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EDITED BY

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THE PERIODIC TABLE.*

PERIODS.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period . .	2 He 4·00	1 H 1·008 3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·000	7 N 14·008	8 O 16·000	9 F 19·00	
Second short period .	10 Ne 20·2	11 Na 22·997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·027	16 S 32·064	17 Cl 35·457	
First long period, Even series .	18 A 39·91	19 K 39·096	20 Ca 40·07	21 Sc 45·10	22 Ti 48·1	23 V 50·96	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
First long period, Odd ,, .		29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·96	34 Se 79·2	35 Br 79·916	
Second long period, Even series .	36 Kr 82·9	37 Rb 85·44	38 Sr 87·63	39 Y 88·9	40 Zr 91·0	41 Nb 93·1	42 Mo 96·0	43 ...	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
Second long period, Odd ,, .		47 Ag 107·880	48 Cd 112·41	49 In 114·8	50 Sn 118·70	51 Sb 121·77	52 Te 127·5	53 I 126·932	
Third long period . .	54 X 130·2	55 Cs 132·81	56 Ba 137·37	57 La 138·90	58 Ce 140·25 59 Pr 140·92	60 Nd 144·27 61 ...	62 Sm 150·43 63 Eu 152·0	64 Gd 157·26 65 Tb 159·2	
Fourth long period . .		66 Dy 162·52 67 Ho 163·4	68 Er 167·7 69 Tm 169·4	70 Yb 173·6 71 Lu 175·0	72 Hf [180·8]	73 Ta 181·5	74 W 184·0	75 ...	76 Os 190·8 77 Ir 193·1 78 Pt 195·23
Fifth long period, Even series .		79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·20	83 Bi 209·00	84 Po [210]	85 ...	
Fifth long period, Odd ,, .	86 Rn 222	87 ...	88 Ra 225·95	89 Ac ...	90 Th 232·15	91 Pa ...	92 U 238·17		
Volume in this series of text-books.	1	2	3	4	5	6	7	8	9

* The International Atomic Weights for 1925 are adopted in this Table.

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME X.

THE METAL-AMMINES.

BY
Miss M. M. J. SUTHERLAND, D.Sc., F.I.C
ROYAL TECHNICAL COLLEGE, GLASGOW

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GENERAL INTRODUCTION TO THE SERIES.

During the past few years the civilized world has begun to realize the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasize their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II, along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV, along with the Elements of Group III, as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II and V respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II under ammonium, and in Volume IX under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.

Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xv–xvii.

The addition of the *Table of Dates of Issue of Journals* (pp. xix–xxvi) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

January 1928.

PREFACE.

In compiling this volume, *The Metal-Ammines*, an endeavour has been made to collect the main points relating to this large class of substances. The ammino-derivatives of chromic and cobaltic salts are well known and are included in most text-books on inorganic chemistry, whilst those of the other metals are barely touched upon. The ammines are treated in the order in which the metals occur in the periodic system, thus keeping this volume in line with the others of the series.

I desire to express my thanks to Dr J. Newton Friend, the editor of the series, for the great help he has given me, and also to Dr Duff, who has kindly read the proofs of the volume.

M. M. J. SUTHERLAND.

January 1928.

CONTENTS.

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE.	JOURNAL.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914 +).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900 +).
Ann. Physik, Beibl.	Annalen der Physik, Beiblättes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin*
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bul. Soc. Stiinte Cluj	Buletinul Societâţei de Ştiinţe din Cluj.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franc. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.

Abbreviated Title.	Journal.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Gilbert's Annalen	Annalen der Physik (1799-1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Geol. Mag.	Geological Magazine.
Helv. Chim. Acta	Helvetica Chimica Acta.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch für Mineralogie.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift für Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mon. scient.	Moniteur scientifique.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Öfvers. K. Vet.-Akad. Forh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Pflüger's Archiv.	Archiv. für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Pharm. Post	Pharmazeutische Post.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824-1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie de Wissenschaften zu Berlin.

Abbreviated Title.	Journal.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift für Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32–35	...	...	...	4–6	...	5–8	90	...
1	...	36–39	...	...	...	7–9	...	8–11	91	...
2	...	40–43	...	...	...	10–12	...	11–14	92	...
3	...	44–47	...	...	...	13–15	...	14–17	93	...
4	...	48–51	...	...	...	16–18	...	17–20	94	...
1805	...	52–55	...	...	...	19–21	...	20–23	95	...
6	...	56–60	...	...	...	22–24	...	23–26	96	...
7	...	61–64	...	...	...	25–27	...	26–29	97	...
8	...	65–68	...	...	...	28–30	...	29–32	98	...
9	...	69–72	...	...	...	31–33	(1) 1*	33, 34	99	...
1810	...	73–76	...	...	...	34–36	2	35, 36	100	...
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13	...	85–88	...	...	...	43–45	5	41, 42	103	...
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29	15, 16	40–42	5, 6	27–30	31–34		15	5, 6	119	15–17

* First series known as *Bulletin de Pharmacie.*

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon.* scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	...
31	19, 20	...	46–48	...	35–39	...	...	39–42	17	...	...	9, 10	121	21–23	...	...	...
32	21, 22	1–4	49–51	(3) 1, 2	40–43	...	...	43–47	18	...	...	11 (3) 1	122	24–26	1	...	...
33	23, 24	5–8	52–55	3, 4	44–47	...	...	48–50	19	...	...	2, 3	123	27–30	2	...	...
34	25–27	9–12	56–57	5, 6	48–50	...	...	51–54	20	1–3	...	4, 5	124	31–33	...	...	...
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36	30, 31	17–20	61–63	9, 10	5–8	...	2, 3	59–62	22	7–9	...	8, 9	126	37–39	...	...	...
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41	40, 41	37–40	(3) 1–3	19, 20	25–28	...	12, 13	79–82	27	22–24	...	18, 19	131	52–54	...	...	...
42	42, 43	41–44	4–6	(4) 1, 2	29–32	...	14, 15	83–86	(3) 1, 2	25–27	...	20, 21	132	55–57	...	...	...
43	44, 45	45–48	7–9	3, 4	33–36	...	16, 17	87–90	3, 4	28–30	...	22, 23	133	58–60	4	...	...
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49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
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59	27, 28	109–112	55–57	15, 16	97–100	1	48, 49	151–154	35, 36	76–78	3	17, 18	149	106–108	9, 10	12	34–38

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1860	...	29, 30	...	113–116	...	58–60	17, 18	101–104	...	2	1, 2	...	...
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67	...	43, 44	...	141–144	5	10–12	11, 12	129–132	...	7, 8	15, 16	...	...
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71	...	(3) 1, 2	...	157–160	...	22–24	19, 20	145–148	4	15, 16	23, 24	...	...
72	...	3, 4	...	161–164	8	25–27	(7) 1, 2	149–150, 201 *	5	17, 18	25, 26	...	...
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1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
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78	86, 87	227–230	8	...	33, 34	27, 28	17, 18	10	...	...	20	17, 18, 19	5, 6
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1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
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64	154	121–123	...	13	Chem. Soc.	...	49, 50	...	...	3	...	...	...
1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127–129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130–132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133–135	...	16, 17	...	...	57, 58	...	...	7	..	...	...
69	159	136–138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139–141	...	18, 19	...	...	61, 62	...	..	9	...	...	...
71	161	142–144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145–147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
73	163	148–150	...	21, 22	...	...	67, 68	...	...	12	...	...	...
74	164	151–153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154–156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
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81	172	...	...	31, 32, 33	...	...	83, 84	1	12–14	20	...	5, 6	...
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83	174	...	...	34, 35, 36	...	2	87, 88	3	18–20	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	4	21–23	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	5	24–26	24	...	10, 11	...
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1890	12	39, 40	15	256–260	19–21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
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1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
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04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
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06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

* See footnote, p. xx.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
01	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
02	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
03	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
04	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
06	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
07	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
08	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
09	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	...	36		55	29	94–98	22	...	91, 92
17	217	18		...	36, 37	...	37		56	30	99–101	23	...	92
18	217	...		...	37	...	38		57	31	102–104	24	No issue*	92
19	...	...		...	38	...	39		58	32	105–109	25		...

* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF

INORGANIC CHEMISTRY

VOLUME X.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. X.

THE METAL-AMMINES.

CHAPTER I.

INTRODUCTORY.

The symbols employed in chemical formulæ to-day are, with a few alterations and additions, those used by Berzelius. The formulæ of simple compounds were represented by writing the symbols of the elements contained in the compound side by side, and this simple representation served for some time. The formulæ used, however, did not denote the proportion of the atoms of one kind to that of another kind, and numerals were therefore introduced to denote the number of each kind of atoms in the molecule. This arose naturally when it was found that more than one compound might contain the same elements, and that the different properties of the compounds were due to the proportion of the elements present in the molecule; as, for example, the two compounds of carbon and oxygen, carbon monoxide and carbon dioxide.

These formulæ are in use at the present day and serve to represent molecules of simple inorganic compounds. They denote the number of atoms of each element in the molecule, and, by the help of atomic weights, also the relative weights of each element in the molecular weight of the compound. So long as the inorganic compounds were simple this nomenclature proved useful and sufficient. Difficulties have arisen, however, in later years owing to the study and isolation of many so-called complex compounds. Now a system is useful so long as that system may be extended to embrace all possible cases, and the present system of formulæ for inorganic substances breaks down when these complex compounds are considered. For example, sodium chloride shows in solution the reactions of sodium ions, but when such compounds as potassium ferrocyanide or hexammino-cobaltic chloride are dealt with it is not possible to write simple formulæ which express their properties; for potassium ferrocyanide when dissolved in water does not show iron ions in solution, neither does a solution of hexammino-cobaltic chloride show all the reactions of the cobalt ions. The possibility of the existence of compound radicles was early recognised, and the initial difficulties of representing more complex substances were overcome by giving a group of elements a separate entity as it were, and a valency of its own. The oxy-acids afford simple examples of this ; sulphuric acid contains the elements hydrogen, sulphur, and oxygen, and is represented as H_2SO_4. Such a compound ought to have in solution hydrogen ions, sulphur ions, and oxygen ions ; but on examination these are not found, and the explanation is given that sulphuric acid in solution breaks up into hydrogen ions and a compound ion, (SO_4). This way out of the difficulty was accepted and the present formula based on it.

With the development of organic chemistry and the discovery of many substances containing the same elements in the same proportions there arose fresh difficulty. The mere empirical formulæ here afforded no clue to the properties of the compound, and structural formulæ were therefore introduced with a view to representing the arrangement of the elements in the molecule. In inorganic chemistry this was not at first necessary, but with the advance of modern chemistry and the examination of compounds such as the metal-ammines, the ferrocyanides, the chlorplatinates, it has become necessary to extend the scope of chemical formulæ. The theory of fixed valency for the elements has been gradually abandoned, but certain conventions regarding valency are still observed, and these more complex compounds seem almost like exceptions to the usual conception of valency of the atoms. Compounds are spoken of as either simple or complex, the name *complex* being given to any compound built up of two or more different molecules, which does not show the individual reactions of the metallic or non-metallic ions contained in it when it is dissolved in a suitable solvent. Abegg and Bodländer [1] gave the following definition of complex compounds : " Complex compounds are those in which a part of the compound, which forms an ion by electrolytic dissociation, consists of a molecular compound of a molecule capable of forming a separate ion with an electrically neutral molecule. By the term *complex ion* we understand this molecular compound when it has taken up its natural electric charge." No sharp line, however, can be drawn between simple and complex compounds.

In the case of salts the terms " simple salt," " double salt," and " complex salt " are employed ; again the distinction is not definite, double salts and complex salts merging one into the other. Generally speaking, if a salt becomes decomposed in solution into simple ions such as sodium ions and chlorine ions from sodium chloride, it is termed a simple salt. A double salt, on the other hand, has a crystalline form different from the component salts, and in this respect, as also in certain other physical properties, it is quite distinct from a mixture of the component salts. But it, also, is decomposed in solution into simple ions, and behaves then as a mixture of the simple salts of which it is composed. Complex salts are not decomposed in solution into metal ions and non-metal ions, and both metal and non-metal may be present in the complex salt in solution without showing the reactions of their ions. Peculiarities of this kind have led to much research on the nature of these compounds and the introduction of theories such as the co-ordination theory and the various electronic theories of valency. The representation of complex substances by formulæ is still far from satisfactory despite the immense amount of work which has been published on the subject. Many graphic formulæ have been suggested, but most of these fit only one series of compounds. The next chapter gives a very

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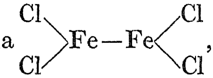
[1] See Jaques, *Complex Ions* (Longmans, 1914), p. 3.

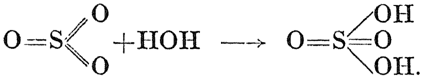
brief summary of the development of the theory of valency from the chemical point of view.

Inorganic chemistry has widened considerably in recent years, and it becomes more and more evident that methods of representation of the type used in organic chemistry must be employed. Physico-chemical measurements have served in many ways to test the accuracy of formulæ, and the introduction from time to time of new theories of valency and affinity of the atoms has led to the elucidation of the behaviour of certain complexes where the elements in the complex appear to react in a manner quite contrary to that of the same elements in their simpler compounds. It should be possible, however, to adopt some convenient method to show graphically the union of the constituents of the complex.

CHAPTER II.

VALENCY.

Following on the dualistic theory of Berzelius came the theory of valency or combining capacity of the atoms, and around this latter theory arose the controversy between a variable and a fixed valency. Frankland regarded valency as probably variable, whilst Kekulé, on the other hand, regarded valency as a fixed and definite property of the element, basing his assumptions on the apparently invariable valency of carbon throughout a large number of compounds. The recognition of a fixed valency for carbon has been of inestimable value in building up structural formulæ for organic compounds, and naturally this invariable valency of carbon led to the extension of the theory to all the elements. The theory fitted many of the simpler compounds, but difficulties soon arose, as some elements appeared to display two different valency values. Such a compound as ferrous chloride had to be represented with two iron atoms in the molecule, and was given the formula Fe_2Cl_4, and a structural formula  , in order to preserve the trivalency of iron. Other compounds, however, were discovered where such an arrangement was not possible, and these were given what were called *molecular formulæ*. These formulæ made no attempt to fit the compounds into the scheme of fixed valency, but represented them as made up of molecules loosely held together in a manner unexplained by valency; for example, phosphorus pentachloride was represented as $PCl_3.Cl_2$, and ammonium sulphate as $2NH_3.H_2SO_4$, for these compounds reverted to simple compounds on heating. Later investigations proved the difficulty of retaining the theory of constant valency, for although phosphorus pentachloride might be given the molecular formula $PCl_3.Cl_2$, phosphorus pentafluoride is not dissociated on heating, and therefore must be given the formula PF_5, thus showing phosphorus as pentavalent. Also, ferrous chloride when in solution was proved in molecular weight determinations by ebullioscopic methods, using pyridine as solvent, to contain only one atom of iron in the molecule, and hence should have the formula $FeCl_2$. It became evident, therefore, that the theory of valency required extension by assuming that certain elements have more than one valency, the exception being carbon, which was generally regarded as tetravalent. It has been shown by examination of the compounds of an element that the valency appears to depend on certain factors; for example, the nature of the other elements in the compound influences the valency, and certain external conditions, notably temperature and pressure, act similarly. For instance, chlorine shows unit valency towards hydrogen and sodium, but it can also apparently exert a valency of seven in the oxide, Cl_2O_7; sulphur is divalent when combined with hydrogen, tetravalent in sulphur dioxide, and hexavalent in sulphur trioxide. If sulphur trioxide be heated to high temperature, however, sulphur appears to revert to tetravalency and the compound loses oxygen. Hence the valency of an element must be regarded as capable of variation, though probably fixed in any special case. Thus, in hydrogen sulphide, sulphur is divalent, and the atom appears unable to exert any other bonds with respect to hydrogen. The theory of valency depends on this principle, and becomes relatively useless if it departs from it. In simple compounds the theory meets most cases, and formulæ were built upon the assumptions outlined above; but when more complex substances are considered, the so-called compounds of higher order referred to by Werner, the theory does not suffice. It cannot explain the union of two or more molecules in which all the valencies of the constituents are already satisfied; it cannot explain, for example, the fact that cobaltous sulphate is able to unite with potassium sulphate, forming the double sulphate, $CoSO_4.K_2SO_4.6H_2O$; or that cobaltic chloride can unite with six molecules of ammonia with formation of the complex salt hexammino-cobaltic chloride, $Co(NH_3)_6Cl_3$; or that silver cyanide dissolves in an aqueous solution of potassium cyanide, yielding the double cyanide, $KAg(CN)_2$. These addition compounds must be looked upon as exceptions to the general idea of valency. The union of oxides and water, such as sulphur trioxide and water, is usually explained in the valency theory by assuming a readjustment of the existing valency bonds. Thus oxygen in sulphur trioxide on combining with water becomes singly linked to sulphur, and hydrogen satisfies the other oxygen valency. The reaction is therefore represented as:



Such an explanation serves for some of the oxides but cannot be made sufficiently general to cover all cases; it does not fully explain the hydration of the oxides themselves, because, as Werner[1] points out, if water is added to the oxides by the formation of hydroxyl groups, sulphur trioxide, which contains three doubly linked oxygen atoms, should be capable of adding *three* molecules of water, whereas it adds on only one. Phosphorus pentoxide contains, according to fixed valency theory, four doubly linked oxygen atoms and unites with only three molecules of water, whilst chlorine heptoxide contains six doubly linked oxygen atoms and adds on only one molecule of water. Further, oxides such as osmium tetroxide, OsO_4, and ruthenium tetroxide, RuO_4, cannot unite with water to form acids. In the cases mentioned the water uniting with the oxide to form an acid is independent of the double linking of the oxygen atoms, and only four oxygen atoms seem capable of being held in combination in the acid. Sulphur trioxide, SO_3, therefore yields sulphuric acid, H_2SO_4; phosphorus pentoxide, P_2O_5, yields orthophosphoric acid, H_3PO_4; and chlorine heptoxide, Cl_2O_7, yields perchloric acid, $HClO_4$. Osmium and ruthenium tetroxides do not yield acids in this way. The addition of water to oxides with formation of

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[1] *New Ideas on Inorganic Chemistry*, A. Werner. Translated by E. P. Hedley (Longmans, 1911), p. 25.

acid thus seems connected with the number of oxygen atoms in the molecule and not with the double linking of the oxygen atoms.

In many cases it is only by forcing an explanation for the particular case that the valency theory can be adhered to, but the formulæ obtained in such circumstances do not indicate the behaviour of the substance chemically. These difficulties in correlating the compounds of higher order with the older valency theory rendered it necessary either to extend the conception of valency still further or to adopt some other theory.

Kolbe gave each element a maximum valency beyond which combination was impossible, but which might not be completely exerted in the compounds of the element. Erlenmeyer and Mendeléeff adopted a somewhat similar view, and assumed that the higher oxygen compounds, with the exception of the peroxides, showed the maximum valency of the elements.

Blomstrand,[1] in 1869, pointed out that elements which are highly electropositive or electronegative have the lowest valency capacity, Van 't Hoff,[2] in 1881, suggested that variable valency might be caused by change in the external form of the atom, and Hinrichsen [3] assumed a connection between the energy content of the atom and its degree of affinity. Abegg [4] assumed that the maximum valency of every element is eight, but he distinguished two kinds of valency, normal or positive valency and contra or negative valency. He further suggested that before combination these valencies are of equal strength, and that when combination takes place between the elements the saturation of one valency of an element weakens the others, the amount of weakening depending on the nature of the element or group with which it has combined. For example, chlorine shows unit valency towards hydrogen and a maximum positive valency of seven towards oxygen. The strength of the two kinds of valency depends upon the chemical nature of the element itself. Alkali metals being too highly electropositive to manifest negative valency, show unit valency. Fluorine is too highly electronegative to manifest positive valency, hence it forms no compound with oxygen. These latent valencies may become active under certain conditions, and this may account for molecular and addition compounds.

Modern theories of valency are electrochemical in character, are concerned with the nature of the atom, and assume union between elements to take place by exchange or sharing of electrons, although theories of how this exchange or sharing takes place differ considerably.

In seeking for an explanation of the fact that certain molecules which were saturated, according to old valency theory, still possessed the power to combine with other molecules, Alfred Werner,[5] in 1891, introduced his co-ordination theory which, altered and added to as it has been developed, he used to explain the existence of complex salts, and especially the large class of compounds known as the metal-ammines. It does not take into account the internal structure of the atoms linked together, but is concerned with the combining capacity

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[1] Blomstrand, *Chemie der Jetztzeit*, 1869, pp. 217, 243.

[2] Van 't Hoff, *Ansichten über die organische Chemie*, 1881.

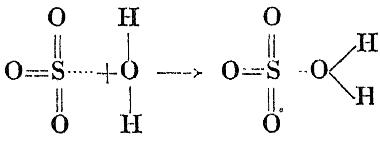
[3] Hinrichsen, *Ueber den gegenwärtigen Stand der Valenzlehre* (Stuttgart, 1902).

[4] Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, **20**, 453; Abegg, *ibid.*, 1904, **39**, 330.

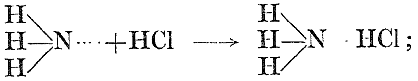
[5] Werner, *Beiträge zur Theorie der Affinität und Valenz*, 1891.

of the elements. The theory is known as the *co-ordination theory of valency*, and has been of great value in dealing with the structure of the complex salts.

Werner assumed that each element possesses two kinds of valency, which he termed *principal* and *auxiliary* respectively. When, therefore, an element is saturated with respect to its principal valency, as, for example, cobalt in cobaltic chloride, $CoCl_3$, it still possesses a certain auxiliary valency which it may or may not exert. It is this auxiliary valency coming into force which gives cobaltic chloride the power to unite with six molecules of ammonia, yielding the complex ammine, $Co(NH_3)_6Cl_3$. Werner in his original statements distinguished between these two kinds of valency, and assumed that principal and auxiliary valencies were possessed of a different energy content; but in his later investigations he had to abandon this assumption and conclude that there was no great fundamental difference between them. When auxiliary valency is exerted it may serve either to increase the stability of the molecule or to weaken it. According to the co-ordination theory, atoms or groups linked to an element by auxiliary valencies are incapable of ionisation in solution, whilst those linked by principal valencies may be dissociated. Also, units of valency cannot be considered as individual forces, for the unit varies with the nature of the atoms it joins together and with the variable amount of affinity possessed by these atoms. Thus, if the total affinity of an atom A in a compound AB is saturated by A becoming linked to other atoms or groups, A has less affinity left over than previously for the bond between A and B. Hence B will have some residual affinity, and if this reaches a certain value it will become able to exert auxiliary valency—that is, it will become capable of forming molecular or addition compounds. This addition will be more possible when the limiting number of principal valencies has been reached, for it is then probable that the last valency bond will be weaker than the others, and hence the atom bound by it will have sufficient residual affinity to form addition compounds. Werner also sought to explain the two kinds of valency from an electronic point of view. He assumed that when principal valencies are saturated two changes take place, one chemical and one electronic. When atoms unite, therefore, by principal valency, that is, when an ionisable group or atom is formed, a passage of electrons takes place from the electropositive to the electronegative element. When atoms unite by auxiliary valency no exchange of electrons takes place and no ionisable group or atom is formed. Additive compounds are formed by assuming that the molecules are united by these auxiliary valencies. Thus, the oxides which unite with water to form acids do so, according to valency theory, by readjustment of the oxygen bonds, whilst, according to Werner's theory, no adjustment takes place, but the residual affinity on the group brings about auxiliary valency between that group and another group or atom. For example, the formation of sulphuric acid from sulphur trioxide takes place thus :



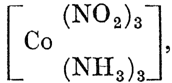
where the broken line represents the auxiliary valency; the union of ammonia and hydrogen chloride thus:

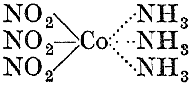


and the union of cobaltic chloride with ammonia thus:

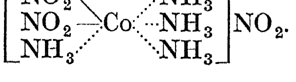
Many objections have been raised to the theory, but in its application to the metal-ammines it has been of great value.

As the result of examining a large number of metal-ammines, Werner was enabled to arrange this class of substances into well-defined groups. He regarded ammonium chloride as the simplest example of the ammino-compounds, and represented it by the formula $H_3N \cdots HCl$. In this, hydrogen is not ionised in solution, but chlorine, being linked by a principal valency bond, can undergo ionisation. This view of the formula of ammonium chloride and ammonium salts has not been generally accepted.

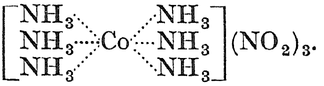
In the metal-ammino-compounds or the complex metal salts there is believed to be a definite number of groups or atoms arranged around a central atom. The most usual number is six, but compounds are known where the number is eight, four, or even two. According to the co-ordination theory these atoms or groups are arranged around a central atom united partly by principal and partly by auxiliary valency bonds, such groups constituting the undissociated zone or *co-ordination complex*. Triammino-cobaltic nitrite, for example, is represented as $[Co(NO_2)_3.(NH_3)_3]$ or  $\left[Co \begin{matrix} (NO_2)_3 \\ \\ (NH_3)_3 \end{matrix}\right]$, the square bracket containing the undissociated or co-ordination complex. To explain the apparent hexavalency of the cobalt atom it is assumed that three groups are united with cobalt by principal valencies and three groups by auxiliary valencies thus:



Triammino-cobaltic nitrite is not ionised in solution, so that in this particular case the principal valency bonds do not show the characteristics at first laid down for them by Werner. If the substance is treated with ammonia, one, two, or even three of the nitro groups may be replaced by ammonia and the following results are obtained. The entrance of one molecule of ammonia causes the compound to become ionised, and in solution one (NO_2) ion may be detected. A nitro-group has therefore been expelled from the undissociated zone with production of a new compound of formula



Further addition of ammonia causes a second and then a third (NO_2) group to pass from the undissociated zone and become ionised in solution, corresponding to the compound



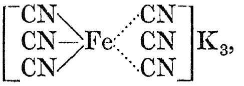
$$\left[\begin{array}{ccc} NH_3 & & NH_3 \\ NH_3 & Co & NH_3 \\ NH_3 & & NH_3 \end{array}\right](NO_2)_3.$$

The number of radicles or atoms attached to the metal in the first zone is termed the co-ordination number, the value for which in the case of the cobalt-ammines is almost invariably six.

The ammines are therefore often classified into types with co-ordination numbers six, four, three, etc.

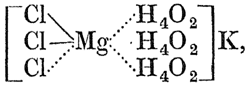
The weak point of the theory is the position of the atoms or groups outside the first zone. These are assumed to arrange themselves indefinitely around the first zone. The ammonia molecules in the metal-ammines in the first zone are firmly attached, inasmuch as many of these compounds can be treated with concentrated acid without removal of ammonia.

The co-ordination theory has also been applied to many complex salts and double salts other than ammines. For example, potassium ferricyanide may be represented by the formula



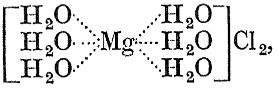
$$\left[\begin{array}{ccc} CN & & CN \\ CN & Fe & CN \\ CN & & CN \end{array}\right]K_3,$$

in which the auxiliary valencies of iron are united with those of the cyanogen radicles already attached to potassium. The double salt, magnesium potassium chloride, $KCl.MgCl_2.6H_2O$, may be represented by the formula



$$\left[\begin{array}{ccc} Cl & & H_4O_2 \\ Cl & Mg & H_4O_2 \\ Cl & & H_4O_2 \end{array}\right]K,$$

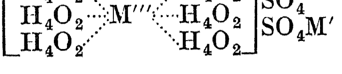
although this salt is unstable and ionises in solution due to splitting off of the undissociated water molecules. These latter are assumed to be double in order to bring the formula into line with hexahydrated single salts, where six molecules of water form the co-ordination complex. Thus, hydrated magnesium chloride is represented as:



$$\left[\begin{array}{ccc} H_2O & & H_2O \\ H_2O & Mg & H_2O \\ H_2O & & H_2O \end{array}\right]Cl_2,$$

in which the acidic radicle lies outside the first zone and is therefore ionisable.

Water molecules are known to associate in pairs in the liquid state, and Werner therefore justified his suggestion that polymerised molecules of dihydrol or H_4O_2 probably occur in hydrates of the former type as also in the alums. These latter are represented as co-ordination derivatives of general formula



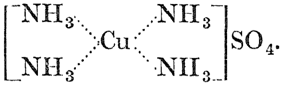
$$\left[\begin{array}{ccc} H_4O_2 & & H_4O_2 \\ H_4O_2 & M''' & H_4O_2 \\ H_4O_2 & & H_4O_2 \end{array}\right]\begin{array}{l} SO_4'' \\ SO_4M' \end{array}$$

where M''' and M' refer to atoms of trivalent and monovalent metals respectively. Potassium chromium alum may therefore be given the co-ordination formula

$$\left[\mathrm{Cr(H_4O_2)_6}\right]\begin{matrix}\mathrm{SO_4K}\\ \mathrm{SO_4}\end{matrix}$$

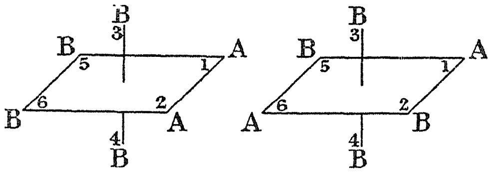
In the examples quoted the co-ordination number is six.

Cupric sulphate unites with ammonia, forming the compound $Cu(NH_3)_4SO_4$. The co-ordination number is again four, and the formula is



$$\left[\begin{matrix}\mathrm{NH_3} & & \mathrm{NH_3}\\ & \mathrm{Cu} & \\ \mathrm{NH_3} & & \mathrm{NH_3}\end{matrix}\right]\mathrm{SO_4}.$$

The *co-ordination number* of the central atom may be the same as the numerical value of the valency of the central atom, or it may be different. The frequent occurrence of the number six or four suggests a definite spatial arrangement for these co-ordinated groups. Compounds with co-ordination number six are assumed to possess an octahedral configuration, whilst those with co-ordination number four are given a tetrahedral or, sometimes, a planar configuration. Werner verified these assumptions by examining many derivatives and showing that they possess the properties of compounds with these particular spatial arrangements. For example, an octahedral grouping with the atoms or groups at the corners of an octahedron ought to exist in two isomeric forms if the central atom be united with two A and four B groups, where A and B are different monovalent groups thus :



Such isomerism has been proved to exist, two and only two isomeric forms being known where A is in the 1-, 2-, or *cis*-position, or in the 1-, 6-, or *trans*-position.

The importance of the theory was further demonstrated by the discovery of the existence of optically active inorganic compounds, and the isolation of the exact number of optical isomers theoretically possible for the spatial arrangement of the atoms.[1] Friend [2] and others criticised the theory on the grounds that in simple compounds, such as sodium chloride or cobaltous chloride, the chlorine is ionised and yet is attached to sodium or cobalt atom directly, whereas in the ammino-compounds the acid capable of ionisation is that which is not directly attached to metal. For instance, in chloro-pentammino-cobaltic chloride, $[CoCl(NH_3)_5]Cl_2$, it is the chlorine outside the first zone which is ionised in solution. Also, the dissociable acidic groups are not attached to any point within the complex, but simply hover round the central complex in an indefinite manner. Thus a definite valency for ionisable

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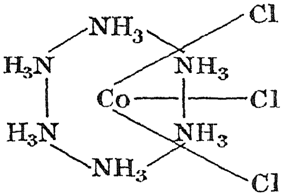
[1] Werner and Kling, *Ber.*, 1911, 44, 1887.

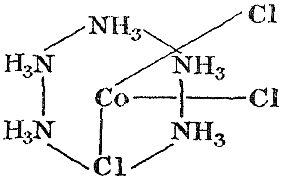
[2] Friend, *Trans. Chem. Soc.*, 1908, 93, 1006; 1916, 109, 715.

acidic groups seemed to be denied. Further, in the example quoted above the chlorine atom directly united with cobalt is not ionised in solution. Reasoning from advance made in organic chemistry by keeping the valency of carbon fixed, Friend therefore advocated formulæ of the same type for inorganic complex substances, as there seemed no apparent reason why one group of complexes should be governed by different laws from another. Cyclic or shell formulæ were suggested for the cobalt-ammines such as the following:—

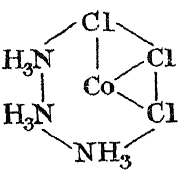
Hexammino-cobaltic chloride,



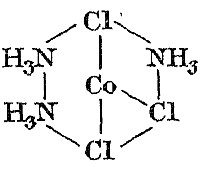
and chloro-pentammino-cobaltic chloride,



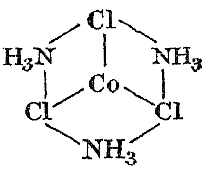
In this way the dissociable chlorine atoms are represented united directly to cobalt, and hence there is no difference between these chlorine atoms and chlorine atoms in cobaltous chloride. The chlorine atom not dissociable is included in the centre shell round the cobalt atom. This shell around the metal is compared to the water molecules associated with some metallic ions which retard their mobility, the complex moving as a whole through a solution. These associated molecules, it is suggested, take the form of shells of water around the atom, the molecules being linked together by oxygen atoms. In the case of trichloro-triammino-cobalt all the chlorine atoms are within the shell and the substance is a non-electrolyte. Three different formulæ are possible, none of which will ionise in solution, viz.:



I

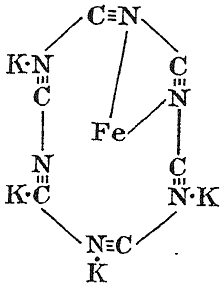


II

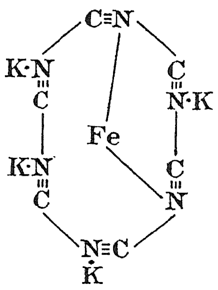


III

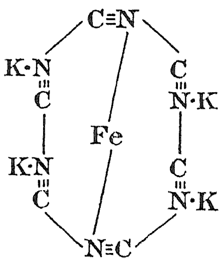
Potassium ferrocyanide was also given a cyclic formula by Friend, where iron is situated at the centre of the ring and is therefore not ionised in solution. The enclosing ring is made up of cyanogen radicles, and potassium is attached to three nitrogen atoms of the ring. Three possible formulæ were represented by Friend thus :



Ortho- or
1-, 2-ferrocyanide.



Meta- or
1-, 3-ferrocyanide.



Para- or
1-, 4-ferrocyanide.

The potassium atoms are attached to the ring itself and not to iron, so that isomerism becomes possible depending on the positions assumed by these atoms. The meta- and para-salts are more evenly balanced and may be expected to show greater stability; the ortho-salt is the double salt, $4KCN.Fe(CN)_2$, and in view of the instability of ferrous cyanide this complex may not be stable. Also, either the meta- or the para- compound may be easily transformed into the nitro-prusside.

The main difference between the two theories lies in Werner's assumption that the co-ordinated groups surrounding the central atom are connected with that atom by valency bonds, whereas Friend assumes them to be connected with one another. The accepted method of writing the formulæ with the central groups within square brackets remains the same in both cases.

Modern physical conceptions of valency are electronic in character, and are intimately connected with the structure of the atom. It is believed that the atom consists of a central nucleus which bears a positive charge, round which are arranged electrons or negative charges of electricity numerically equal to the number of positive charges on the nucleus. In the case of hydrogen the nucleus bears unit positive charge, and there is one electron at some distance away which neutralises this charge and thus renders the atom electrically neutral. This electron is regarded as a valency electron, and in some manner is connected with the unit valency manifested by hydrogen. Helium has a net double positive charge on its nucleus and two external electrons. These form a stable pair which do not readily enter into chemical combination, and hence helium has a valency of 0. Lithium has a positive nuclear charge of three units and three electrons external to the nucleus, two forming, as in helium, a stable pair, and one outside of these, further removed from the nucleus. This outside electron is thus analogous to the electron of the hydrogen atom, and lithium has unit valency. Beryllium has two, boron three, carbon four external electrons in addition to the stable central electrons; and the valencies of these elements are two, three, and four respectively, and so on. Eight is regarded as the maximum number of electrons an atom can retain in any one shell, and an element with a complete outer shell of eight will tend neither to take up nor part with any electrons. This is presumed to be the cause of chemical inactivity, and such an element will be inert like helium. Neon is the first of these, having ten electrons, two of the helium type and eight others. Sodium has eleven electrons, that is, ten plus one ; the last named being the first electron of a new shell still further removed from the nucleus. It is thus isolated from the others, and the sodium atom therefore exerts unit valency in a similar manner to lithium. Calcium has twelve electrons, that is, 2+8+2, the two outermost giving to calcium its double valency, and so on. As soon as a ring or shell of eight electrons has been completed another shell is begun, and hence the valency ranges from *nil* to seven in each of the horizontal series of the periodic table. As the atomic weights of the elements increase the atoms become increasingly complex, and the arrangement of the electrons somewhat modified, although the octave rule is still believed to apply, the outermost electrons being those that cause the effect known as valency. For physical and allied purposes it seems essential to assume that the electrons are in a rapid state of motion, and the so-called Bohr atom [1] has been constructed with this essential feature in view. On the other hand, the chemist feels that valency is best explained on the assumption that the electrons do not move to any appreciable distance from fixed points. The theories of Lewis [2] and Langmuir [3] are in consequence based on this. At the present time it is difficult to harmonise these views.

Once the modern conception of the atom, as outlined above, had been accepted, it became clear that the earlier views as to the mechanism of valency required revision.

Three kinds of valency are now recognised,[4] namely :

1. *Ionised Valency.*—This is exemplified by sodium chloride, the sodium atom functioning as a donor by giving its single-valency electron to the chlorine atom, thereby increasing the number of the outer-shell electrons of this latter atom to eight.

2. *Co-valency*, in which each of two adjacent atoms shares an electron with the other. The simplest examples of this are afforded by molecules such as H_2, O_2, etc.

3. *Co-ordinate Valency*, in which two adjacent atoms share a pair of electrons, both of which, however, are supplied by one only of the atoms, namely, the donor, the acceptor atom offering none in return.

It is a tribute to the prevision of Werner that these developments have not materially affected the essential features of his theory.

In this volume it has been found convenient to retain, in many cases, Werner's original conception of principal and auxiliary valencies.

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[1] Bohr, *Phil. Mag.*, 1913, [6], 26, 857.

[2] Lewis, *Proc. Nat. Acad. Sci.*, 1916, 2, 586.

[3] Langmuir, *J. Amer. Chem. Soc.*, 1919, 41, 868 ; 1920, 42, 274.

[4] See summary by Sidgwick, *J. Soc. Chem. Ind.*, 1927, 46, 799.

CHAPTER III.

GENERAL CHARACTERISTICS OF THE METAL-AMMINES.

THE metal-ammines, formed by the addition of ammonia molecules or molecules of organic amines, constitute an exceedingly large class of substances of the complex type.

The class has received, in recent times, much attention, and has been a fruitful source of research into the constitution of inorganic compounds, and also in the elaboration of modern theories of valency. As has been said already, the classical formulæ used to express the constitution of simple compounds, and the reactions of these one with another, are found inadequate to represent the constitution and behaviour of these complex derivatives. The original ideas of fixed valency introduced by Kekulé in his researches on the carbon compounds must be abandoned when the metal-ammines are considered. Take, for example, one of the simplest cases of the metal-ammines, that of the compound formed by the addition of two molecules of ammonia to platinic chloride, $PtCl_4.2NH_3$. In platinic chloride all the valency of platinum, according to the classical theory of simple salts, is fully saturated in linking four atoms of chlorine to the metal. Yet, under certain conditions, two molecules of ammonia may be added. The supporters of fixed valency explained the substance as a molecular compound in which the ammonia is loosely bound to the molecule in some different manner by forces akin to cohesion but not those usually regarded as valency. Such a formula as $PtCl_4.2NH_3$, however, does not explain the properties of the substance, for whereas pure platinic chloride ionises in aqueous solution and gives a highly conducting liquid which shows the reactions for chlorine ions, the diammine, $PtCl_4.2NH_3$, in aqueous solution conducts electricity so badly that it cannot be regarded as ionised to any appreciable extent. Also, the presence of chlorine cannot be proved by the usual analytical reactions depending upon the presence of chlorine ions. Consequently it must be concluded that the entrance of ammonia into the molecule has fixed the chlorine atoms so firmly to the rest of the molecule that they are no longer able to exist as free ions in solution.

Again, cobaltic chloride can be produced, but the compound is unstable and readily passes into the more stable cobaltous chloride; when dissolved in water the presence of cobalt and chlorine ions can be detected, and conductivity measurements indicate that the salt is completely ionised. If, however, cobaltous chloride is treated with ammonia and then oxidised, stable derivatives of cobaltic chloride containing ammonia are obtained. For example, when united with six molecules of ammonia the well-known salt hexammino-cobaltic chloride is produced. According to the fixed valency theory, however, cobaltic chloride is already a fully saturated compound and should not unite further with other atoms or groups. The ammino-compound is highly stable, and a study of the electric conductivity of its aqueous solution indicates that the complex molecule has dissociated into four ions, of which the halogen can be precipitated completely by silver nitrate. On the other hand, cobalt ions cannot be detected in solution, and the only feasible assumption is that cobalt has formed a complex ion with the ammonia molecules.

Additive compounds of ammonia and cobalt salts were first observed by Tassaert in 1799, although at that time the reaction which takes place when an aqueous ammoniacal solution of cobalt salt is exposed to air was not recognised as one involving the addition of ammonia to the molecule. From that time onwards research has been carried out on these complexes.[1]

One of the first important steps in unravelling the problem was taken by Berzelius with regard to ammonia compounds of the platinum salts. Reasoning from the dualistic theory, he believed these substances to be complexes formed by the union of ammonia with another complex; this complex was not decomposed on treatment with acids, and it did not affect the saturation capacity of the base. He used formulæ of a special type to express the nature of the complex. Thus, the union of platinum chloride and ammonia was represented by

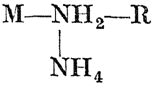
$$\mathrm{Pt.}\cancel{\mathrm{NH}}_2.\cancel{\mathrm{NH}}_4.\cancel{\mathrm{Cl}}.$$

These ideas were subsequently abandoned, but were revived later, in 1869, by Blomstrand,[2] who, however, modified Berzelius' formulæ and suggested the following scheme for the above compound:—

$$\mathrm{Pt.}\cancel{\mathrm{NH}}_3.\cancel{\mathrm{NH}}_3.\cancel{\mathrm{Cl}}.$$

In these formulæ it is assumed that the (NH_3) group has a capacity for forming homologous chains much like the methylene (CH_2) group in the carbon compounds. The metal-ammines were represented, therefore, as built up of chains of ammonia molecules. By adopting such formulæ he recognised that two different forms of chain formation are possible just as in the case of the carbon compounds, namely, the *normal* form and the *iso* or branched form. Thus:

$$\mathrm{M{-}NH_3{-}NH_3{-}R} \quad \text{and}$$



$$\begin{array}{l}\mathrm{M{-}NH_2{-}R}\\ \qquad\;\, |\\ \qquad \mathrm{NH_4}\end{array}$$

where M represents metal and R an acid radicle.

The second formula, he pointed out, was not probable owing to the fact that the fifth valency of the nitrogen atom in other well-known compounds is always attached to a negative radicle, so that the radicle NH_4 was hardly likely to unite with another nitrogen atom. Thus,

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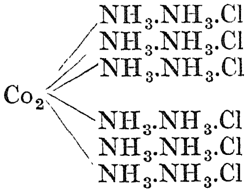
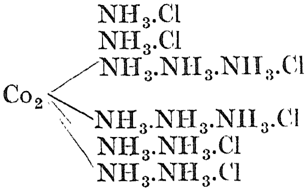
[1] Reitzenstein (*Zeitsch. anorg. Chem.*, 1898, 18, 152) has given a very complete account of the older theories and formulæ of the metal-ammines, and has traced the development of those compounds up to the position at that time.

[2] Blomstrand, *Ber.*, 1871, 4, 40.

taking the cobalt-ammines as example, hexammino-cobaltic chloride was given the constitutional formula (1)

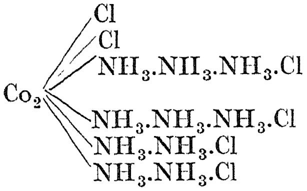


(1)

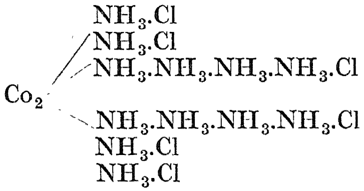


(2)

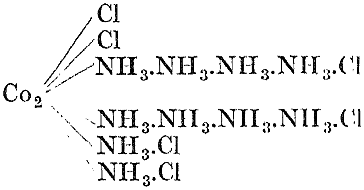
This formula he afterwards modified to (2) in order to explain the fact that if two ammonia molecules fewer are present in the molecule, two acid residues become inactive and therefore must be directly linked to cobalt. Removing two ammonia molecules from scheme (2) yields the formula at that time given to the pentammino-salts, namely, in the case of chloro-pentammino-cobaltic chloride,



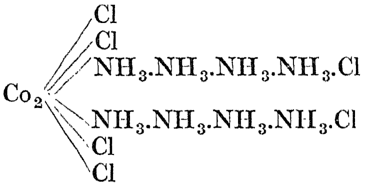
Again the formula had to be modified, when it was found that by removing two more ammonia molecules another pair of acid residues lost their ionic character, and an octammino-salt, the present tetrammino-salt, was formed. Jörgensen therefore, in order to show their relationship to the octammino-salt, suggested the following schemes :—[1]



Luteo-salt.
(Present hexammino-salt.)
(1)



Purpureo-salt.
(Present chloro-pentammino-salt.)
(2)



Octammino-salt.
(Present dichloro-tetrammino-salt.)
(3)

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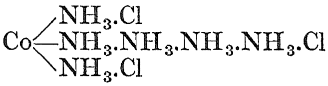
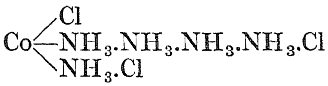
[1] In the early days of research the metal-ammines known were supposed to contain two metallic atoms. The cobalt-ammines were therefore represented as $Co_2Cl_6.10NH_3$, $Co_2Cl_6.12NH_3$, and so on, and the formulæ proposed by Blomstrand were based on this assumption.

An attempt to clear up the constitution of these salts was then made, and Jörgensen,[1] with the help of molecular-weight determination, proved that the substances contained only one cobalt atom in the molecule. The formulæ were then halved and written as :



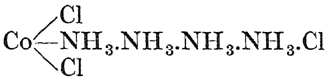
$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{NH_3.Cl}\\ \mathrm{NH_3.NH_3.NH_3.NH_3.Cl}\\ \mathrm{NH_3.Cl}\end{matrix}\right.$$

(1)



$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{NH_3.NH_3.NH_3.NH_3.Cl}\\ \mathrm{NH_3.Cl}\end{matrix}\right.$$

(2)



$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{NH_3.NH_3.NH_3.NH_3.Cl}\\ \mathrm{Cl}\end{matrix}\right.$$

(3)

Jörgensen based his formula on the different behaviour of the halogen atoms towards chemical reagents in the pentammino- and tetrammino-salts. Thus, when the pentammino-salts, for instance, undergo metathetical decomposition one halogen atom takes no part in the reactions but remains associated with metal and ammonia. Further, concentrated sulphuric acid will remove two atoms of halogen as halogen acid, but the third is not attacked. Finally, if chlorine be replaced by bromine two series of salts are obtained which differ in molecular volume according to the type of chlorine replaced. For example, chloro-pentammino-cobaltic chloride yields the following results :—

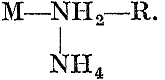
$ClCo(NH_3)_5Cl_2$	molecular volume 277·7
$BrCo(NH_3)_5Cl_2$	molecular volume 281·6

that is a difference of 3·9 per molecule. If, on the other hand, ionisable chlorine is replaced by bromine the results are as follows :—

$ClCo(NH_3)_5Cl_2$	molecular volume 277·7
$ClCo(NH_3)_5Br_2$	molecular volume 319·9

yielding a difference in this case of 42·2 per molecule, that is of 21·1 for each atom of chlorine replaced. This was assumed to be due to the different ways in which the halogen atoms are linked in the two cases.

The problem as to whether the ammonia chains are straight or branched was now tackled. If the latter, then one hydrogen must be more labile than the others, and therefore able to leave one ammonia group and attach itself to another ammonia group. For example, a compound $M—NH_3—R$ on addition of a molecule of ammonia would become



$$\mathrm{M}—\underset{\substack{|\\ \mathrm{NH_4}}}{\mathrm{NH_2}}—\mathrm{R}.$$

That this reaction does not take place in the metal-ammines was proved in the following way.[2] A tertiary amine was chosen, namely, pyridine, in which no labile hydrogen is possible, and therefore no forked chain could be formed if the compound were united with metal salt. It was found that when pyridine and the metallic salt are allowed to interact, metal-pyridine compounds are obtained analogous in every way to the metal-ammines. It seemed probable, therefore, that the metal-ammines do not contain the (NH_4) group.

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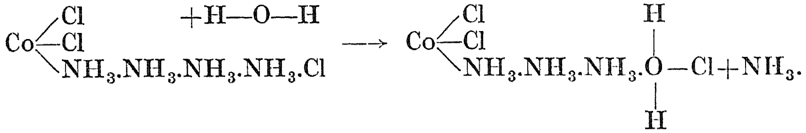
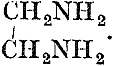
[1] Jörgensen, *J. prakt. Chem.*, 1890, [2], 41, 440.
[2] Jörgensen, *ibid.*, 1886, [2], 33, 489.

Just as ammonia groups may be replaced by acid, so ammonia groups may be replaced by water molecules. These "aquo" salts, as they are called, were represented by Jörgensen [1] as oxonium salts. For instance, dichloro-tetrammino-cobaltic chloride is transformed into aquo-dichloro-triammino-cobaltic chloride by replacement of one ammonia molecule by one water molecule, a reaction which was represented thus:



This theory of the constitution of the metal-ammines is known as the Jörgensen-Blomstrand theory, and was generally accepted until 1893, when Werner put forward his hypothesis of co-ordination. According to **Werner's theory,** the ammonia molecules in the metal-ammines are joined directly to, or "co-ordinated" with, the metal, the whole constituting a "co-ordination complex." The complex is stable within itself, and may pass from one reaction to another as a whole, or it may undergo reactions whereby one or more molecules or groups within the complex are replaced by others. Each metal has a maximum co-ordination number, and only that number of ammonia molecules, or acidic or neutral groups in place of ammonia, can be associated with the metal in the complex. The co-ordination number in the ammines may be six, five, four, three, or two, six being the number in the majority of the compounds. Werner assumes that the ammonia molecules and any acid or water molecules in the co-ordination complex are symmetrically disposed around the central metal atom. Thus, in the case of metals of co-ordination number six the groups or atoms are presumed to occupy the angular points of a regular octahedron with the metal at the centre. Further, the acidic radicles outside the complex are combined with the complex as a whole and not with any particular atom or group in it.

The valency of the complex radicle is the same as that of the central metallic atom when the complex contains only ammonia, substituted ammonia, water, or other neutral group. For example, cobalt in cobaltic salts is trivalent, and the cobalt complex with ammonia, $[Co(NH_3)_6]^{\cdot\cdot\cdot}$, is likewise trivalent; copper in cupric sulphate is divalent, and the copper complex, $[Cu(NH_3)_4]^{\cdot\cdot}$, is also divalent. In the same way $[Co(NH_3)_5.H_2O]^{\cdot\cdot\cdot}$ and $[Co(NH_3)_4.(H_2O)_2]^{\cdot\cdot\cdot}$ are trivalent, as also $[Co(NH_3)_2.en_2]^{\cdot\cdot\cdot}$ and $[Co.en_3]^{\cdot\cdot\cdot}$, where en represents ethylenediamine,  $\begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix}$. When acidic radicles enter the complex, however, the valency is diminished by a corresponding amount thus:

$[Co(NH_3)_5.Cl]^{\cdot\cdot}$ and $[Co(NH_3)_5.(NO_2)]^{\cdot\cdot}$ are divalent, $[Co(NH_3)_4.Cl_2]^{\cdot}$ and $[Co(NH_3)_4.(NO_2)_2]^{\cdot}$ are monovalent, and $[Co(NH_3)_3.(NO_2)_3]$ has no free valency and is a non-electrolyte, all valency in this case being used up within the complex.

The valency of the complex, therefore, is found by subtracting the number of acidic radicles from the total valency of the metal. Thus, $[Co(NH_3)_4.(NO_2)_2]^{\cdot}$ has two acidic radicles, the valency of the central

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1897, 11, 448; 1900, 14, 417.

atom is three, hence valency of the complex is three minus two, that is unity. In the case of a divalent acidic radicle the problem is more difficult, because the acid may occupy either one or two co-ordinate positions. For instance, the complex $[Co(NH_3)_5.SO_4]^{\cdot\cdot}$ has an apparent valency of three minus one, that is two, since the SO_4— radicle occupies only one co-ordinate position, whilst the complex $[Co(NH_3)_4.SO_4]^{\cdot}$ would have unit valency, since the SO_4— radicle occupies two co-ordinate positions.

In some instances the metal complex may become the anode instead of the cathode. The acidic radicles have, in this case, increased at the expense of ammonia until there is a greater number of acidic radicles in the complex than corresponds to the valency of the metallic atom thus: $[Co(NH_3)_2.(NO_2)_4]'$. If valency is determined by the above method it is found, since cobalt is trivalent, and $(NO_2)_4$ has a total valency of four, that the valency of the complex, namely, three minus four, has a unit negative value. The complex is thus anodic and unites with one atom of a monovalent metal or its equivalent. The complex radicle cited, therefore, united with potassium yields the substance $[Co(NH_3)_2.(NO_2)_4]K$, or potassium tetranitrito-diammino-cobalt.

Nomenclature.—A definite system of nomenclature has been adopted for metal-ammines, and the old names derived from the colour of the compounds have, in the main, been abandoned, as they lead to confusion. The system adopted is that suggested by Werner. Ammonia molecules present in the complex are indicated by the terms "monammino," "diammino," "triammino," "tetrammino," "pentammino," "hexammino," the word *ammino*, written with a double *m*, having been adopted to show the relationship with ammonia and to distinguish from the ammonium salts and the substituted ammonia compounds, namely, the amines.

The co-ordination complex is placed within square brackets, and the acidic, metallic, or other radicles, not included in the complex, are placed outside the bracket. Thus the complex derivative of cobaltic chloride containing six ammonia molecules is represented as $[Co(NH_3)_6]Cl_3$. Where the ammine contains other groups besides ammonia in the complex the ammonia molecules are always placed next to the metal, then follow acidic, water, or neutral groups. In describing the compound it is usual to name the groups in the co-ordination complex before the metal, and the ionisable groups, that is those not included in the complex, after the metal. The above example is therefore designated hexammino-cobaltic chloride. When part of the ammonia in the complex is replaced by acidic or water molecules the acid or water is named before ammonia, and, furthermore, if both acid and water are present the acidic group is named before the water. For example, the substance, $[Cr(NH_3)_4.Cl.H_2O]Cl_2$, is monochloro-aquo-tetrammino-chromic chloride. The number of each radicle in the complex is denoted by prefixes thus: $[Co(NH_3)_3.Cl.(H_2O)_2]Cl_2$ is monochloro-diaquo-triammino-cobaltic chloride. In some cases it is not necessary to use a prefix for all the radicles, and the above compound would be correctly named, and its formula could be written from the name chloro-diaquo-triammino-cobaltic chloride, as it is known that the co-ordination number for cobalt in this series of compounds is six. Further, certain conventions are observed to distinguish radicles in the complex from those outside of it. The acidic radicles are given the termination *o* thus: chlorine in the complex is "chloro"; sulphate is "sulphato"; nitrate is "nitrato"; nitrite is "nitrito" or "nitro"; whilst water in the complex is distinguished as "aquo," and the hydroxyl group as "hydroxo."

A few examples will illustrate the use of these terms. Chloro-pentammino-cobaltic chloride is written as $[Co(NH_3)_5.Cl]Cl_2$, nitrito-aquo-tetrammino-cobaltic chloride as $[Co(NH_3)(NH_3)_4(NO_2).H_2O]Cl_2$, and chloro-aquo-tetrammino-cobaltic chloride as $[Co(NH_3)_4Cl(H_2O)]Cl_2$. It will be observed that the co-ordination number in each of the complexes is six, and this is characteristic not only of cobalt-ammines, but also of many other complexes. Some metals, however, yield complexes with co-ordination number four. For example, tetrammino-cupric sulphate, $[Cu(NH_3)_4]SO_4$, and tetrammino-platinous chloride, $[Pt(NH_3)_4]Cl_2$, belong to this class. On the other hand, the co-ordination number of hexammino-platinic chloride, $[Pt(NH_3)_6]Cl_4$, is six, but the central metallic atom is tetravalent, hence there are four chlorine atoms in the outer dissociable zone.

Complexes are also known in which the co-ordination numbers are one, two, three, five, seven, and even eight respectively, but these are less frequent. As examples may be mentioned sulphito-copper potassium, $[Cu(SO_3)]K$, and the unstable nitroso-ferrous sulphate, $[Fe(NO)]SO_4$, each of which possess unit co-ordination number. Diammino-silver chloride, $[Ag(NH_3)_2]Cl$, and triammino-silver chloride, $[Ag(NH_3)_3]Cl$, possess co-ordination numbers two and three respectively. In penta-phenylhydrazino-zinc sulphate, $[Zn(NH_2.NH.C_6H_5)_5]SO_4$, and octammino-strontium chloride, $[Sr(NH_3)_8]Cl_2$, the co-ordination numbers are five and eight respectively.

Stability of the Metal-ammines.—Most metallic salts combine with ammonia, forming ammines of varying stability. The alkaline earth salts, for instance, unite with ammonia, yielding such compounds as $CaCl_2.6NH_3$ and $CaCl_2.8NH_3$, which are known only in the solid state and decompose when dissolved in water. On the other hand, the metals of group eight form ammines which are so stable that they may be treated, in many cases, with concentrated acid without removal of ammonia. Between these two classes there are ammino-compounds of all grades of stability. Numerous theories have been advanced to account for the different stability of the ammines. According to Ephraim,[1] the stability of the metal-ammines depends on the atomic volume of the central atom of the complex. He assumes that if the pressure is kept constant the temperature at which decomposition takes place is a measure of the strength of the auxiliary valencies. Experiments were carried out to determine the temperature at which the hexammino-derivatives of the chlorides of the metals beryllium, nickel, cobalt, iron, copper, manganese, zinc, cadmium, and magnesium each exert an ammonia vapour pressure of 500 mm. The results indicated that the temperature decreases as the atomic volume increases. It is therefore assumed that the strength, or energy, of auxiliary valency is a function of the atomic volume of the central atom of the complex. Similar results were obtained for the hexammino-bromides, iodides, and sulphates.

It is pointed out, however, that the atomic volume of the central

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[1] Ephraim, *Ber.*, 1912, 45, 1322.

atom cannot be the only factor, for copper and iron have the same atomic volume, and yet the hexammino derivatives have different dissociation temperatures; whilst beryllium, which has the least atomic volume of the metals quoted, gives a hexammino-chloride which is so unstable that it decomposes before the dissociation pressure of 500 mm. is reached. Further, those metals with an atomic volume greater than 14 do not yield stable hexammino-compounds at ordinary temperatures, and the effect of the atomic volume on the stability appears to diminish with increased atomic volume of the metallic atom. It is also influenced by the anion, for experiment shows that the ratio of the absolute temperatures at which the hexammino-chlorides and the hexammino-bromides exert the same vapour pressure is $^{T}NiBr_2 : {}^{T}NiCl_2 = 1{\cdot}073$, and for the corresponding cobalt compounds is $^{T}CoBr_2 : {}^{T}CoCl_2 = 1{\cdot}086$. This constant Ephraim named the "tension modulus," and the moduli observed for the ratio Cl : I, Br : I, and SO_4 : I vary between 1·08 and 1·10.

The ability of a substance to form addition compounds seems also to be connected with the magnitude of the space occupied by various parts of the molecule. If the anion be large the additive capacity of the atom becomes much more than it was originally, and a large anion may render a small cation capable of addition reactions.[1]

Ephraim and Müller [2] describe some results obtained with the groups $-SO_4$, $-SeO_4$, $-MoO_4$, $-WO_4$, and $-CrO_4$. These anions were united with the hexammino-nickel complex, and the temperature measured at which the ammonia tension is equal to atmospheric pressure. The stability of the complex is apparently independent of the atomic volumes of selenium, sulphur, chromium, molybdenum, and tungsten, but increases proportionally with the molecular volume of the corresponding trioxides.

Ephraim and Bolle [3] find that the stability of the ammines of general formula $[M(NH_3)_n]R_2$ depends not only on the central atom but also on the anion. These influences oppose one another, and the stability of the whole molecule is therefore the resultant of the two influences; consequently, very little parallelism may appear between analogous compounds. For instance, the temperatures of decomposition of the hexammino-salts of nickel decrease in the order perchlorate, iodide, bromide, chlorate, nitrate, chloride, sulphate; whilst in the case of the hexammino-salts of zinc, the order for decreasing stability is iodide, bromide, chloride, perchlorate, sulphate, nitrate, chlorate.

In general it is found that salts of strong acids yield more stable ammines than do those of weak acids, and in most cases the stability of the ammine is parallel with the stability of the corresponding ammonium salt. For instance, both hexammino-nickel iodide, $[Ni(NH_3)_6]I_2$, and ammonium iodide decompose at higher temperatures than hexammino-nickel bromide, $[Ni(NH_3)_6]Br_2$, and ammonium bromide. The more stable ammines are also the least soluble in water.

No sharp line can be drawn between double and complex salts, the difference being merely a difference in the amount of ionisation. In the metal-ammines the complex may be very little ionised, and the central atom is therefore not present, to any appreciable extent, as

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[1] Ephraim and Rosenberg, *Ber.*, 1918, 51, 644; Ephraim and Moser, *ibid.*, 1920, 53, 548.

[2] Ephraim and Müller, *ibid.*, 1921, 54, 973.

[3] Ephraim and Bolle, *ibid.*, 1915, 48, 638.

metal ion. Take, for example, hexammino-cobaltic chloride; the substance in solution does not react with cold sodium hydroxide, but ammonium sulphide causes the precipitation of cobaltous sulphide. By employing different reagents, therefore, the concentration of metal ion in solution may be determined. The complex ion, $[Co(NH_3)_6]^{\cdots}$, to a certain extent ionises to give cobalt ion and ammonia. The most stable of the metal-ammines are little ionised in solution, and give mostly the complex ion and acidic or basic ion without the complex. On the other hand, the unstable ammines in solution yield a large proportion of free metal ion from the complex; that is, secondary ionisation has gone further. The stability of the ammines has been determined by measuring the secondary ionisation by the employment of reagents of differing sensitiveness.[1]

It is difficult, in view of the above observations, however, to make any safe generalisation regarding the stability of the ammines.

Formation of Metal-ammines.—The compounds may be formed in several ways, such as treating the dry metal salts with ammonia gas until absorption is complete; by treating the salts with liquid ammonia; or from an aqueous solution of the salt and aqueous ammonia. The method of formation depends on the stability of the ammine. In some cases the ammine has not been isolated in the solid state, and its presence in solution is only indicated by the behaviour of the liquid.

Isomerism in the Metal-ammines.—Werner claimed for the co-ordination theory that in certain cases isomerism should occur, that isomerism being brought about by different causes. He divided isomerism in the ammines into five groups, namely, structure isomerism, ionisation isomerism, hydrate isomerism, polymerism, and stereo-isomerism.

Structure Isomerism.—Many examples of this type of isomerism occur thus: aquo-pentammino-cobaltic chloride, $[Co(NH_3)_5.H_2O]Cl_3$, if treated with nitrous acid yields a red unstable compound which, on standing, changes to a brown stable substance, the change being as follows :—

$$\begin{array}{lll} [Co(NH_3)_5.H_2O]Cl_3+HNO_2 & \longrightarrow & [Co(NH_3)_5(ONO)]Cl_2+HCl \\ & & \quad\big\downarrow \text{ Red unstable.} \\ & & [Co(NH_3)_5NO_2]Cl_2 \\ & & \quad \text{Brown stable.} \end{array}$$

Other more stable salts of this type, such as the substances $[Co\,en_2(ONO)_2]R$ and $[Co\,en_2(NO_2)_2]R$, contain the (ONO) and the (NO_2) group respectively. The former are brick-red in colour, the latter are brown. The isomerism is due to these groups which are distinguished as nitrito, (ONO), and nitro, (NO_2).[2, 3]

Salts containing the nitrito-group are easily decomposed by dilute acids, those containing the nitro-group are stable towards acid. Further, on standing, or more readily on heating, the nitrito-compounds pass into the nitro-derivatives.

Isomerism of this kind occurs wherever tautomeric acidic radicles are introduced into the molecule. Isomeric thiocyanato-compounds

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[1] Bodländer, *Zeitsch. physikal. Chem.*, 1903, 39, 602.
[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1893, 5, 168; 1899, 19, 149.
[3] Werner, *Ber.*, 1907, 40, 768.

are known; for instance, the two series of salts, $[\mathrm{Co\ en_2(NCS)_2}]\mathrm{R}$ and $[\mathrm{Co\ en_2(SCN)_2}]\mathrm{R}$.

The constitution of these is determined by oxidation, the thiocyanato-compounds being easily oxidised by chlorine, whereas the isothiocyanato-derivatives are not.

Ionisation Isomerism.—This type of isomerism is very common in the metal-ammines. If two or more different acidic radicles are present in a molecule of metal-ammine, the acidic radicles may be firmly fixed in the co-ordination complex or may be outside of this. If they are outside the complex they are easily ionised and easily freed by other acids; if, on the other hand, they are within the complex they are not ionised and are difficult to free by other acids. This distribution of the acidic radicles in the complex, or outside of it, gives rise to ionisation isomerism. For example, the compound $\mathrm{Co(NH_3)_5Br(SO_4)}$ is known in two forms, one violet and the other red. The violet modification in aqueous solution contains $-\mathrm{SO_4}''$ ions, which may be precipitated by barium chloride. The red variety gives no $-\mathrm{SO_4}''$ ions in aqueous solution, and barium sulphate is not precipitated by barium chloride. These two substances, bromo-pentammino-cobaltic sulphate and sulphato-pentammino-cobaltic bromide, are ionisation isomers, and are represented as:

$$\underset{\text{Violet.}}{[\mathrm{Co(NH_3)_5Br}]\mathrm{SO_4}} \quad \text{and} \quad \underset{\text{Red.}}{[\mathrm{Co(NH_3)_5SO_4}]\mathrm{Br}}.$$

In the same way chloro-pentaquo-chromic sulphate, $[\mathrm{Cr(H_2O)_5Cl}]\mathrm{SO_4}$, is isomeric with sulphato-pentaquo-chromic chloride, $[\mathrm{Cr(H_2O)_5SO_4}]\mathrm{Cl}$.

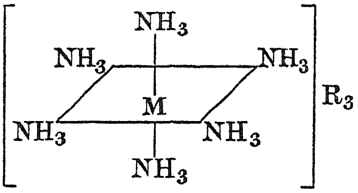
Hydrate Isomerism.—As its name implies, this depends on the position of water in the molecule, just as in the case of the acido compounds. If two or more molecules of water are present in a molecule of ammine, the water may be present within the co-ordination complex or outside of it. For instance, the compound $\mathrm{Cr\ en_2.(H_2O)_2.Br_3}$ exists in isomeric forms. It may have all the water within the complex, in which case the formula will be $[\mathrm{Cr\ en_2(H_2O)_2}]\mathrm{Br_3}$. In solution the whole of the bromine is precipitated by silver nitrate. On the other hand, the compound may have one molecule of water in the complex and the other outside, in which case the formula is $[\mathrm{Cr\ en_2(H_2O)Br}]\mathrm{Br_2.H_2O}$, and only two-thirds of the bromine are precipitated by silver nitrate. Another example of this kind occurs in the cobalt series: chloro-aquo-tetrammino-cobaltic chloride, $[\mathrm{Co(NH_3)_4Cl.H_2O}]\mathrm{Cl_2}$, is violet in colour, and is isomeric with dichloro-tetrammino-cobaltic chloride monohydrate, $[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl.H_2O}$, which is green.

Polymerism.—This may be regarded as similar to polymerism in organic compounds. The best example of this type of isomerism is shown in triammino-trinitro-cobalt, $[\mathrm{Co(NH_3)_3(NO_2)_3}]$. Polymers have been prepared which are dimolecular, trimolecular, up to pentamolecular, thus:

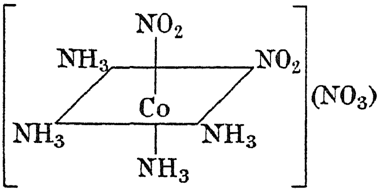
$$\begin{aligned}
&[\mathrm{Co(NH_3)_3(NO_2)_3}]_2 &&\text{or}\quad [\mathrm{Co(NH_3)_6}][\mathrm{Co(NO_2)_6}],\\
&[\mathrm{Co(NH_3)_3(NO_2)_3}]_3 &&\text{or}\quad [\mathrm{Co(NO_2)(NH_3)_5}][\mathrm{Co(NO_2)_4(NH_3)_2}]_2,\\
&[\mathrm{Co(NH_3)_3(NO_2)_3}]_4 &&\text{or}\quad [\mathrm{CO(NH_3)_6}][\mathrm{Co(NO_2)_4(NH_3)_2}]_3,\\
&[\mathrm{Co(NH_3)_3(NO_2)_3}]_5 &&\text{or}\quad [\mathrm{Co(NH_3)_5NO_2}]_3[\mathrm{Co(NO_2)_6}]_2.
\end{aligned}$$

Polymers of chromium compounds of this type are also known. Thus, $[\mathrm{Cr(NH_3)_3(SCN)_3}]$, which has been prepared up to pentamolecular form.

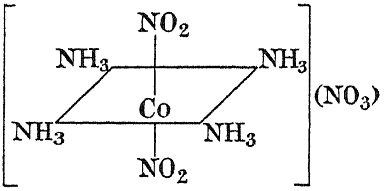
Stereo-isomerism.—Werner gave to the elements with co-ordination number six, which constitute the largest and most important class of the metal-ammines, a spatial configuration where the six co-ordination groups are arranged around the central metal atom, which is situated at the centre of a regular octahedron with the co-ordinated groups at the angles of the figure. That is, to the compounds of general formulæ $[M(NH_3)_6]R_3$ is given the configuration :



Such a configuration should on replacement of one ammonia molecule by acidic or other monovalent radicle yield only one compound, and this is proved to be the case. On the other hand, if two acidic or other groups replace two ammonia groups in the complex, isomerism should be possible, yielding two isomers of the formula $[M(NH_3)_4R_2]R$. In the case of dinitro-tetrammino-cobaltic nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3$, two isomeric forms are known to exist, one brown in colour, the other yellow. The two substances may be represented by the following formulæ :—

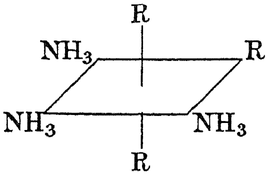


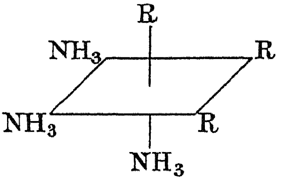
1-, 2-, dinitro-, or *cis*.



1-, 6-, dinitro-, or *trans*.

When three ammonia groups are substituted by acidic groups two isomers are theoretically possible, and this is again proved by experimental evidence. The configuration of the complex is represented thus :





The isomers of type $[M(NH_3)_4R_2]R$ differ in properties, solubility, colour, and reactivity. For instance, the dichloro-tetrammino-cobaltic chlorides are green and violet respectively. The violet-coloured salt is known as the " violo " salt and the green as the " praseo " salt.

Werner [1] endeavoured to determine the structure of these isomers, and concluded that the isomerism of these compounds was of the *cis-trans* type of organic substances. Reasoning from this, he replaced the two

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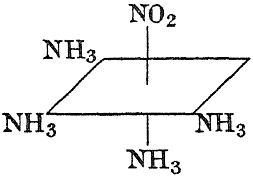
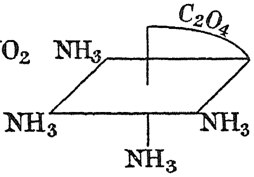
[1] Werner and Humphrey, *Ber.*, 1901, 34, 1720.

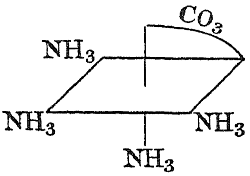
substituted groups by a divalent group which occupied two co-ordinate positions, and found that only one form allowed replacement to take place readily. Hence he concluded that the form which reacted easily was the form with the acidic radicles in the adjacent positions; thus, by substituting two nitro groups by an oxalate or carbonate group the following configurations were obtained :—



1-, 2-, dinitro-, or *cis*.



Oxalato-.

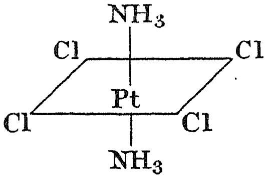


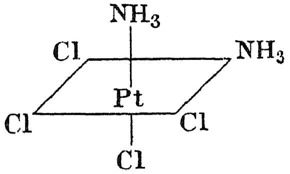
Carbonato-.

Also, on replacement of oxalato- or carbonato-group by nitro-, chloro-, or bromo-radicles, brown salts are obtained with acid and sodium nitrite, and violet salts on treatment with concentrated hydrochloric or hydrobromic acid. The brown nitro-compounds are therefore given a formula with the nitro-groups in the 1-, 2-, or *cis*-position, and the violet halogen salts the formula with halogen in the *cis*-position. The *cis*-form may be transformed into the *trans*-modification by intramolecular rearrangement. Concentrated hydrochloric acid converts carbonato-tetrammino-cobaltic salts first into violo-salts, and on standing, or on rise of temperature, these pass into the praseo- or 1-, 6-salts.

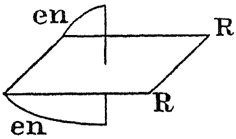
In the triacido-triammino-metallic salts two isomers are possible, according as the three similar groups lie in one plane or in different planes. Many of these isomers have been isolated.

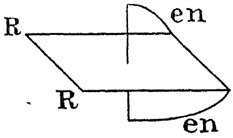
The two isomeric tetrachloro-diammino-platinum salts also belong to this class of isomerism, the configurations being :





If in the complex, $[M(NH_3)_4R_2]$, ammonia be replaced by a divalent basic group such as ethylenediamine, a further type of isomerism is possible; that is, the *cis*-form should exist in two enantiomorphous forms related thus :





as these configurations are related as object to mirror image.

Werner and Kling [1] found that two such isomers can be obtained from the *cis*-salt of type $[M(NH_3)_4R_2]R$. They prepared the compounds 1-chloro-2-ammino-diethylenediamino-cobaltic chloride,

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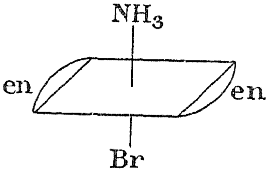
[1] Werner and Kling, *Ber.*, 1911, 44, 1887 ; 1912, 45, 3287.

$[Co(NH_3)en_2Cl]Cl$, and 1-bromo-2-ammino-diethylenediamino-cobaltic bromide, and found that these can be resolved into the optical isomers by means of d-bromo-camphorsulphonic acid. The salts of the bromo-ammino series were more easily resolved, as there is greater difference between the solubility of the d-bromo-camphorsulphonates. In both cases the d-isomer is more sparingly soluble. These active compounds are stable, and aqueous solutions of the bromides of the bromammine series may be kept for long at ordinary temperature.

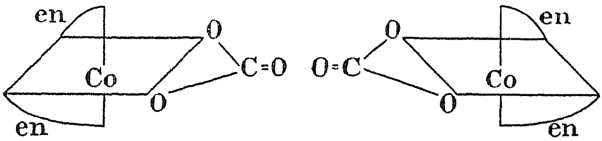
Further, the *trans*-series of salts has never been found to give isomers, as they are symmetrical, and therefore such isomerism should not exist. 1-bromo-6-ammino-diethylenediamino-cobaltic bromide therefore exists in only one form, and the configuration is given by



1-, 6-, or *trans*-form.

The asymmetry of the two *cis*-forms manifests itself in the form of crystals which are enantiomorphous, and in the action of the substances in solution on plane polarised light.

All compounds, therefore, with complex radicle $[Co\,en_2R_2]$, in which the two groups R are in the *cis*-position, can be resolved into optically active forms. Further, by replacing the two groups in the *cis*-position by a divalent acidic radicle such as carbonato-radicle, a compound is produced which does not exist in *cis*- and *trans*-forms but which may be resolved into optical isomers. Thus, carbonato-diethylenediamino-cobaltic salts are known in two optically active forms [1] represented by the structural formulæ



After the resolution of 1-2-chloro-ammino-diethylenediamino-cobaltic chloride many analogous resolutions of optically active compounds of octahedral symmetry were carried out, and active isomers of substances containing central cobalt, chromium, platinum, rhodium, iron atoms are known. The asymmetry is not confined to ammines alone, but is found in salts of complex type ; for example, potassium trioxalato-chromium, $[Cr(C_2O_4)_3]K_3$, exists in two optically active forms. These forms were separated by Werner [2] by means of the base strychnine. More than forty series of compounds possessing octahedral symmetry have been proved to exist in optically active forms, so that the spatial configuration for co-ordination number six is firmly established.

Among polynuclear ammines optical activity also occurs, and in

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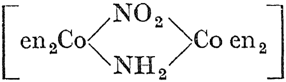
[1] Werner and McCutcheon, *Ber.*, 1912, 45, 3281.

[2] Werner, *ibid.*, 1912, 45, 3061.

accordance with Werner's theory the compounds containing two metallic central atoms should exist in four forms—two optically active isomers, l- and d-, and two inactive forms, one being the *meso*-form inactive by internal compensation, the other the racemic form, a mixture of equal quantities of the d- and l-forms. Werner's expectation was fulfilled, for he obtained four distinct isomers of the compound  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NO_2}\\ \\ \mathrm{NH_2}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{R_4}$. These corresponded exactly with the four possible isomers of tartaric acid, and gave further proof of the correctness of the co-ordination theory.[1]

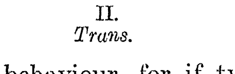
Doubt was thrown on the reason for optical activity in these compounds, as all those considered contained a carbon residue of some sort, such as the $C_2H_4(NH_2)_2$, the C_2O_4, or pyridyl group. In 1914, however, Werner [2] succeeded in preparing optically active isomers containing none of these groups, a purely inorganic compound. In this compound the complex $[Co(NH_3)_4(OH)_2]$ replaced ethylenediamine or other basic group, and three such complex radicles were co-ordinated with cobaltic bromide, giving the substance $Co[Co(NH_3)_4(OH)_2]_3Br_6.2H_2O$. This was successfully resolved by means of bromo-camphorsulphonic acid, proving conclusively that optical activity in these compounds is not due to the presence of special groups but is a geometric property of the complex.

Since then even more complex cases of isomerism have been discovered. For instance, a series of compounds containing asymmetric cobalt and asymmetric carbon in the molecule have been prepared,[3] and here again the theoretical number of isomers is obtained. In the metal-ammines of co-ordination number four the configuration is assumed to be planar. The co-ordinated groups are arranged at the corners of a plane figure with the metal atom at the centre. *Cis* and *trans* isomerism is possible with such a configuration, thus the compound dichloro-diammino-platinum exists in two isomeric forms which differ in colour, one being orange-yellow, the other yellow. They may be represented as :

$$\left[\begin{matrix}\mathrm{NH_3} & & \mathrm{Cl}\\ & \mathrm{Pt} & \\ \mathrm{NH_3} & & \mathrm{Cl}\end{matrix}\right]$$

I.
Cis.

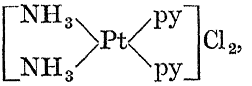
and



$$\left[\begin{matrix}\mathrm{NH_3} & & \mathrm{Cl}\\ & \mathrm{Pt} & \\ \mathrm{Cl} & & \mathrm{NH_3}\end{matrix}\right].$$

II.
Trans.

These isomers differ in chemical behaviour, for if two molecules of pyridine are caused to act upon Compound I., dichloro-diammino-platinum, the chlorine is replaced in the complex by two molecules of pyridine, and the substance dipyridino-diammino-plato-chloride is formed:



$$\left[\begin{matrix}\mathrm{NH_3} & & \mathrm{py}\\ & \mathrm{Pt} & \\ \mathrm{NH_3} & & \mathrm{py}\end{matrix}\right]\mathrm{Cl_2},$$

where py represents pyridine.

Formula II. also reacts with pyridine, yielding dipyridino-diammino-

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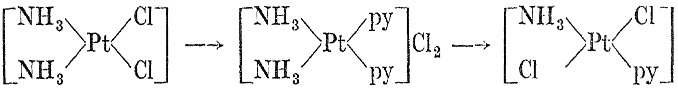
[1] Werner, *Ber.*, 1913, 46, 3674.
[2] Werner, *Compt. rend.*, 1914, 154, 426.
[3] Werner, *Helv. Chim. Acta.*, 1918, 1, 5.

plato-chloride, but the compound is not identical with that obtained from Formula I. The first pyridine compound on heating loses one molecule of pyridine and one molecule of ammonia; the second pyridine derivative loses either two molecules of ammonia or two molecules of pyridine, yielding a mixture of dichloro-dipyridino-platinum and dichloro-diammino-platinum.[1]

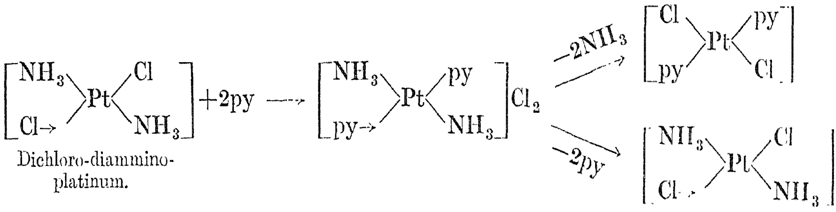
The transformation may be represented in the following manner:—

I.



Dichloro-diammino-platinum. *Cis.* *Trans.*

II.



Dichloro-diammino-platinum. *Trans.*

In this way the configuration of the ammines of divalent platinum is deduced, and this agrees with theoretical considerations. A number of this type is known.

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[1] Werner, *Zeitsch. anorg. Chem.*, 1893, 3, 310.

CHAPTER IV.

METAL-AMMINES OF THE ELEMENTS OF GROUP I.

THE AMMINES OF COPPER, SILVER, AND GOLD.

THE metals copper, silver, and gold show a marked tendency to form double and complex salts, the tendency being greatest in the case of gold, the member of the group with highest atomic weight.

Ammino-derivatives of Copper Salts.

It is well known that metallic copper is attacked by ammonia in aqueous solution, yielding a deep blue solution; that cupric hydroxide dissolves in aqueous ammonia, yielding a blue solution known as Schweizer's reagent; and that a solution of cupric sulphate, when treated with excess of ammonia, gives a deep blue solution from which dark blue prismatic crystals may be obtained of composition $CuSO_4.4NH_3.H_2O$. These observations are explained by the fact that the salts readily form complex derivatives with ammonia known asouprammines.[1]

By the action of ammonia on cuprous or on cupric salts, substances are formed containing varying amounts of ammonia. Cuprous ammines are colourless, unstable, and readily turn blue, passing into the more stable cupric ammines. The cupric ammines are deep blue in colour and dissolve in water, yielding dark blue solutions. In the dry state many of them are stable. The most important ammines of copper are those of the salts, cupric chloride and cupric sulphate.

Ammino-derivatives of Cupric Sulphate.—Cupric sulphate forms with ammonia four ammino derivatives, namely, *pentammino-cupric sulphate*, $[Cu(NH_3)_5]SO_4$; *tetrammino-cupric sulphate*, $[Cu(NH_3)_4]SO_4$; *diammino-cupric sulphate*, $[Cu(NH_3)_2]SO_4$; and *monammino-cupric sulphate*, $[Cu(NH_3)]SO_4$. The tetrammino salt is the best known and the one most easily obtained. It exists both in the anhydrous and in the hydrated state.

Monohydrated Tetrammino-cupric Sulphate, $[Cu(NH_3)_4]SO_4.H_2O$.—The compound was first described by Stisser in 1693 and later analysed by Berzelius, who proved it to contain four molecules of ammonia and one molecule of water. It is formed by treating an aqueous solution of cupric sulphate with excess of ammonium hydroxide and precipitating the deep blue compound by the addition of alcohol. The same derivative may be obtained by passing ammonia gas into an aqueous solution of cupric sulphate, when, as the ammonia concentration

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[1] Dawson, *Trans. Chem. Soc.*, 1906, 89, 1666.

increases, crystals of the ammine are precipitated. This process is the one usually adopted for the preparation of the compound. The crystals are collected and dried over lime. They cannot be dried over sulphuric acid, *in vacuo*, or over calcium chloride without decomposition. Even in air the salt is unstable, and can be dried between filter-paper or on porous tile only in small quantity.

The ammine crystallises in dark blue prisms belonging to the rhombic system. In the dry state it has no odour, but loses ammonia on exposure to moist air, the crystals becoming opaque and much lighter in colour, passing finally into a green powder composed of ammonium sulphate and basic cupric sulphate. It may be kept over lime in a closed vessel without loss of ammonia. On heating in dry air it is stable up to 30° C., thereafter it gradually loses ammonia. Dawson and McCrae [1] state that between 100° and 125° C. it loses one molecule of water and two molecules of ammonia, whilst Horn and Taylor [2] claim that between 125° and 149° C. ammonia is gradually lost, and that from 149° to 260° C. the whole of the ammonia is eliminated; but no definite compounds can be obtained at the various temperatures, and the decomposition products seem to consist of mixtures of salts. If the mono- and di-ammine are formed they appear to be mixed with other products. The tetrammine is fairly soluble in water, 18·05 grams dissolving in 100 grams of water at 21° C. Decomposition in aqueous solution occurs, probably due to hydrolysis, as, if kept in solution, basic salts are gradually precipitated. Some controversy has arisen regarding the water content of the tetrammine; Berzelius assigned to it the composition $CuSO_4.4NH_3.1H_2O$, whilst Bouzat [3] suggested that the compound contained more water, and gave it the composition $CuSO_4.4NH_3.1\frac{1}{2}H_2O$. Later investigators [4] proved the substance to contain only one molecule of water.

Anhydrous Tetrammino-cupric Sulphate, $[Cu(NH_3)_4]SO_4$.—The anhydrous tetrammino salt is prepared by passing ammonia gas over dehydrated cupric sulphate at a temperature between 90° and 150° C.,[5] or by keeping pentammino-cupric sulphate in a desiccator over sulphuric acid.

It is a bluish-violet powder, stable up to 140·5° C., but when heated above 150° C. it dissociates, yielding diammino-cupric salt and ammonia.[6] It is soluble in water, but much water causes decomposition and precipitation of basic salts.

Pentammino-cupric Sulphate, $[Cu(NH_3)_5]SO_4$.—Anhydrous cupric sulphate is insoluble in liquid ammonia, but both anhydrous and hydrated salt absorb ammonia gas. At first the reaction is vigorous, the white anhydrous salt becomes blue and then absorption of ammonia gradually slows down; the product formed is assumed to be the pentammino-sulphate.

Pentammino-cupric sulphate is prepared by allowing carefully dried ammonia gas to act upon cooled, dry cupric sulphate.[7] The product is stable if kept over sulphuric acid, but is decomposed by moist

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[1] Dawson and McCrae, *Trans. Chem. Soc.*, 1901, 79, 496.

[2] Horn and Taylor, *Amer. Chem. J.*, 1904, 32, 253.

[3] Bouzat, *Ann. Chim. Phys.*, 1903, [7], 29, 305.

[4] Horn and Taylor, *ibid.*; H. M. Dawson, *Trans. Chem. Soc.*, 1906, 89, 166.

[5] Bouzat, *Ann. Chim. Phys.*, 1903, [7], 29, 372.

[6] Ephraim, *Ber.*, 1919, 52, 940.

[7] Bouzat, *loc. cit.*

air, when water gradually replaces ammonia, forming the substances $[Cu(NH_3)_4]SO_4.H_2O$ and $[Cu(NH_3)_2]SO_4.3H_2O$.

Pentammino-cupric sulphate melts below 200° C., darkens in colour, and at 400° C. completely decomposes, leaving a residue of metallic copper. It is stable up to 99° C., and when heated between 99° and 141° C. loses one molecule of ammonia and passes into tetrammino-cupric sulphate.[1]

Diammino-cupric Sulphate, $[Cu(NH_3)_2]SO_4$, is formed when tetrammino-cupric sulphate is heated above 150° C. It is an apple-green powder, which absorbs moisture from the air and becomes blue in colour.

Hydroxylamine Derivatives.—Several derivatives of cupric sulphate containing hydroxylamine in place of ammonia are known. Thus, cupric sulphate unites with hydroxylamine, giving a mono-hydroxylamino-compound $Cu[NH_2OH]SO_4$, a dihydroxylamino-salt, $[Cu(NH_2OH)_2]SO_4$, and a pentahydroxylamino-salt, $[Cu(NH_2OH)_5]SO_4$. The latter is unstable, but the two former compounds are stable in the dry state and even in solution up to 0° C. Above that temperature reduction of the salts occurs.

Cupro-ammino-sulphates.—Cuprous sulphate unites with ammonia, forming complex salts. **Tetrammino-cuprous sulphate,** $[Cu_2(NH_3)_4]SO_4$, and **mono-hydrated tetrammino-cuprous sulphate,** $[Cu_2(NH_3)_4]SO_4.H_2O$, are known. These salts are prepared by reducing ammoniacal cupric sulphate solution with hydroxylamine or with metallic copper and hydrogen, or from cuprous oxide. Péchard[2] prepared the compounds by adding hydroxylamine sulphate to an alcoholic, ammoniacal solution of cupric sulphate, when the tetrammine, $[Cu_2(NH_3)_4]SO_4$, is precipitated mixed with some ammonium sulphate. It is obtained free from ammonium sulphate by reducing basic cupric carbonate with hydroxylamine sulphate in ammonia solution at a temperature of 80° C., when, on cooling, and adding alcohol, the ammine is precipitated. The same ammine is formed by adding alcohol to a mixture of cuprous oxide and aqueous ammonium sulphate at 50° C. in an atmosphere of hydrogen.[3]

The ammine crystallises in hexagonal plates which are colourless, readily oxidised in air, insoluble in alcohol, and decomposed by water. It is stable up to 100° C., but above that temperature loses ammonia, liberating Cu_2SO_4, which then decomposes. The salt reduces nitric acid, and is broken down by dilute sulphuric acid, copper being precipitated and cupric ammonium sulphate formed.

The *hydrated salt* is obtained by passing a weak electric current through a strongly ammoniacal solution of cupric sulphate.[4] It forms colourless needle-shaped crystals and behaves like the anhydrous form.

Ammino-salts of Cupric Halides.—When an aqueous solution of cupric chloride is treated with an aqueous solution of ammonia the hydroxide is precipitated, but if excess of ammonia be added the precipitate dissolves, forming a deep blue solution. The liquid contains the tetrammino-chloride and higher ammino compounds, depending on the concentration of the ammonia in solution and the temperature.

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[1] Ephraim, *Ber.*, 1919, 52, 940.

[2] Péchard, *Compt. rend.*, 1903, 136, 505.

[3] Bouzat, *ibid.*, 1908, 146, 76.

[4] Förster and Blankenberg, *Ber.*, 1906, 39, 4435.

Anhydrous cupric chloride, like anhydrous cupric sulphate, absorbs ammonia rapidly; the absorption is accompanied by increase in bulk, and the brown chloride changes to a blue powder having the composition $CuCl_2.6NH_3$. The following compounds of cupric chloride with ammonia are known :—

Hexammino-cupric chloride, $[Cu(NH_3)_6]Cl_2$.
Pentammino-cupric chloride, $[Cu(NH_3)_5]Cl_2$.
Pentammino-cupric chloride sesquihydrate, $[Cu(NH_3)_5]Cl_2.1\frac{1}{2}H_2O$.
Pentammino-cupric chloride hemihydrate, $[Cu(NH_3)_5]Cl_2.\frac{1}{2}H_2O$.
Tetrammino-cupric chloride, $[Cu(NH_3)_4]Cl_2$.
Tetrammino-cupric chloride monohydrate, $[Cu(NH_3)_4]Cl_2.H_2O$.
Tetrammino-cupric chloride dihydrate, $[Cu(NH_3)_4]Cl_2.2H_2O$.
Diammino-cupric chloride, $[Cu(NH_3)_2]Cl_2$.
Decammino-tricupric chloride, $[3Cu(NH_3)_{10}]Cl_6$.

Hexammino-cupric Chloride, $[Cu(NH_3)_6]Cl_2$.—This salt was prepared by Faraday in 1818 by allowing ammonia gas to act upon fused cupric chloride. Increase in bulk immediately took place and a blue powder was formed. The compound may be conveniently prepared by allowing dry ammonia to act on a solution of the cupric salt in ethyl acetate, when a green precipitate of hexammino-chloride is formed which is washed with ethyl acetate and dried.[1] The same compound is obtained by the action of liquid ammonia on anhydrous cupric chloride previously saturated with ammonia gas.[2]

The substance is a pale blue powder which is insoluble in liquid ammonia, soluble in water, and decomposed by much water. It gradually dissociates, yielding the tetrammine, $[Cu(NH_3)_4]Cl_2$. On heating it loses ammonia, but there is some divergence of opinion amongst investigators regarding the temperature at which decomposition begins and the final product left. It is variously stated that the substance first melts, then gives off ammonia and leaves a residue of cupric chloride; that ammonium chloride is formed; that the final residue consists of cuprous chloride. The hexammine is stable up to 20° C. and dissociates at 46·7° C.[3]

Pentammino-cupric Chloride, $[Cu(NH_3)_5]Cl_2$, is said to be formed by saturating cupric chloride at low temperature with ammonia gas and gradually raising the temperature. Certain points are reached where evolution of ammonia occurs and where the temperature remains constant during the evolution, thus indicating the existence of a definite compound. Pentammino-cupric chloride appears to exist below 105° C. and to decompose sharply at 105° C., yielding decammino-tricupric chloride.[4]

Pentammino-cupric Chloride Sesquihydrate, $[Cu(NH_3)_5]Cl_2.1\frac{1}{2}H_2O$, is prepared by cooling an ammoniacal solution of cupric chloride to $-15°$ C., or by the action of ammonia on the ammoniacal liquid at 0° C. It is a dark blue crystalline substance and decomposes above 0° C., with formation of diammino-cupric chloride. It is soluble in water and in aqueous ammonia, and the crystals remain unaltered in an atmosphere of dry ammonia. If allowed to stand in a desiccator over

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[1] Alexander and Naumann, *Ber.*, 1899, 32, 1002.
[2] Bouzat, *Compt. rend.*, 1902, 135, 292.
[3] Horn, *Amer. Chem. J.*, 1908, 39, 203.
[4] Ephraim, *Ber.*, 1919, 52, 940.

potassium hydroxide and a mixture of lime and ammonium chloride, **pentammino-cupric chloride hemihydrate**, $[Cu(NH_3)_5]Cl_2.\frac{1}{2}H_2O$, is produced.[1]

Tetrammino-cupric Chloride, $[Cu(NH_3)_4]Cl_2$.—This is the best known of the cuprammino-chlorides. It is obtained by heating hexammino-cupric chloride to a temperature of 90° C. in a closed vessel,[2] or from the dihydrate by keeping it over a mixture of lime and ammonium chloride. The salt is blue in colour and is immediately decomposed by water. If heated to 140° C. it loses two molecules of ammonia, forming the diammine $[Cu(NH_3)_2]Cl_2$.

Tetrammino-cupric Chloride Monohydrate, $[Cu(NH_3)_4]Cl_2.H_2O$.—When ammonia is passed into a hot saturated solution of cupric chloride a dark blue solution is formed, and, on cooling, dark blue crystals are deposited. The salt crystallises in blue quadratic prisms which lose water on drying, giving the anhydrous salt described above. If heated it loses ammonia, passing into the diammino-derivative, and finally, on further heating, decomposes completely. Water attacks the substance and converts it into cupric ammonium chloride, ammonium chloride, and basic cupric chloride.

A tetrammino-salt containing two molecules of water is formed by evaporating an ammoniacal solution of cupric chloride in an atmosphere of ammonia at ordinary temperature.[3] The crystals are deep blue in colour, and lose both ammonia and water below 100° C., being transformed into the diammino-compound.

Diammino-cupric Chloride, $[Cu(NH_3)_2]Cl_2$, is obtained by heating the higher ammino-derivatives to 150° C. or less, or by the action of ammonia on a concentrated solution of cupric chloride, when the diammine is gradually precipitated from the liquid.[4]

Diammino-cupric chloride is greenish blue in colour and is not changed in air. On heating to high temperatures it decomposes, evolving ammonia and nitrogen, whilst cuprous chloride remains. Water decomposes the salt, yielding basic cupric chloride, $CuO.CuCl_2.6H_2O$, some tetrammino-cupric chloride, and ammonium chloride. It dissolves in excess of aqueous ammonia with formation of the complex ion, $[Cu(NH_3)_4]^{\cdot\cdot}$.

Decammino-tricupric Chloride, $[Cu_3(NH_3)_{10}]Cl_6$, is formed by saturating cupric chloride with ammonia at low temperature and gradually raising the temperature to 105° C. It decomposes at 124° C. with formation of the diammine.[5]

Ammino-cupric Bromides.—Cupric bromide, like cupric chloride, absorbs ammonia gas, forming complex ammino-compounds. The following ammines of cupric bromide have been described: *Hexammino-cupric bromide*, $[Cu(NH_3)_6]Br_2$; *pentammino-cupric bromide*, $[Cu(NH_3)_5]Br_2$; *diammino-cupric bromide*, $[Cu(NH_3)_2]Br_2$; and *decammino-tricupric bromide*, $[Cu_3(NH_3)_{10}]Br_6$.

Hexammino-cupric Bromide, $[Cu(NH_3)_6]Br_2$, is formed when dry, finely divided cupric bromide is exposed to ammonia gas at ordinary temperature. It is stable up to 20° C., but above that temperature

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[1] Bouzat, *Ann. Chim. Phys.*, 1903, [7] 29, 312.
[2] Bouzat, *Compt. rend.*, 1902, 135, 292.
[3] Sabbatini, *Ann. Chim. Farm.*, 1897, 26, 337.
[4] Kohlschütter, *Ber.*, 1904, 37, 1156.
[5] Ephraim, *ibid.*, 1919, 52, 940.

begins to dissociate. Rammelsberg[1] claimed to have obtained the pentammino-derivative by exposing dry cupric bromide to dry ammonia gas ; increase in bulk took place and a voluminous blue powder was formed. This was afterwards proved to be impure hexammino-cupric bromide and not the pentammino-derivative. The hexammine decomposes partially even at ordinary temperature, and decomposition is complete above 115° C.[2]

Diammino-cupric Bromide, $[Cu(NH_3)_2]Br_2$.—On exposure to air hexammino-cupric bromide and other alleged higher ammines lose ammonia and are transformed into the more stable diammino-bromide.

Diammino-cupric bromide is very dark in colour ; it is soluble in a concentrated aqueous solution of ammonium bromide, from which it may be crystallised ; water alone decomposes the ammine completely. It is capable of absorbing ammonia gas, forming the higher ammino-derivatives, and it may be heated to 200° C. without decomposition. At 260° C. it begins to decompose, and above that temperature it loses ammonia, leaving a residue of cupric bromide and some cupric oxide.[2]

Ammino-cupric Iodides.—A solution of ammonia in water does not dissolve cuprous iodide, but if air be allowed access to the mixture a blue solution is formed, and if the solution be cooled colourless crystals of **diammino-cupric iodide** separate. From the mother-liquor hydrated tetrammino-cupric iodide may be precipitated by means of alcohol.

Tetrammino-cupric Iodide is produced by adding potassium-iodide solution to an aqueous ammoniacal solution of cupric sulphate and then saturating the mixture with ammonia gas at 0° C.[3]

Tetrammino-cupric Iodide Monohydrate, $[Cu(NH_3)_4]I_2.H_2O$, crystallises in dark blue tetrahedra and decomposes rapidly in air, with loss of ammonia and formation of a dark brown compound. If the solution of the salt in ammonia be warmed it changes in colour, and, on cooling, crystals of **decammino-tricupric iodide,** $[Cu_3(NH_3)_{10}]I_6$, separate. This substance on heating is transformed into diammino-cupric iodide.

A polyiodide, **tetrammino-cupric polyiodide,** $[Cu(NH_3)_4]I_2 4I_2$, is also known. It separates from a solution of tetrammino-cupric iodide in ammonia and excess of iodine as a blackish-brown crystalline mass.[4]

Ammino-cuprous Chlorides.—It has long been known that cuprous chloride is soluble in aqueous ammonia, giving a solution which is capable of absorbing carbon monoxide and hence used in gas analysis. Cuprous chloride is also soluble in liquid ammonia.[5]

At least five different ammino-cuprous chlorides have been described. By studying the vapour pressures obtained by saturating cuprous chloride with ammonia and measuring the vapour pressure between 0° and 150° C., Lloyd found that only three ammino-derivatives existed, namely, *hexammino-cuprous chloride,* $[Cu_2(NH_3)_6]Cl_2$; *triammino-cuprous chloride,* $[Cu_2(NH_3)_3]Cl_2$; *monammino-cuprous chloride,* $[Cu_2(NH_3)]Cl_2$.

Hexammino-cuprous Chloride, $[Cu_2(NH_3)_6]Cl_2$, is formed by exposing cuprous chloride to ammonia gas at temperatures below 0° C.

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[1] Rammelsberg, *Pogg. Annalen*, 1842, 55, 246.
[2] Ephraim, *Ber.*, 1919, 52, 940.
[3] D. W. Horn, *Amer. Chem. J.*, 1908, 39, 184.
[4] Ephraim, *Ber.*, 1921, 54, 385.
[5] Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 827.

It melts at 123° C., is green in colour, and has a vapour pressure of 760 mm. at 46·3° C.[1]

Triammino-cuprous Chloride, $[Cu_2(NH_3)_3]Cl_2$, is prepared by saturating cuprous chloride with ammonia gas at low temperature under a pressure of 650 mm. It is light brown in colour and melts about 144° C.[1]

Monammino-cuprous Chloride, $[Cu_2(NH_3)]Cl_2$, is obtained by saturating cuprous chloride with ammonia and removing the excess until the pressure of the gas is 522 mm. at 90° C., when a dark brown powder remains of melting-point 162° C.

Ammino-cuprous Bromides.—Cuprous bromide forms three definite compounds which correspond to the chlorides, namely, *hexammino-cuprous bromide*, $[Cu_2(NH_3)_6Br_2$; *triammino-cuprous bromide*, $[Cu_2(NH_3)_3]Br_2$; and *diammino-cuprous bromide*, $[Cu_2(NH_3)_2]Br_2$.

Hexammino-cuprous Bromide, $[Cu_2(NH_3)_6]Br_2$, is made either by saturating finely powdered cuprous bromide with ammonia gas at low temperature,[2] or by removing ammonia gas from cuprous bromide which has been saturated with ammonia till the pressure reaches 87·6 mm. at 100° C.[3] The substance is described by Richards and Merigold as a black, unstable powder, whereas Lloyd describes it as a green powder of melting-point 115° C. The vapour pressure of the salt at 49·3° C. is 760 mm., or, at temperature of 283° C., the dissociation pressure is 100 mm.[4]

Ammino-cuprous Iodides.—Cuprous iodide, like the other halides of copper, absorbs ammonia gas, forming ammino-compounds. If the iodide be saturated with ammonia gas at 0° C. two ammines appear to be formed, **hexammino-cuprous iodide,** $[Cu_2(NH_3)_6]I_2$, and **triammino-cuprous iodide,** $[Cu_2(NH_3)_3]I_2$. These are the only compounds formed according to Lloyd's examination by measuring change of pressure with change of composition.

Hexammino-cuprous Iodide, $[Cu_2(NH_3)_6]I_2$, is prepared by passing dry ammonia gas slowly over cuprous iodide at a temperature below 0° C. It is a pale green compound which readily absorbs moisture from the air, and, if heated to 51° C., it loses ammonia, assumes a dark brown colour, becomes hygroscopic, and is transformed into triammino-cuprous iodide, $[Cu_2(NH_3)_3]I_2$, which melts at 117° C.[5]

The stabilities of the triammino-cuprous halides are almost identical, and the dissociation pressures of the ammino-cupric halides lie very near together.[6] The stabilities of hexammino-copper halides is also almost identical; the compounds are very readily decomposed by water, and hence do not seem to be formed in aqueous solution. Ammino-derivatives of cupric carbonate, cupric acetate, cupric oxide, and cuprous cyanide and thiocyanate are known. These have the general characteristics of the ammines already described.

Allied to the cuprammines is **Schweizer's reagent,** which is prepared by dissolving cupric hydroxide in an aqueous solution of ammonia, when a deep blue liquid is obtained which has the property of dissolving

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[1] S. J. Lloyd, *J. Physical Chem.*, 1908, 12, 398.

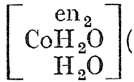
[2] Richards and Merigold, *Zeitsch. anorg. Chem.*, 1898, 17, 245.

[3] Lloyd, *J. Physical Chem.*, 1908, 12, 298.

[4] Ephraim, *Ber.*, 1919, 52, 236; Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1921, 119, 97.

[5] Ephraim, *Ber.*, 1919, 52, 236, 940.

[6] Ephraim and Bolle, *ibid.*, 1915, 48, 1770.

cellulose.[1] It is interesting to note that copper is the only heavy metal which gives ammino-hydroxides capable of dissolving cellulose. Other bases, as, for example, $[Co\ en_3](OH)_3$ and  $\left[\begin{matrix}en_2\\ CoH_2O\\ H_2O\end{matrix}\right](OH)_3$, are unable to exert solvent powers on cellulose, from which is drawn the conclusion that copper complexes are different in structure.[2]

When freshly precipitated cupric hydroxide is digested with aqueous ammonia a blue solution is formed. Dawson and McCrae[3] assume that the compound formed is diammino-cupric hydroxide, $[Cu(NH_3)_2](OH)_2$, which ionises in solution yielding $[Cu(NH_3)_2]^{\cdot\cdot}$ and $(OH)'$ ions. Bonsdorff[4] investigated the electrical conductivity of cupric hydroxide in aqueous ammonia, and concluded that when only a small excess of ammonia is present the above complex exists in solution, but with large amounts of ammonia the complex substance $[Cu(NH_3)_4](OH)_2$ is probably formed. This solution of cupric hydroxide or cupric oxide in aqueous ammonia is often called Schweizer's reagent. The liquid contains one or more cupric ammino-oxides, and the base, which has not been isolated, is probably $[Cu(NH_3)_4](OH)_2$. It is a fairly strong base, for cellulose is deposited from solution in ammoniacal cupric hydroxide on the addition of a potassium salt. This is possibly due to the acid ion of the salt neutralising or replacing the basic ion of the complex. Hence cellulose is only soluble in a solution of the free base.[5]

Ammino-derivatives of Silver Salts.

The best known of the silver ammines is the compound obtained by dissolving silver chloride in aqueous ammonia.

In 1818 Faraday obtained a compound by the direct union of precipitated silver chloride and ammonia gas. He found that silver chloride absorbed ammonia readily, 6·48 grams of chloride absorbing 2·13 litres of ammonia; the compound had the composition represented by the formula $2AgCl.3NH_3$, and the ammonia so absorbed was liberated again at a temperature of 37° C. This was utilised in the preparation of liquid ammonia.

Silver chloride forms with ammonia the following derivatives :—

Triammino-silver chloride, $AgCl.3NH_3$ or $[Ag(NH_3)_3]Cl$; *sesquiammino-silver chloride,* $2AgCl.3NH_3$ or $[Ag_2(NH_3)_3]Cl_2$; and probably *diammino-silver chloride,* $AgCl.2NH_3$ or $[Ag(NH_3)_2]Cl$; and *monammino-silver chloride,* $AgCl.NH_3$ or $[AgNH_3]Cl$.

Sesquiammino-silver Chloride, $[Ag_2(NH_3)_3]Cl_2$, is prepared by allowing ammonia gas to pass over dry powdered silver chloride at a temperature of 20° C. Increase in bulk takes place and ammonia is absorbed. The compound is white in colour, and when exposed to air gradually loses ammonia, leaving, finally, a residue of silver chloride. The same derivative is formed by dissolving precipitated silver chloride in an aqueous solution of ammonia at 20° C. and then cooling the solution to 0° C. or precipitating from solution with alcohol.[6] It is

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[1] Schweizer, *J. prakt. Chem.*, 1857, 72, 109.

[2] Kurt Hess, *Helv. Chim. Acta.*, 1920, 3, 866.

[3] Dawson and McCrae, *Trans. Chem. Soc.*, 1900, 77, 1257.

[4] Bonsdorff, *Zeitsch. anorg. Chem.*, 1904, 41, 184.

[5] Bouzat, *Compt. rend.*, 1902, 134, 1502.

[6] Jarry, *Compt. rend.*, 1897, 124, 288; *Ann. Chim. Phys.*, 1899, [7], 17, 327.

a colourless, crystalline substance which, when exposed to air, loses ammonia, becomes powdery, and leaves a residue of silver chloride. If heated in a sealed tube it fuses between 88° and 95° C., increases in bulk, and finally melts at 103° C. Unlike the simple salt the sesquiammine is not affected by light. If a solution of silver chloride in aqueous ammonia be evaporated quickly the ammine is decomposed and only silver chloride separates ; on the other hand, if the liquid be evaporated slowly, colourless prisms of the sesquiammine separate.

Triammino-silver Chloride, $[Ag(NH_3)_3]Cl$.—When silver chloride is dissolved in liquid ammonia, in which it is sparingly soluble, and the solution evaporated at $-40°$ to $-20°$ C., long, colourless needles of the triammine are deposited.[1] The same compound is formed by dissolving silver chloride in aqueous ammonia, maintaining the temperature between 0° and 20° C.,[2] or from highly concentrated solutions of silver chloride in ammonia.

The triammine is colourless, and crystallises in long needles which are birefractive and not affected by light.

Diammino-silver Chloride, $[Ag(NH_3)_2]Cl$.—If silver chloride be heated with concentrated aqueous ammonia in a sealed tube and then cooled, crystals separate which were at first regarded as diammino-silver chloride.[3] The substance was later found to be the sesquiammine, which partially dissociates.

Biltz[4] carried out a series of investigations on the vapour pressures of solutions of silver chloride and ammonia, and came to the conclusion that silver chloride forms the triammine, $[Ag(NH_3)_3]Cl$, at atmospheric pressure below 20° C., and the sesquiammine, $2AgCl(NH_3)_3$, at temperatures between 20° and 60° C. Above 60° C. silver chloride does not unite with ammonia.

Monammino-silver Chloride, $[Ag(NH_3)]Cl$.—Biltz and Stollenwerk[5] report the existence of the monammine, and state that sesquiammino- and monammino-silver chloride form mixed crystals at 30° C., whilst Bodländer and Fittig[6] have shown that a solution of silver chloride in aqueous ammonia contains the diammine in solution even when solid sesquiammine has separated from the liquid. A certain amount of doubt, therefore, surrounds the existence of the monammine and the diammine of silver chloride, although both appear to exist in aqueous ammoniacal solution.

Ammino-silver Bromides.—Silver bromide, like the chloride, unites with ammonia; the triammine, $[Ag(NH_3)_3]Br$, the sesquiammine, $[Ag_2(NH_3)_3]Br_2$ or $2AgBr.3NH_3$, the diammine, $[Ag(NH_3)_2]Br$, and the monammine, $[Ag(NH_3)]Br$, have all been obtained.

These resemble the chlorides.

Triammino-silver Bromide, $[Ag(NH_3)_3]Br$.—Silver bromide treated with liquid ammonia below 4° C. yields the triammine, or it may be formed in solution if the bromide be treated with water saturated with ammonia gas under pressure.[7]

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[1] Jarry, *loc. cit.*

[2] Isambert, *Compt. rend.*, 1878, 86, 968.

[3] Terreil, *ibid.*, 1884, 98, 1279.

[4] Biltz, *Zeitsch. physikal. Chem.*, 1909, 57, 561.

[5] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1920, 114, 174.

[6] Bodländer and Fittig, *Zeitsch. physikal. Chem.*, 1902, 39, 597.

[7] Jarry, *Compt. rend.*, 1898, 126, 1138; Joannis and Crozier, *ibid.*, 1894, 118, 1149.

The triammine is a white substance, and on raising the temperature above 4° C. passes into the sesquiammine, $2AgBr.3NH_3$.

Sesquiammino-silver Bromide, $2AgBr.3NH_3$ or $[Ag_2(NH_3)_3]Br_2$, is obtained from the triammine on heating between 4° and 34° C., or by the action of gaseous ammonia on dry silver bromide.

It is a white crystalline compound which, like the corresponding chloride, is not sensitive to light. It is decomposed by water, and dissociates at 34° C. with formation of the monammine.

Monammino-silver Bromide, $[Ag(NH_3)]Br$, is produced on the decomposition of the above derivative by heating between the temperatures 34° and 50° C. Above that temperature it decomposes, losing ammonia and leaving a residue of silver bromide.

Ammino-silver Iodides.—Silver iodide forms the following ammino-derivatives :—

Triammino-silver iodide, $[Ag(NH_3)_3]I$; *sesquiammino-silver iodide,* $[Ag_2(NH_3)_3]I$ or $2AgI.3NH_3$; *monammino-silver iodide,* $[Ag(NH_3)]I$; *hemiammino-silver iodide,* $[Ag(NH_3)]I.AgI$ or $2AgI.NH_3$.

These compounds are all unstable and lose ammonia on heating. Silver iodide is readily soluble in liquid ammonia, and on evaporating the solution at −40° to −10° C. white lamellar crystals of monammino-silver iodide separate.[1]

The monammine loses ammonia at 4° C. and is transformed into the hemiammine, $2AgI.NH_3$. Both compounds are unstable, the monammine dissociating under ordinary pressure at 3·5° C. and the hemiammine at 90° C. If treated with water or exposed to moist air ammonia is lost and a residue of silver iodide remains.

Sesquiammino-silver iodide, $[Ag_2(NH_3)_3]I_2$, and triammino-silver iodide, $[Ag(NH_3)_3]I$, have been prepared by Biltz and Stollenwerk,[2] whereas Ephraim,[3] in his investigations on the vapour pressures of the triammino-silver salts, denied the existence of triammino-silver iodide.

The ammino-iodides of silver show great tendency to form mixed crystals; for instance, sesquiammino-silver chloride and monammino-silver chloride form mixed crystals at 30° C.[4]

Comparing the stability of the triammines of silver halides, the chloride is more stable than the bromide, and the iodide either does not exist or is very unstable. This is contrary to the usual observations in the ammines, where the stability of the ammine rises from chloride to iodide. In the case of the ammines of the oxy-halogen salts of silver the most unstable is the iodate, which is non-existent at ordinary pressure, then comes the bromate, and the most stable is the chlorate.[3]

Ammino-derivatives of other Silver Salts. Ammino-silver Nitrates.—Silver nitrate unites with ammonia, forming the *diammino-silver nitrate,* $[Ag(NH_3)_2]NO_3$, and *triammino-silver nitrate,* $[Ag(NH_3)_3]NO_3$.

The existence of monammino-silver nitrate is doubtful.

Rechler, in 1883, obtained a compound containing ammonia which was assumed to be the monammine, by adding aqueous ammonia to a solution of silver nitrate until a precipitate is formed, filtering off the

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[1] Jarry, *Ann. Chim. Phys.*, 1899, [7], 17, 327.

[2] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1920, 114, 174.

[3] Ephraim, *Ber.*, 1918, 51, 706.

[4] Biltz and Stollenwerk, *loc. cit.*

precipitate, and evaporating the filtrate. This was later proved to be the diammine in solid solution with silver nitrate.[1]

Diammino-silver Nitrate, $[Ag(NH_3)_2]NO_3$.—When aqueous ammonia is added to a solution of silver nitrate until the precipitate first formed redissolves and the solution is evaporated, a crystalline substance separates of composition $[Ag(NH_3)_2]NO_3$. The compound can also be formed by dissolving silver oxide in an ammoniacal solution of ammonium nitrate, or by dissolving silver nitrate in benzonitrile and passing ammonia gas into the solution.[2]

Diammino-silver nitrate forms glistening rhombic or prismatic crystals which blacken on exposure to light. It is fairly stable, and may be heated to 100° C. without loss of ammonia. Further heating causes it to decompose, and finally to melt with evolution of nitrogen and ammonia, leaving a residue of metallic silver and ammonium nitrate. It is soluble in water, but partial dissociation takes place so that the solution is alkaline in reaction, and it therefore yields a precipitate of silver chloride and soluble chlorides. Certain of the metals—for example, zinc, cadmium, and copper—quickly reduce the ammine in solution to metallic silver.

Triammino-silver Nitrate, $[Ag(NH_3)_3]NO_3$.—The compound is formed when silver nitrate is exposed to dry ammonia gas; much heat is developed, increase in bulk takes place, and sufficient heat may be produced to fuse the mass.[3] It exhibits considerable heat of formation, is soluble in water, and loses ammonia on heating, dissociating at 63° C. under ordinary pressure, and is soluble in liquid ammonia below $-10°$ C.[4] Only the diammine exists in solution, the triammine being completely dissociated into the diammine and ammonia.

Many other ammines of silver salts have been prepared; thus, silver sulphate forms with ammonia diammino-silver sulphate, $[Ag_2(NH_3)_2]SO_4$, and tetrammino-silver sulphate, $[Ag(NH_3)_2]_2SO_4$.

Silver chlorate forms the triammine, $[Ag(NH_3)_3]ClO_3$; silver carbonate the tetrammine, $[Ag(NH_3)_2]_2CO_3$; and silver oxide itself forms diammino-silver oxide, $Ag_2O.2NH_3$, and the hydroxide, $[Ag(NH_3)_2]OH$.[5] Diammino-silver hydroxide appears to be more strongly dissociated than barium hydroxide.[6]

Ammino-derivatives of Gold Salts.

Gold has a more marked tendency to form complex salts than either copper or silver, but the ammines of gold are somewhat unstable. Gold forms two series of salts where the metal is monovalent or divalent respectively; from both series of salts ammines have been obtained.

The ammines of the halides of gold are taken as the type of the aurammines.

Ammino-aurous Chlorides.—Aurous chloride unites with ammonia, forming *dodecammino-aurous chloride*, $AuCl.12NH_3$; *triammino-*

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[1] Kuriloff, *Bull. Acad. St Petersburg*, 1903, 17, 149.
[2] Hantzsch, *Zeitsch. anorg. Chem.*, 1899, 19, 104.
[3] Bruni and Levi, *Gazzetta*, 1916, [2], 46, 17.
[4] Joannis and Crozier, *Compt. rend.*, 1894, 118, 1149.
[5] Dervin and Ohner, *ibid.*, 1921, 172, 1662.
[6] Bonsdorff, *Ber.*, 1903, 36, 2322.

aurous chloride, $AuCl.3NH_3$; *diammino-aurous chloride*, $AuCl.2NH_3$; and *monammino-aurous chloride*, $AuCl.NH_3$.

When aurous chloride is mixed with liquid ammonia at a temperature below $-28°$ C. the salt absorbs ammonia, yielding an addition compound containing twelve molecules of ammonia, $AuCl.12NH_3$. This substance is stable only below $-28°$ C., and when the temperature rises to $+20°$ C. nine molecules of ammonia are eliminated, forming the compound **triammino-aurous chloride,** $[Au(NH_3)_3]Cl$.[1]

Prepared in the above manner, triammino-aurous chloride is a white powder which is comparatively stable. It may be heated to 180° C. without decomposition, but above that temperature it dissociates, yielding gold and ammonium chloride. It is decomposed by water, and dilute acids cause it to lose ammonia with formation of the unstable monammino-aurous chloride. When treated with potassium hydroxide ammonia is evolved and a brown explosive substance formed.

Diammino-aurous Chloride, $[Au(NH_3)_2]Cl$, is formed by saturating dry aurous chloride with ammonia gas at ordinary temperature. The diammine is a white voluminous powder, and has dissociation temperature 113·5° C.[2]

Monammino-aurous Chloride, $[Au(NH_3)]Cl$.—When aurous chloride is dissolved in an aqueous solution of ammonia and the mixture acidified with hydrochloric acid a white crystalline precipitate separates; the precipitate is unstable and cannot therefore be completely dried.[3]

Monammino-aurous chloride is a white crystalline powder, sparingly soluble in water, soluble in an aqueous solution of ammonia, and precipitated by the addition of hydrochloric acid. It is unstable in the dry state, and decomposes completely on heating between 150° and 200° C. Aurous bromide and aurous iodide also unite with ammonia. The former yields only one ammino-derivative, the diammine, $[Au(NH_3)_2]Br$, and the latter two ammino-derivatives, namely, hexammino-aurous iodide, $[Au(NH_3)_6]I$, and monammino-aurous iodide, $[Au(NH_3)]I$.

Diammino-aurous Bromide, $Au(NH_3)_2Br$, may be formed by passing ammonia gas over aurous bromide at a temperature of 18° C. If the temperature be allowed to rise the ammine is decomposed, and metallic gold, nitrogen, and ammonium bromide are formed. The ammine is a white powder which readily decomposes on heating, on exposure to air, or on treatment with water.[1]

Hexammino-aurous Iodide, $[Au(NH_3)_6]I$.—When liquid or gaseous ammonia is allowed to act upon aurous iodide a white crystalline or powdery substance is obtained containing ammonia and having the composition $AuI.6NH_3$. It decomposes at $-28°$ C. under ordinary pressure, and if heated from $-28°$ C. to $+20°$ C. it loses five molecules of ammonia and is transformed into the monammine, $[Au(NH_3)]I$.

The monammine is stable at ordinary temperature, but on heating decomposes, yielding ammonia, iodine, and gold, and on treating with water breaks down into ammonium iodide and metallic gold.

Ammino-derivatives of Auric Salts and Oxides.—Auric chloride, like platinic chloride, combines with hydrochloric acid and alkali chlorides with formation of chlorauric acid, $HAuCl_4$, and alkali chlor-

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[1] Meyer, *Compt. rend.*, 1906, 143, 280.

[2] Ephraim, *Ber.*, 1919, 52, 252.

[3] Diemer, *J. Amer. Chem. Soc.*, 1913, 35, 552.

aurate, for example, $KAuCl_4$. Potassium chloraurate, $KAuCl_4$, slowly absorbs ammonia, yielding an orange compound, potassium triammino-chloraurate, $KAuCl_4.3NH_3$, which loses ammonia *in vacuo.*[1] At a temperature of −18° C. potassium chloraurate absorbs a larger amount of ammonia, forming an orange-red compound containing twelve molecules of the gas. This substance immediately decomposes in water with evolution of nitrogen.

It is suggested that substances such as potassium chloraurate are dissociated first by ammonia into simple halides, for the alkali chloraurates and bromaurates behave towards ammonia like the auric salts.[2] Auric bromide, obtained by dissolving precipitated gold in bromine, also absorbs ammonia, the amount depending on the temperature.

Several explosive nitrogen compounds of gold have long been known; thus, when concentrated ammonia is added to auric oxide the substance **fulminating gold** is produced which has the composition $AuN_2H_3.3H_2O$. This derivative is an ammine possibly of composition $[Au(NH_3)_2(OH)_2]OH$. When ammonia is added to an aqueous solution of auric chloride an explosive substance is produced which is a mixture of fulminating gold with imino-auric chloride, $Au(NH)Cl$.

Pure fulminating gold is best prepared by treating auric hydroxide with concentrated ammonia and drying over phosphorus pentoxide; it is a dark, olive-green powder which explodes on heating or on percussion. Weitz[3] has examined the explosive nitrogen compounds of gold, has criticised the formulæ adopted for these substances, and has attempted to formulate these compounds in accordance with the co-ordination theory.

By treating an aqueous solution of chlorauric acid with ammonia a precipitate is obtained containing gold, nitrogen, and chlorine; as the amount of ammonia is increased the quantity of chlorine in the precipitate diminishes, but the ratio of gold to nitrogen remains constant at 1 : 1·5. The precipitate obtained in this way is given the general name of *explosive gold chloride.* It seems to be a mixture of two substances in varying proportions, the two being **diamino-imino-diauric chloride,** $NH(AuClNH_2)_2$, and **sesquiammino-auric oxide,** $Au_2O_3.3NH_3$. From the mixture the chlorine-free substance has been isolated, and, when dried in air, has the composition $2Au(OH)_3.3NH_3$ or $[2Au(NH_3)_3](OH)_3$. It is comparatively stable, but if dried at 105° to 110° C., or *in vacuo* over phosphorus pentoxide, it loses water, and in the dry condition is exceedingly explosive. Other mixtures have been obtained where nitrate or bromide radicle takes the place of chlorine, and again the ratio of gold to nitrogen is 1 : 1·5.

If dilute chlorauric acid containing ammonium chloride is added to a cold saturated solution of ammonium chloride saturated with ammonia only one compound is obtained, namely, diamino-auric chloride, $Au(NH_2)_2Cl$. This is a yellow powder which is non-explosive and is decomposed by washing with water, forming a derivative of aurous oxide of composition $3AuO.2NH_3.xH_2O$, which is explosive.

Both diamino-imino-diauric chloride, $NH(AuClNH_2)_2$, and diamino-auric chloride, $Au(NH_2)_2Cl$, if treated with successive quantities of

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[1] Peters, *Ber.*, 1908, 41, 3182.
[2] Ephraim, *ibid.*, 1919, 52, 241.
[3] Weitz, *Annalen*, 1915, 410, 117.

aqueous ammonia are converted into **sesquiammino-auric hydroxide**, $[2Au(NH_3)_3](OH)_3$, and this, if treated with hot water, is transformed into the explosive compound $Au_2O_3.2NH_3$, to which Weitz gave the name monammino-auric oxide. Warm dilute hydrochloric acid transforms the sesquiammino-auric hydroxide into chlorauric acid, explosive gold chloride being formed as an intermediate product. The hydroxide is scarcely attacked by dilute sulphuric acid in the cold, but on warming ammonia is eliminated and the explosive product obtained. Cold concentrated sulphuric acid and nitric acid do not decompose the complex, but transform it into the sulphate or the nitrate.

Several tetrammino-derivatives of gold salts have been prepared. When dilute chlorauric acid saturated with ammonium nitrate is added to a cold saturated solution of ammonium nitrate and the mixture treated with ammonia gas at ordinary temperature, a precipitate of **tetrammino-auric nitrate**, $[Au(NH_3)_4](NO_3)_3$, is obtained. Tetrammino-auric nitrate is soluble in water and may be crystallised from warm water. It may be precipitated from solution by the addition of any soluble nitrate, but with potassium, sodium, or ammonium nitrate it forms double salts. Thus, potassium nitrate if added to a concentrated solution of tetrammino-auric nitrate forms the compound $[Au(NH_3)_4](NO_3)_3.KNO_3$, which crystallises from solution in needles.

Tetrammino-auric nitrate is comparatively stable, and may be converted into other salts containing the cation $[Au(NH_3)_4]^{\cdots}$ on the addition of soluble salts of the acid required.

Tetrammino-auric Phosphate, $[Au(NH_3)_4]PO_4.H_2O$, is a white crystalline substance; **tetrammino-auric perchlorate**, $[Au(NH_3)_4](ClO_4)_3$, forms short prismatic crystals, and is claimed to be specially useful for the preparation of other tetrammino-auric salts.

Salts have also been obtained containing more than one acid radicle combined with the cation, $[Au(NH_3)_4]^{\cdots}$. For example, **tetrammino-auric oxalate perchlorate**, $[Au(NH_3)_4](C_2O_4)(ClO_4)$, which crystallises in leaflets, and **tetrammino-auric sulphate nitrate**, monohydrate and dihydrate, $[Au(NH_3)_4](SO_4)(NO_3).H_2O$, $[Au(NH_3)_4](SO_4)(NO_3).2H_2O$. The salts containing the tetrammino-auric radicle are all very stable, and retain ammonia even when treated with concentrated acids. The salts of the strong acids have a neutral action in solution. The corresponding hydroxide, namely, tetrammino-auric hydroxide, has not been isolated, but as the nitrate is more soluble in aqueous alkali hydroxide than in water and is precipitated from the alkaline solution on addition of nitric acid, it is possible that tetrammino-auric hydroxide, $[Au(NH_3)_4](OH)_3$, exists in solution.

When an alkaline solution of tetrammino-auric salt is kept it becomes yellow in colour, and a yellow precipitate which is explosive is formed. This appears to have composition similar to that of explosive gold chloride.

The halogen acids do not form salts with the tetrammino-auric ion in solution, for if an aqueous solution of potassium chloride be added to tetrammino-auric nitrate a yellow colour is produced, and a yellow precipitate formed which apparently is a derivative of explosive gold chloride.

Salts of hydrobromic and hydriodic acid produce similar results.

AMMINO-DERIVATIVES OF THE ALKALI METAL SALTS.

With the exception of lithium the alkali metals do not readily form ammines.

Sodium and potassium chlorides absorb ammonia, but there is no evidence of chemical reaction, and on exposure to air ammonia is completely lost. If, however, sodium chloride is dissolved in liquid ammonia at −10° C. and the solution evaporated at −24° C., small needle-shaped crystals separate which have a composition corresponding to **pentammino-sodium chloride,** $[Na(NH_3)_5]Cl$. Lithium salts, on the other hand, readily absorb ammonia, forming ammino-derivatives.

Ammino-lithium Halides.—Lithium halides absorb gaseous ammonia in the dry state. The chloride forms four compounds depending on the temperature at which absorption takes place. Below 13° C. *tetrammino-lithium chloride,* $[Li(NH_3)_4]Cl$, is produced. *Triammino-lithium chloride,* $[Li(NH_3)_3]Cl$, is formed between 20° and 60° C.; *diammino-lithium chloride,* $[Li(NH_3)_2]Cl$, between 60° and 85° C.; and at 85° C. the *monammine,* $[Li(NH_3)]Cl$, is produced. These are white unstable substances.[1]

Lithium bromide also combines with gaseous ammonia to form four solid deliquescent substances. The *monammine,* $[Li(NH_3)]Br$, is formed above 95° C.; the *diammine,* $[Li(NH_3)_2]Br$, between 87° and 95° C.; the *triammine,* $[Li(NH_3)_3]Br$, between 71° and 87° C.; and the tetrammine about −18° C.[2] Ephraim prepared other ammino-salts of lithium, as, for example, *tetrammino-lithium nitrate,* $[Li(NH_3)_4](NO_3)$, which is a colourless syrup at ordinary temperature and is more stable than the chloride; *tetrammino-lithium chlorate,* $[Li(NH_3)_4]ClO_3$, which is a fairly mobile liquid; and *tetrammino-lithium perchlorate,* $[Li(NH_3)_4]ClO_4$, a white solid which liquefies and decomposes at ordinary temperature.[3]

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[1] Bonnefoi, *Compt. rend.*, 1898, 127, 367.

[2] Bonnefoi, *ibid.*, 1900, 130, 1394.

[3] Ephraim, *Ber.*, 1919, 52, 236.

CHAPTER V.

METAL-AMMINES OF THE ELEMENTS OF GROUP II.

Relatively few ammines occur in this group. The alkaline earth metals, namely, Subgroup A, show little tendency to form complex salts. A few have been prepared, such as strontium fluorochloride, $SrF_2.SrCl_2$, or potassium tetrachlorobariate, K_2BaCl_4, but these are not readily formed. The subgroup further shows little tendency to unite with ammonia, and the ammino-derivatives obtained are very unstable. Beryllium and magnesium, on the other hand, form double salts and complex salts analogous to the metal-ammines, and some ammino-compounds are known. In the Subgroup B the tendency to form complex salts and metal-ammines is much more marked. Zinc forms many complex salts and also several ammines; cadmium forms ammines similar to those of zinc; whilst mercury forms compounds with ammonia of various types, some of which have been classified as additive compounds of the metal-ammine type.

Beryllium. Magnesium.	
Subgroup A.	*Subgroup B.*
Calcium.	Zinc.
Strontium.	Cadmium.
Barium.	Mercury.

AMMINO-DERIVATIVES OF BERYLLIUM AND MAGNESIUM SALTS.

Although beryllium and magnesium salts do not form stable metal-ammines yet they unite with ammonia, forming additive compounds of the hydrate type which are sometimes referred to as *ammoniates* or *ammonio-compounds*. These appear to be of the same type as the metal-ammines, and the difference seems to be merely one of stability. The ammonio-compounds are formed by the addition of ammonia gas to dry or fused salt, and most of them decompose with liberation of ammonia when dissolved in water.

Ammino-derivatives of Beryllium Salts.

The halogen salts of beryllium unite readily with ammonia, yielding various products.

Hexammino-beryllium Chloride, $BeCl_2.6NH_3$ or $[Be(NH_3)_6]Cl_2$, is formed by treating dehydrated beryllium chloride with ammonia gas until no further increase in weight occurs.[1] Beryllium chloride which has been sublimed, on treatment with ammonia gas in the cold forms **tetrammino-beryllium chloride,** $[Be(NH_3)_4]Cl_2$, and, if the

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[1] Ephraim, *Ber.*, 1912, 45, 1322.

temperature is allowed to rise during absorption of ammonia, **diammino-beryllium chloride**, $[Be(NH_3)_2]Cl_2$, is formed.[1]

Beryllium bromide also absorbs gaseous ammonia and the iodide unites with dry ammonia. If dry gas be passed slowly over beryllium iodide in the cold, increase in bulk takes place, and a white powder of composition $2BeI_2.3NH_3$ is left. By slightly warming and passing more ammonia gas over the compound a further quantity is absorbed and a white crystalline mass is formed.

Only the halogen salts of beryllium appear capable of uniting with ammonia.

Ammino-derivatives of Magnesium Salts.

Magnesium salts, like those of beryllium, can absorb ammonia gas, forming additive products distinct from the ammonium double salts. Thus, magnesium chloride forms double salts with ammonium chloride and absorbs ammonia gas, forming ammines containing four or six molecules of ammonia.

Tetrammino-magnesium Chloride, $[Mg(NH_3)_4]Cl_2$.—This compound is produced when magnesium chloride is volatilised in a stream of ammonia gas; the ammine condenses as a white meal of composition $MgCl_2.4NH_3$. It decomposes quickly with loss of ammonia if exposed to air, but is capable of sublimation in an atmosphere of ammonia.

Hexammino-magnesium Chloride, $[Mg(NH_3)_6]Cl_2$, is formed by saturating pure, dry magnesium chloride with ammonia at room temperature. The substance produced is extraordinarily voluminous.[2] The same compound is obtained by exposing specially dry magnesium chloride to ammonia gas for fifteen hours at room temperature.[3] It dissociates at 142° C. into the *diammine*, $[Mg(NH_3)_2]Cl_2$. Determinations of heats of formation during the addition of ammonia show the existence of *diammino-* and *monammino-magnesium chlorides*.

Aquo-pentammino-magnesium Chloride, $[Mg(NH_3)_5H_2O]Cl_2$.—A colourless crystalline aquo salt is described which is produced by passing ammonia gas into an alcoholic solution of magnesium chloride at ordinary temperature.[4]

Magnesium bromide and iodide unite with ammonia, forming salts corresponding to the chloride, but the monammine of magnesium iodide does not appear to exist.[3] Complex salts containing hydroxylamine, pyridine, and ethylenediamine in place of ammonia have been prepared.[5] Also some complex salts of magnesium sulphate containing ammonia are known. Thus, *tetraquo-diammino-magnesium sulphate*, $[Mg(NH_3)_2(H_2O)_4]SO_4$, and *triaquo-triammino-magnesium sulphate*, $[Mg(NH_3)_3(H_2O)_3]SO_4$.

AMMINO-DERIVATIVES OF SALTS OF SUBGROUP A.

The halides of these elements absorb ammonia readily.

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[1] Mieleitner and Steinmetz, *Zeitsch. anorg. Chem.*, 1913, 80, 71.

[2] Ephraim, *Ber.*, 1912, 45, 1322.

[3] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1921, 119, 115.

[4] Spacu and Ripan, *Bul. Soc. Stiinte. Cluj.*, 1922, 1, 267.

[5] Spacu and Ripan, *ibid.*, 1922, 1, 72, 247.

Ammino-derivatives of Calcium Halides.

Calcium chloride forms with ammonia octammino-, hexammino-, tetrammino-, and diammino-calcium chloride, the best known of these being the octammine.

Octammino-calcium Chloride, $[Ca(NH_3)_8]Cl_2$.—Anhydrous calcium chloride absorbs ammonia rapidly, increase in bulk takes place, and finally the mass falls to a white voluminous powder. Fused calcium chloride also absorbs ammonia at first rapidly, but as the reaction nears completion absorption is very slow. The composition corresponds to the octammine.

Octammino-calcium chloride decomposes on heating with complete loss of ammonia; it dissolves in water with loss of ammonia, although from physical measurements it has been shown that the dissolved calcium ion is capable of fixing some ammonia.[1, 2] If brought into chlorine gas it inflames with liberation of nitrogen and hydrochloric acid.

Hexammino-calcium Chloride, $[Ca(NH_3)_6]Cl_2$, is not stable, but tetrammino-calcium chloride, $[Ca(NH_3)_4]Cl_2$, and diammino-calcium chloride, $[Ca(NH_3)_2]Cl_2$, exist in the stable state.[3]

The corresponding bromide addition compounds have been prepared, namely, *octammino-calcium bromide,* $[Ca(NH_3)_8]Br_2$; *hexammino-calcium bromide,* $[Ca(NH_3)_6Br_2$; *diammino-calcium bromide,* $[Ca(NH_3)_2]Br_2$; and *monammino-calcium bromide,* $[Ca(NH_3)]Br_2$.

All four dissociate on heating, with loss of ammonia. The hexammine is formed by absorption of ammonia gas by anhydrous calcium bromide.

Ammino-derivatives of Strontium Halides.

The halides of strontium resemble those of calcium, and unite with ammonia gas in the dry state. All are decomposed by water with liberation of ammonia. The chloride, on exposure to ammonia gas, yields **octammino-strontium chloride,** $[Sr(NH_3)_8]Cl_2$. It is a voluminous white powder which loses ammonia on heating, leaving a residue of strontium chloride. If degraded isothermally, constancy of pressure indicates the existence of **monammino-strontium chloride,** $[Sr(NH_3)]Cl_2$, which on further heating loses ammonia completely. The monammine at a temperature of 45·5° C. has a dissociation pressure of 100 mm.[4]

Strontium bromide also absorbs ammonia in the dry state, yielding **octammino-strontium bromide,** $[Sr(NH_3)_8]Br_2$, and if this be degraded isothermally, the existence of the *diammine,* $[Sr(NH_3)_2]Br$, and the *monammine,* $[Sr(NH_3)]Br_2$, may be shown. The temperatures at which these ammines exert a dissociation pressure of 100 mm. are 30°, 68°, and 146° C. respectively.[4]

The existence of the following ammino iodides has been proved in the same way: *octammino-strontium iodide,* $[Sr(NH_3)_8]I_2$; *hexammino-strontium iodide,* $[Sr(NH_3)_6]I_2$; *diammino-strontium iodide,* $[Sr(NH_3)_2]I_2$; and *monammino-strontium iodide,* $[Sr(NH_3)]I_2$.

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[1] Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 1910.

[2] Dawson and McCrae, *Trans. Chem. Soc.*, 1900, 77, 1240.

[3] Hüttig, *Zeitsch. anorg. Chem.*, 1922, 123, 31.

[4] Hüttig, *ibid.*, 1922, 124, 322.

The temperatures at which the dissociation pressure of these is 100 mm. are 31°, 75°, 134°, and 204° C. respectively.

The ammino-iodides behave towards water and heat like the chlorides.

Ammino-derivatives of Barium Halides.

The following ammino-barium halides have been described:

Tetrammino-barium chloride, $[Ba(NH_3)_4]Cl_2$; *octammino-barium bromide*, $[Ba(NH_3)_8]Br_2$; *hexammino-barium iodide*, $[Ba(NH_3)_6]I_2$.

Barium chloride under ordinary conditions absorbs gaseous ammonia very slowly, but under pressure it absorbs considerable quantities of ammonia gas, which is very quickly lost on exposure to air.

Tetrammino-barium Chloride, $[Ba(NH_3)_4]Cl_2$, is prepared by melting barium chloride in a stoppered tube and, whilst it is still warm, condensing on it liquid ammonia. Ammonia is absorbed, and when reaction is complete the tube is heated to 0° C. and excess of ammonia allowed to escape. The residue is tetrammino-barium chloride. This loses ammonia on exposure to air, and by measuring the dissociation pressure Joannis[1] showed that compounds containing fewer than four molecules of ammonia do not exist.

Octammino-barium Bromide, $[Ba(NH_3)_8]Br_2$.—This compound is prepared in the same way as tetrammino-barium chloride by condensing ammonia on fused barium bromide at −30° C. and allowing the excess of ammonia to escape at 0° C. On exposure to air ammonia is completely lost.[1] According to the investigation of Hüttig,[2] barium bromide forms four ammino derivatives, namely, the *octammine*, $[Ba(NH_3)_8]Br_2$; the *tetrammine*, $[Ba(NH_3)_4]Br_2$; the *diammine*, $[Ba(NH_3)_2]Br_2$; and the *monammine*, $[Ba(NH_3)]Br_2$. Whilst the following derivatives of barium iodide exist, namely, the *decammine*, $[Ba(NH_3)_{10}]I_2$; the *nonammine*, $[Ba(NH_3)_9]I_2$; the *octammine*, $[Ba(NH_3)_8]I_2$; the *heptammine*, $[Ba(NH_3)_7]I_2$; the *hexammine*, $[Ba(NH_3)_6]I_2$; the *tetrammine*, $[Ba(NH_3)_4]I_2$; and the *diammine*, $[Ba(NH_3)_2]I_2$.

The method used in examination of these ammines is described by Biltz and Hüttig.[3]

THE AMMINES OF ZINC, CADMIUM, AND MERCURY.

The tendency to form complex salts is more marked for these elements than for those of the alkaline earths or the first two members of the group, and the ammino-derivatives are more stable than those just described.

Ammino-derivatives of Zinc Salts.

Zinc halides unite with ammonia, readily forming a number of metal-ammines containing one, two, four, five, or six molecules of ammonia for every molecule of zinc salt. The ammino-derivatives of the chlorides are best known, although some of these described appear to be of doubtful individuality.

Monammino-zinc Chloride, $[Zn(NH_3)]Cl_2$.—The compound was first obtained by Déherain, who prepared it by allowing ammonia gas to act upon anhydrous zinc chloride. It may be prepared by distilling

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[1] Joannis, *Compt. rend.*, 1891, 112, 339.
[2] Hüttig, *Zeitsch. anorg. Chem.*, 1922, 125, 269.
[3] Biltz and Hüttig, *ibid.*, 1919, 109, 111.

diammino-zinc chloride, $[Zn(NH_3)_2]Cl_2$, or tetrammino-zinc chloride, $[Zn(NH_3)_4]Cl_2$; both derivatives lose ammonia, leaving a residue of the monammine, which becomes partially crystalline.

Monammino-zinc chloride is a white crystalline solid which is very hygroscopic. It may be distilled at a red heat without decomposition and is stable in air; on treatment with water it is decomposed, yielding tetrammino-zinc chloride and zinc oxychloride.

Diammino-zinc Chloride, $[Zn(NH_3)_2]Cl_2$, is obtained by evaporation of the solution from which the tetrammino-derivative is separated (see under). It may also be prepared by heating tetrammino-zinc chloride to a temperature of 149° C., or by dissolving zinc in an aqueous solution of ammonium chloride with the aid of metallic copper or silver, or by passing ammonia gas into a concentrated solution of zinc chloride in acetone.[1]

Diammino-zinc chloride crystallises in glistening prisms which are stable in air but lose ammonia on heating. It is not completely soluble in water, but may be recrystallised from a hot aqueous solution of ammonium chloride. In the moist state it gradually decomposes with formation of zinc oxychloride. This ammine was at one time regarded as one of the substances found in the Leclanché cell, but Davis[2] afterwards contradicted the statement.

Various hydrated diammino derivatives have been described, such as $[Zn(NH_3)_2]Cl_2.H_2O$, $[Zn(NH_3)_2]Cl_2.\frac{2}{5}H_2O$, and $[Zn(NH_3)_2]Cl_2.\frac{1}{2}H_2O$,[3] but these are doubtful.

Tetrammino-zinc Chloride, $[Zn(NH_3)_4]Cl_2$, is produced by passing ammonia gas into a hot concentrated solution of zinc chloride until the precipitate first formed dissolves; on cooling the liquid, pearly crystals of $[Zn(NH_3)_4]Cl_2.H_2O$ separate.[4] The tetrammine is unstable and easily loses ammonia, forming the more stable lower ammine. It is decomposed by water, but may be recrystallised from an ammoniacal solution. The existence of tetrammino-zinc chloride is confirmed by examining the dissociation pressure.[5]

Pentammino-zinc Chloride, $[Zn(NH_3)_5]Cl_2.H_2O$, may be obtained by dissolving zinc chloride in cold concentrated aqueous ammonia, or by passing ammonia gas into a solution of zinc chloride. The substance crystallises in large octahedra, which are deliquescent and rapidly lose ammonia on exposure to air.

Hexammino-zinc Chloride, $[Zn(NH_3)_6]Cl_2$, cannot be formed in solution, but if ammonia gas be passed over dry zinc chloride increase in volume takes place, heat is developed, and hexammino-zinc chloride is obtained.[5] It is not stable and easily dissociates.[6]

Ammino-zinc Bromides.—The ammino-derivatives of zinc bromide are unstable and easily decomposed. Diammino-zinc bromide, $[Zn(NH_3)_2]Br_2$, is the best known of these ammines. It may be produced in colourless octahedral crystals, when a concentrated solution of zinc bromide is treated with aqueous ammonia. It is decomposed completely by warm water, whilst on heating alone it melts and loses ammonia.

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[1] Naumann, *Ber.*, 1904, 37, 4338.

[2] Davis, *Chem. News*, 1872, 25, 265.

[3] André, *Ann. Chim. Phys.*, 1884, [6], 3, 66; Kane, *ibid.*, 1839, [2], 72, 290.

[4] Blanchard, *J. Amer. Chem. Soc.*, 1904, 26, 1326.

[5] Kuriloff, *Zeitsch. anorg. Chem.*, 1897, 15, 344; *Ann. Chim. Phys.*, 1906, 7, 568.

[6] Bouzat, *Compt. rend.*, 1903, 136, 1396.

Ammino-zinc Iodides.—These are prepared in the same way as those of zinc chloride. *Pentammino-zinc iodide*, $[Zn(NH_3)_5]I_2$, and *hexammino-zinc iodide*, $[Zn(NH_3)_6]I_2$, are easily obtained.

Pentammino-zinc Iodide, $[Zn(NH_3)_5]I_2$, is formed by passing dry ammonia gas over dry zinc iodide; increase in volume takes place and rise of temperature. The pentammine is unstable and is readily decomposed by water. A hydrate which does not easily decompose on treatment with water, $[Zn(NH_3)_5]I_2.3H_2O$, is formed by the action of an aqueous solution of ammonium iodide and ammonia on zinc oxide.[1]

Tetrammino-zinc Iodide, $[Zn(NH_3)_4]I_2$, is prepared by dissolving zinc iodide in aqueous ammonia and evaporating the solution, when white glistening leaflets containing no water separate. The crystals are stable in air but decompose on heating. They dissolve easily in acids and are decomposed by cold water.

Ammino-zinc Sulphates.—Zinc sulphate forms, with ammonia, *pentammino-zinc sulphate*, $[Zn(NH_3)_5]SO_4$; *tetrammino-zinc sulphate*, $[Zn(NH_3)_4]SO_4$; and *diammino-zinc sulphate*, $[Zn(NH_3)_2]SO_4$.

Pentammino-zinc Sulphate, $[Zn(NH_3)_5]SO_4$, is formed by allowing anhydrous zinc sulphate to absorb dry ammonia gas; heat is developed, the substance increases in bulk, and a white powder is obtained. The compound is soluble in water, but gradually decomposes with formation of zinc hydroxide.

Tetrammino-zinc Sulphate, $[Zn(NH_3)_4]SO_4$, is produced by passing ammonia gas into a well-cooled solution of zinc sulphate in aqueous ammonia. A precipitate of small felted needles is formed, consisting of the trihydrate of the *tetrammine*, $[Zn(NH_3)_4]SO_4.3H_2O$. A dihydrate of the ammine has also been obtained. The tetrammine is unstable in air and loses ammonia readily.

Diammino-zinc Sulphate, $[Zn(NH_3)_2]SO_4$, is obtained by keeping the tetrammine at its melting-point for some time. At higher temperatures ammonia is completely eliminated, and on heating the diammine with water it decomposes, with formation of the oxy-salt of zinc, tetrammino-zinc sulphate, and ammonium sulphate.

A hydrated form of the compound $[Zn(NH_3)_2]SO_4.H_2O$ is also described, and if a solution of this be evaporated slowly at ordinary temperature, transparent crystals of hydrated tetrammino-zinc sulphate, $[Zn(NH_3)_4]SO_4.4H_2O$, are formed.

Zinc sulphite also unites with ammonia, forming *monammino-zinc sulphite*, $[Zn(NH_3)]SO_3$; *diammino-zinc sulphite*, $[Zn(NH_3)_2]SO_3$; and *triammino-zinc sulphite*, $[Zn(NH_3)_3]SO_3$.[2]

Ammino-zinc Nitrates are obtained in the same way as the ammino-zinc chlorides. By saturating a concentrated solution of zinc nitrate with ammonia at low temperature, a colourless crystalline substance separates which is tetrammino-zinc nitrate, $[Zn(NH_3)_4](NO_3)_2$. If more ammonia is used and the temperature is kept below 0° C., hexammino-zinc nitrate, $[Zn(NH_3)_6](NO_3)_2$, is obtained.

Ephraim and Bolle[3] examined the stability of the zinc-ammines and found that the temperatures at which the hexammine and pentammine salts of zinc decompose decrease in the order : iodide, bromide, chloride,

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[1] Tasilly, *Compt. rend.*, 1896, **122**, 323.

[2] Ephraim and Bolle, *Ber.*, 1915, 48, 640.

[3] Ephraim and Bolle, *ibid.*, 1915, 48, 638.

thiosulphate, perchlorate, sulphate, nitrate, oxalate, chlorate, nitrite. The metal-ammines of copper are most nearly related to the zinc-ammines in stability. A large number of compounds of zinc with organic bases in place of ammonia are known.

Ammino-derivatives of Cadmium Salts.

Cadmium salts form with ammonia addition compounds which correspond, for the most part, to those of zinc.

Ammines of Cadmium Halides.—Cadmium chloride unites with ammonia with formation of the following compounds: *Monammino-cadmium chloride*, $[Cd(NH_3)]Cl_2$; *diammino-cadmium chloride*, $[Cd(NH_3)_2]Cl_2$; *triammino-cadmium chloride*, $[Cd(NH_3)_3]Cl_2$; *tetrammino-cadmium chloride*, $[Cd(NH_3)_4]Cl_2$; *hexammino-cadmium chloride*, $[Cd(NH_3)_6]Cl_2$.[1]

Monammino-cadmium Chloride, $[Cd(NH_3)]Cl_2$, is formed when diammino-cadmium chloride is distilled.

Diammino-cadmium Chloride, $[Cd(NH_3)_2]Cl_2$, has been obtained in several ways. If cadmium chloride be dissolved in hot aqueous ammonia and the liquid cooled, a crystalline substance separates which is a mixture of diammino-salt and cadmium hydroxide; if, however, a clear aqueous solution of cadmium chloride be saturated with ammonia gas and allowed to evaporate spontaneously, the diammine is obtained free from hydroxide. The same ammino-salt is formed by adding a saturated solution of cadmium chloride to liquid ammonia and evaporating off the excess of ammonia by allowing the temperature to rise. The diammine is also formed by passing ammonia gas into an alcoholic solution of cadmium chloride.[2]

Diammino-cadmium chloride is a white crystalline compound which is stable in dry air up to 210° C. Above that temperature it decomposes, but even at 360° C. decomposition is not complete, and at 400° C. it melts. By distilling the substance monammino-cadmium chloride is produced.

Triammino-cadmium Chloride, $[Cd(NH_3)_3]Cl_2$, is prepared by carefully heating hexammino- or tetrammino-cadmium chloride until the requisite amount of ammonia is lost.

Tetrammino-cadmium Chloride, $[Cd(NH_3)_4]Cl_2$, is obtained by heating the hexammine until two molecular proportions of ammonia are eliminated.

Hexammino-cadmium Chloride, $[Cd(NH_3)_6]Cl_2$.—When anhydrous cadmium chloride is exposed to an atmosphere of dry ammonia the gas is rapidly absorbed, the mass increases in bulk, heat is developed, and the hexammine produced. It has also been prepared by exposing anhydrous cadmium chloride to dry gaseous ammonia for two hours in a tube cooled to very low temperature. A layer of liquid ammonia forms on the surface of the solid, and the tube is sealed and kept for some time at −70° C. On opening and allowing the temperature to rise to −30° C. to remove the condensed ammonia a residue of the hexammino-salt is left.[2]

Hexammino-cadmium chloride is a white crystalline powder, only slightly soluble in cold water. On exposure to air it loses ammonia,

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[1] Lang and Rigault, *Trans. Chem. Soc.*, 1899, 75, 883.

[2] Kwasnik, *Arch. Pharm.*, 1891, 229, 310.

and if left so exposed until the odour of ammonia can no longer be detected, it is found to have formed the more stable diammino-cadmium chloride. The hexammine melts on heating, and loses ammonia completely above 620° C. A pentammino-derivative has been described, but this has since been identified as the hexammine.

Cadmium bromide unites with ammonia, forming three compounds, namely, *diammino-cadmium bromide*, $[Cd(NH_3)_2]Br_2$; *triammino-cadmium bromide*, $[Cd(NH_3)_3]Br_2$; and *tetrammino-cadmium bromide*, $[Cd(NH_3)_4]Br_2$. These correspond in chemical behaviour to the ammino-chlorides.

Diammino-cadmium Bromide, $[Cd(NH_3)_2]Br_2$, is obtained in small colourless crystals by saturating a concentrated solution of cadmium bromide in water with ammonia and allowing the solution to evaporate. The compound is unstable and loses ammonia on heating, and on treatment with water is partially decomposed with formation of cadmium hydroxide. The same product is formed by saturating an acetone solution of cadmium bromide with ammonia gas.[1]

Triammino-cadmium Bromide, $[Cd(NH_3)_3]Br_2$, is formed when ammonia gas is passed into an ammoniacal solution of cadmium bromide. It is a colourless crystalline substance which, on exposure to air, decomposes, the crystals becoming opaque and powdery.

Tetrammino-cadmium Bromide, $[Cd(NH_3)_4]Br_2$, is prepared by passing dry ammonia gas over dry powdered cadmium bromide. The salt swells up, absorbs ammonia, and is transformed into tetrammine. It is unstable, and on heating loses ammonia completely. If dissolved in water ammonia is eliminated and precipitation of cadmium hydroxide takes place.

Ammino-derivatives of Cadmium Iodide.—Cadmium iodide forms with ammonia *diammino-cadmium iodide*, $[Cd(NH_3)_2]I_2$; *tetrammino-cadmium iodide*, $[Cd(NH_3)_4]I_2$; and *hexammino-cadmium iodide*, $[Cd(NH_3)_6]I_2$.

Diammino-cadmium Iodide, $[Cd(NH_3)_2]I_2$, is obtained by heating cadmium hydroxide for a long time with a solution of ammonium iodide, or by dissolving cadmium iodide in acetone and passing ammonia gas into the solution,[2] when small colourless crystals of the ammine separate. The substance melts and loses ammonia on heating.

Tetrammino-cadmium Iodide, $[Cd(NH_3)_4]I_2$, is formed when cadmium iodide is treated with a large excess of ammonia ; it crystallises in colourless plates.[3]

Hexammino-cadmium Iodide, $[Cd(NH_3)_6]I_2$, is produced like the corresponding hexammino-chloride when dry ammonia gas is passed over dry cadmium iodide at ordinary temperature. Rise in temperature and increase in volume takes place and a fine white powder is formed. It loses ammonia completely on warming, and on treatment with water decomposes with precipitation of cadmium hydroxide ; the solution, however, still retains cadmium salt, from which more ammonia may be evolved.

Cadmium sulphate also forms ammino-derivatives; a diammino-, a tetrammino-, and a hexammino-derivative are known.

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[1] Naumann, *Ber.*, 1904, 37, 1337.

[2] Naumann and Müller, *ibid.*, 1904, 37, 4338.

[3] Dawson and McCrae, *Trans. Chem. Soc.*, 1900, 77, 1246.

Diammino-cadmium Sulphate, $[Cd(NH_3)_2]SO_4$, is formed by heating hexammino-cadmium sulphate to 100° C. The compound is stable at 100° C. and no ammonia is liberated.

Tetrammino-cadmium Sulphate, $[Cd(NH_3)_4]SO_4.2H_2O$, is prepared by evaporation of an aqueous ammoniacal solution of cadmium sulphate, or by passing ammonia gas into a well-cooled ammoniacal solution of the sulphate. A hydrate containing four molecules of water may be obtained, when an aqueous ammoniacal solution of cadmium sulphate is poured into alcohol and the ammonia allowed to evaporate in air. The hexammine is prepared by the method already described for hexammino-zinc chloride. It loses ammonia when fused and completely decomposes; water hydrolyses it with precipitation of cadmium hydroxide.

Cadmium nitrate forms complex salts with ammonia, such as *hexammino-cadmium nitrate*, $[Cd(NH_3)_6](NO_3)$, and the hydrate, $[Cd(NH_3)_6](NO_3).H_2O$.[1] These are crystalline substances, easily decomposed by water. The hydrated salt loses water on heating, becomes dark in colour, and finally decomposes with explosion.

The cadmium ammino-derivatives all behave towards heat and water like the corresponding zinc ammines. Ammonia in some cases has been replaced by hydrazine or hydroxylamine; the addition products so formed have the same general characteristics as the ammine themselves.

Ammino-derivatives of Mercury Salts.

Several mercurous salts absorb ammonia in the dry state or react with ammonia in aqueous solution. The products formed have been described from time to time as ammino-mercurous compounds. It appears, however, that these supposed mercuro-ammines are non-existent, and that the substances produced by the action of ammonia are really mercuric derivatives mixed with mercury. For instance, mercurous fluoride in the dry state is blackened by ammonia gas, forming a compound $HgF(NH_3)$. This substance gives off ammonia at 100° C. and is black in colour; the colour is now regarded as being due to finely divided mercury, and the compound as a derivative of mercuric fluoride and not of mercurous fluoride. Numerous instances of the same kind may be quoted. For example, mercurous chloride with aqueous ammonia yields a black compound; this again has been proved to be a mixture of finely divided mercury and mercuric chloroamide. The reaction may be represented thus:

$$2HgCl+2NH_3=Hg+Hg(NH_2)Cl+NH_4Cl.$$

The only salt corresponding to the mercuro-ammines which seems capable of existence is the hydrazine derivative of mercurous nitrate, $[Hg(N_2H_4)_2]NO_3$, prepared by Hoffmann and Marburg.[2] The corresponding ammonia derivative has not been obtained.

Ammino-mercuric Salts.—Several types of ammoniacal derivatives of mercuric salts have been described, but little is known of their constitution. Many of them are insoluble in ordinary solvents and decompose on volatilisation; hence, molecular-weight determinations are difficult. Originally all compounds were shown as derivatives

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[1] André, *Compt. rend.*, 1887, 104, 987.

[2] Hoffmann and Marburg, *Ber.*, 1897, 30, 2030.

of dimercuriammonium salts, in which four hydrogen atoms of the ammonium radicle were replaced by two divalent mercury atoms thus : $NH_4R \longrightarrow Hg_2NR$, where R represents a monacidic radicle.[1, 2] Further derivatives were produced owing to the tendency of dimercuriammonium compounds to form double salts with ammonium salts and mercuric salts. This view was subjected to serious criticism, and in 1907 Franklin [3] rejected the ammonium theory and extended the substituted ammonia theory, bringing out an analogy between reactions where ammonia takes part and where water takes part. In this theory ammonia is therefore represented as "ammonia of crystallisation," like water of crystallisation in hydrated salts. The nature of the mercuric ammonia compounds is varied, but according to Franklin,[3] and later Holmes,[4] they seem to fall into three definite classes, namely :

1. Additive compounds of mercuric salt and ammonia, the ammino-mercuric salts such as $[Hg(NH_3)_2]Cl_2$.
2. Compounds described as "ammonolysed compounds," a term introduced by Franklin to indicate analogy to hydrolysis. For example, infusible precipitate, $ClHgNH_2$, where ammonia has entered the molecule much as hydroxyl does on hydrolysis.
3. Compounds where both ammonolysis and hydrolysis take place. For example, the chloride of Millon's base, $NH_2HgO.HgCl$.

The first class represents the true ammino-derivatives of mercuric salts.

It has been found on examination of the ammino-derivatives of mercuric halides that the nature of the halogen present has a marked effect on the stability of the compound. Thus, diammino-mercuric chloride, $[Hg(NH_3)_2]Cl_2$, is stable and does not readily lose ammonia, whereas the corresponding iodide, diammino-mercuric iodide, $[Hg(NH_3)_2]I_2$, readily loses ammonia at ordinary temperature. The stability decreases in the order: chloride, bromide, iodide.

Ammino-mercuric Chlorides.—Six ammino-salts of mercuric chloride are known. These are: *monammino-mercuric chloride*, $[Hg(NH_3)]Cl_2$; *diammino-mercuric chloride*, $[Hg(NH_3)_2]Cl_2$; *triammino-mercuric chloride*, $[Hg(NH_3)_3]Cl_2$; *tetrammino-mercuric chloride*, $[Hg(NH_3)_4]Cl_2$; *triammino-dimercuric chloride*, $[Hg_2(NH_3)_3]Cl_4$; [5] and *dodecammino-mercuric chloride*, $HgCl_2.12NH_3$. This last derivative is only stable if kept under pressure, and if pressure is released ammonolysis takes place in accordance with the equation

$$HgCl_2.12NH_3 \longrightarrow ClHgNH_2+NH_4Cl+10NH_3.$$

The ammonium chloride formed dissolves in the liquid ammonia used in the preparation of the addition compound.[6]

Mercuric bromide and mercuric iodide yield the same type of compounds. The stability of these, however, is less than that of the chlorides. The fluorine analogue to fusible precipitate has been prepared,[7] to which the composition $Hg(NH_2)F$ is given. *Dimercuric fluoramide*, $(HgF)_2NH.H_2O$, has also been prepared.

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[1] Pesci, *Gazz. Chim. Ital.*, 1891, [2], 21, 571.

[2] Rây, *Trans. Chem. Soc.*, 1902, 81, 647.

[3] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 35 ; 1912, 47, 361.

[4] Holmes, *Trans. Chem. Soc.*, 1918, 113, 74.

[5] Naumann and Kammerer, *Ber.*, 1914, 47, 1373 ; 1904, 37, 3603 ; 1910, 43, 315.

[6] Franklin and Kraus, *Amer. Chem. J.*, 1900, 23, 300.

[7] Böhm, *Zeitsch. anorg. Chem.*, 1905, 43, 327 ; Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 51.

The best known and most important compound belonging to the ammino-mercuric salts is the so-called *fusible precipitate* of composition $HgCl_2.2NH_3$, *diammino-mercuric chloride.* It was originally represented as a double salt of dimercuriammonium chloride and ammonium chloride, $Hg_2NCl.NH_4Cl$, but this has been proved to be incorrect, and the addition formula is now accepted as the one which bears out its chemical behaviour.

Diammino-mercuric Chloride, Fusible Precipitate, $[Hg(NH_3)_2]Cl_2$, is obtained by adding an aqueous solution of mercuric chloride drop by drop to a boiling solution of ammonium chloride, containing ammonia, as long as the precipitate dissolves. On cooling the liquid, colourless rhombic crystals separate. The same substance may be prepared by dissolving mercuric chloride in liquid ammonia. Fusible precipitate is stable and is not altered on heating to 125° C., but at a temperature of 180° C. ammonia is evolved, and the mass melts at 300° C. to a yellow liquid with loss of nitrogen and ammonia. On boiling with alkali it decomposes with elimination of ammonia. According to some investigators all the ammonia is evolved,[1] whilst Pesci states that only three-quarters of the nitrogen is evolved as ammonia.[2] Related compounds containing mercuric bromide, mercuric nitrate, and mercuric iodide are known.

Diammino-mercuric Iodide, $[Hg(NH_3)_2]I_2$, behaves like the ammines of zinc and loses ammonia on exposure to air; the monammino derivative from examination of vapour-pressure measurements does not appear to exist.

The ammonolysed compounds or ammonio bases are formed when a solution of mercuric salt is treated with slight excess of ammonia. This does not give an addition compound such as metal-ammine, but a substituted derivative. For instance, from mercuric chloride infusible precipitate $Hg(NH_2)Cl$ is formed. The same substance may be produced from diammino-mercuric chloride if an excess of ammonia be present after fusible precipitate is formed.

Conversely, $Hg(NH_2)Cl$ may be transformed into the diammino-derivative by means of ammonium chloride dissolved in liquid ammonia thus:

$$[Hg(NH_3)_2]Cl_2 \rightleftharpoons NH_4Cl + Hg(NH_2)Cl.$$

Infusible precipitate or mercuric amido-chloride, $Hg(NH_2)Cl$, is very sparingly soluble in water, a fact which is one of the arguments against the old formula where the compound was represented by Rammelsberg[3] as a double salt of dimercuriammonium chloride and ammonium chloride, $Hg_2NCl.NH_4Cl$, for the ammonium salt of the complex acid, $H(HgNCl_2)$, ought to be more soluble than the acid.

When heated, mercuric amido-chloride decomposes with loss of ammonia and nitrogen, leaving a residue of mercuric chloride. It does not melt during decomposition, and if boiled with aqueous sodium hydroxide all the nitrogen is eliminated as ammonia. Water hydrolyses it, giving ammonium chloride and oxydimercuriamido-chloride thus:

$$2Hg(NH_2)Cl + H_2O \longrightarrow NH_4Cl + HgONH_2.HgCl, \text{ or } Hg(OH).NH.HgCl$$

(the chloride of Millon's base).

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[1] Hoffmann and Marburg, *Ber.*, 1897, 30, 2030.

[2] Pesci, *Gazz. Chim. Ital.*, 1891, [2], 21, 571.

[3] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 563.

Millon's base itself is regarded by Franklin and others as the hydroxyl compound, dimercurihydroxy-ammonium hydroxide, $Hg(OH)_2.NH_2OH$. It is obtained in yellow crystals by allowing ammonia in aqueous solution to act on mercuric oxide :

$$2HgO + NH_4OH = Hg(OH)_2.NH_2OH.$$

Rammelsberg gave the base the formula $Hg_2NOH.2H_2O$, showing it to contain two molecules of water of hydration; but this does not agree with its behaviour nor with that of its chloride, which can be heated to 125° C. without loss of water.

Nessler's precipitate belongs to the same class of compounds, and may be represented as $Hg(OH).NH.HgI$, mercuric hydroxy-iodoamide.

CHAPTER VI.

METAL-AMMINES OF THE ELEMENTS OF GROUP III.

THE metal-ammino-derivatives in Group III. are few, and many of these described are of doubtful composition, also they are unstable compounds and obtainable only in the dry state.

Ammino-derivatives of Boron Salts.

The first element of the group, boron, behaves mostly as a non-metal, but in its compounds with the halogens it shows some of the properties of a metal, for the halides are not readily acted upon by water.

The halogen derivatives of boron unite with ammonia, forming ammines. Boron trifluoride combines with ammonia, forming the substances $BF_3.NH_3$, $BF_3.2NH_3$, $BF_3.3NH_3$; the two latter are liquid, and easily lose ammonia with formation of the monammine.

Monammino-boron Fluoride, $BF_3.NH_3$, is a white solid which may be sublimed without decomposition in a closed tube. The vapour of the substance is stated by Mixter [1] to attack glass; it is decomposed on exposure to moist air, and dissolves in water with formation of oxy-fluoborate. It is probable that these compounds of boron trifluoride and ammonia are mixtures of the same type as those formed from boron trichloride described by Joannis.

Ammino-boron Trichlorides.—Berzelius observed that boron trichloride absorbed ammonia gas with formation of a compound of composition $2BCl_3.3NH_3$.

Sesquiammino-boron Trichloride, $2BCl_3.3NH_3$, is also formed when dry ammonia gas is passed into liquid boron trichloride. The ammine does not fume on exposure to air, is less volatile than ammonium chloride, and may be sublimed without decomposition. Water decomposes it with formation of ammonium chloride, hydrochloric acid, and a borate. Besson [2] described a substance of composition $2BCl_3.9NH_3$, which he obtained from boron phosphino-chloride and ammonia. This is not attacked by moist air and does not lose ammonia below 50° C., but water decomposes it immediately.

In 1902 Joannis [3] examined the products formed when ammonia acts upon boron trichloride, and concluded that the reaction is more complex than mere addition of ammonia.

When hydrogen carrying boron trichloride vapour is passed into liquid ammonia at —50° C. and the temperature then raised to —23° C.

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[1] Mixter, *Amer. Chem. J.*, 1881, 2, 153.

[2] Besson, *Compt. rend.*, 1890, 110, 517.

[3] Joannis, *ibid.*, 1902, 135, 1106.

to remove excess of ammonia, a residue containing fifteen molecules of ammonia for every molecule of the chloride is obtained. On raising the temperature to 0° C. nine molecules of ammonia are removed and the composition becomes $BCl_3.6NH_3$. During the loss of ammonia the vapour pressure is found to be the same as that of an additive compound, $NH_4Cl.3NH_3$. Hydrogen and nitrogen are not evolved during the reaction, and by determination of increase in weight and the formation of boric acid on treatment with water, it is concluded that for three ammonium groups formed three amino groups are produced which unite with boron. The reaction at −23° C. is assumed to take place thus :

$$BCl_3+15NH_3 \longrightarrow 3(NH_4Cl.3NH_3)+B(NH_2)_3,$$

and at 0° C. according to the equation

$$BCl_3+6NH_3 \longrightarrow 3NH_4Cl+B(NH_2)_3.$$

The compounds described, therefore, are not simple addition substances, and this may explain the different results obtained. The ammonium chloride formed may be removed by liquid ammonia, in which it is soluble, but the removal is not complete.

Ammino-boron Tribromides.—Ammonia gas combines directly with boron tribromide, heat is developed, and some boron nitride is produced.[1] By keeping the temperature low a product may be produced containing no nitride. Dry ammonia gas cooled to 0° C. is passed into a cold solution of boron tribromide in carbon tetrachloride, a white solid separates, and on removal of the solvent by evaporating in a current of air a white amorphous substance remains of composition $BBr_3.4NH_3$, tetrammino-boron tribromide. It decomposes if heated in oxygen below 150° C., and a mixture of boron nitride and ammonium bromide is formed. Water and alkali also decompose the ammine. Joannis[2] throws doubt on the existence of this compound, and explains the absorption of ammonia in the same manner as that for boron trichloride, the substance produced in this case being boronimide, $B_2(NH)_3$. He assumes that the reaction at 0° C. takes place according to the equation

$$2BBr_3+27NH_3 \longrightarrow 6(NH_4Br.3NH_3)+B_2(NH)_3.$$

If the temperature be raised to 20° C. the ammoniacal ammonium bromide dissociates, and for every molecule of boron tribromide present nine molecules of ammonia are evolved.

Ammino-boron Tri-iodides.—Boron iodide and ammonia unite with development of heat. If dry ammonia gas is passed into a solution of boron tri-iodide in carbon tetrachloride, cooled to 0° C., a white amorphous substance of composition $BI_3.5NH_3$ is formed,[3] which turns brown on exposure to light and is decomposed by water. This compound is capable of absorbing more ammonia, being transformed into a liquid of composition $BI_3.15NH_3$, which is exceedingly unstable and rapidly loses ammonia on exposure to air. These derivatives also are most probably mixtures of ammonium iodide and boron triamide.

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[1] Besson, *Compt. rend.*, 1891, **112**, 1002.
[2] Joannis, *ibid.*, 1904, **139**, 364.
[3] Besson, *ibid.*, 1892, **114**, 542.

Ammino-derivatives of Aluminium Salts.

Aluminium forms numerous series of complex derivatives, the halogen salts showing a marked tendency to form molecular compounds with other metallic halides, with acid chlorides, with chlorides of organic acids, and with ammonia.

Ammino-aluminium Fluoride.—Aluminium fluoride combines slowly with ammonia; one compound is reported, the monammine, $[Al(NH_3)]F_3$, which was prepared by Clark.[1]

Ammino-aluminium Chlorides.—Anhydrous aluminium chloride combines readily with dry ammonia gas, heat is evolved, and the chloride increases greatly in volume. Several compounds of aluminium chloride and ammonia are described of composition $AlCl_3.9NH_3$, $AlCl_3.6NH_3$, $AlCl_3.5NH_3$, $AlCl_3.4NH_3$, $AlCl_3.3NH_3$, $AlCl_3.2NH_3$.

Aluminium chloride in aqueous solution does not appear to unite with ammonia, and the compounds described are formed by the action of ammonia gas or liquid ammonia on the anhydrous salt.

Franklin in early research on ammonia and aluminium chloride stated that the anhydrous salt did not dissolve in liquid ammonia. Persoz [2] investigated the action of ammonia on aluminium chloride and described a substance of composition $AlCl_3.3NH_3$.

Stillmann and Yoder [3] and Baud [4] have examined the compounds obtained, and find that a series of derivatives exists depending on the temperature at which addition of ammonia takes place. According to these investigators the following compounds exist: $[Al(NH_3)_9]Cl_3$, $[Al(NH_3)_6]Cl_3$, $[Al(NH_3)_5]Cl_3$, $[Al(NH_3)_2]Cl_3$.

If well-dried ammonia gas is passed over freshly sublimed aluminium chloride ammonia is rapidly absorbed, heat is developed, and the whole mass fuses and then gradually solidifies as more ammonia is absorbed, leaving a white voluminous powder of composition $AlCl_3.6NH_3$ or $[Al(NH_3)_6]Cl_3$. Hexammino-aluminium chloride is stable at ordinary temperature and is much less hygroscopic than the chloride. It is decomposed by water with formation of aluminium hydroxide, and when heated in dry air is oxidised, yielding the oxide and ammonium chloride. If heated in an atmosphere of dry hydrogen it loses ammonia and passes into diammino-aluminium chloride, $[Al(NH_3)_2]Cl_3$.[5] Triammino-aluminium chloride obtained in this way by Persoz was not found by Stillmann and Yoder.

The hexammine may be prepared by treating anhydrous salt at ordinary temperature with excess of dry ammonia gas.[6] On heating the compound to 180° C. it loses one molecule of ammonia, yielding pentammino-aluminium chloride, $[Al(NH_3)_5]Cl_3$.

Pentammino-aluminium chloride if heated in an atmosphere of dry hydrogen melts at 380° C. and boils at 450° C., leaving a white powdery residue of monammino-aluminium chloride, $[Al(NH_3)]Cl_3$. If the distillation is carried out without hydrogen the residue consists of a mixture of pentammino- and monammino-chloride.

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[1] G. L. Clark, *Amer. J. Sci.*, 1924, 7, 1.

[2] Persoz, *Ann. Chim. Phys.*, 1830, 44, 319.

[3] Stillmann and Yoder, *Amer. Chem. J.*, 1895, 17, 748.

[4] Baud, *Compt. rend.*, 1901, 132, 134, 690.

[5] Stillmann and Yoder, *Amer. Chem. J.*, 1895, 17, 749.

[6] Baud, *Compt. rend.*, 1901, 132, 134.

Pentammino-aluminium chloride absorbs more ammonia at the boiling-point of liquid ammonia, forming an unstable compound containing about eighteen molecules of ammonia. At −23° C. aluminium chloride absorbs ammonia, yielding the unstable derivative $AlCl_3.9NH_3$. This cannot exist at ordinary temperature, for its dissociation pressure even at −14° C. is 760 mm.[1]

All the compounds formed decompose immediately in water with formation of aluminium hydroxide. The most stable derivative is the hexammine; gaseous hydrogen chloride at −15° C. has little action upon it, at 0° C. the compound is attacked slowly, and at 15° C. it is rapidly converted into ammonium chloride and aluminium chloride.

Ammino-aluminium Bromide.—If aluminium bromide is exposed to ammonia gas at ordinary temperature the gas is absorbed slowly at first and then more rapidly; the mass increases in bulk and a white powder is formed of composition $AlBr_3.NH_3$ or $[Al(NH_3)]Br_3$. The monammine loses ammonia on exposure to air, but may be sublimed in a sealed tube without decomposition.

Ammino-aluminium Iodides.—Aluminium iodide is soluble in liquid ammonia, forming a colourless solution from which, on cooling to −33° C., a crystalline solid of composition $AlI_3.20NH_3$ separates. On rise of temperature it loses ammonia, and at 8° to 13° C. the composition is that of hexammino-aluminium iodide, $[Al(NH_3)_6]I_3$. Weber[2] found that aluminium iodide absorbs ammonia gas slowly at first, and on warming a white voluminous powder was formed which contains at least four molecules of ammonia for every molecule of the iodide. It decomposes with loss of ammonia on treatment with water.

Ammino-derivatives of Indium Chloride.

Anhydrous indium trichloride on volatilising in a stream of dry ammonia gas gives a white, crystalline, volatile, additive product. The composition of the substance is not discussed and the properties are not described.[3] Indium halogen salts have a tendency to form complex salts with the alkali chlorides. For example, the salt potassium indium chloride, $K_6[(InCl_3)_2Cl_6].3H_2O$, is produced by evaporating an aqueous solution containing potassium and indium chlorides in presence of hydrochloric acid. Also the ammonium salt, $(NH_4)_2[InCl_3.Cl_2].H_2O$, is described. These complex salts are easily soluble in water, but it is not known if the complex anion exists in aqueous solution or not.

Renz[4] describes an additive compound of indium trichloride and pyridine, tripyridino-indium trichloride, $[In(C_5H_5N)_3]Cl_3$, which is prepared by adding pyridine to a solution of indium trichloride in alcohol. After standing for a short time, small needle-shaped crystals separate of melting-point 253° C. The compound is not hygroscopic like indium chloride, is somewhat sparingly soluble in alcohol, and is insoluble in ether. It decomposes on warming with water with formation of indium hydroxide, $In(OH)_3$. Aluminium trichloride and iron trichloride form similar addition products.

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[1] Baud, *Compt. rend.*, 1901, 132, 690.

[2] Weber, *Pogg. Annalen*, 1857, 103, 263.

[3] Dennis and Geer, *Ber.*, 1904, 37, 961.

[4] Renz, *ibid.*, 1903, 36, 101; 1904, 37, 2110.

Ammino-derivatives of Thallium Salts.

Thallium halides and a few other salts of thallium form addition compounds with ammonia.

Thallous halides do not absorb ammonia at ordinary temperature, but in liquid ammonia these salts form triammino-thallous halides of composition $[Tl(NH_3)_3]Cl$, $[Tl(NH_3)_3]Br$.[1] The triammino-derivatives formed are somewhat soluble in liquid ammonia, and the solubility increases with rise of temperature and increase in atomic weight of the halogens. No lower ammino-derivatives are known. Thallic halides absorb ammonia gas readily. If ammonia gas is passed into an alcoholic solution of thallic chloride, or if dry ammonia gas is passed over dry thallic chloride, the gas is absorbed and a white crystalline substance is formed of composition $[Tl(NH_3)_3]Cl_3$. The crystals may be washed with alcohol containing ammonia and then with absolute alcohol, and finally dried *in vacuo*. On coming in contact with water the triammine is decomposed with precipitation of violet-black oxide thus :

$$2[Tl(NH_3)_3]Cl_3+3H_2O=Tl_2O_3+6NH_4Cl.$$

The triammine is soluble in hydrochloric acid, forming ammonium thallic chloride, $3NH_4Cl.TlCl_3$, and on heating decomposes with loss of ammonia and formation of ammonium chloride and thallous chloride.

Triammino-thallic Bromide, $[Tl(NH_3)_3]Br_3$, is prepared in the same way. It becomes very quickly yellow in colour, due to partial decomposition. Water transforms it into the oxide, Tl_2O_3, and on heating to 100° C. it loses ammonia and bromine, leaving a residue of thallous bromide.

Meyer [2] prepared tripyridino-thallic chloride by mixing an aqueous or ethereal solution of thallic chloride with pyridine, when a white crystalline precipitate of the tripyridino-derivative, $[Tl(C_5H_5N)_3]Cl_3$, is formed. Renz [3] obtained the same compound by mixing thallic chloride and pyridine in alcoholic solution. The compound is stable in air, and crystallises in small white needles which are insoluble in ether and soluble in alcohol. It dissolves fairly easily in water, but the aqueous solution decomposes readily. Thallic bromide also forms a tripyridino-compound, $[Tl(C_5H_5N)_3]Br_3$, and thallic iodide gives the corresponding iodide, $[Tl(C_5H_5N)_3]I_3$. Similar derivatives are known containing three molecules of quinoline.

AMMINO-DERIVATIVES OF THE RARE EARTH SALTS.

The rare earths which are included in Group III. form a few complex derivatives containing ammonia or organic bases. These have, however, not been fully investigated.

Ammino-derivatives of Neodymium Chloride.

Anhydrous neodymium chloride unites with ammonia gas at low temperature, or if kept in a sealed tube with liquid ammonia, yielding a voluminous rose-coloured powder of composition $[Nd(NH_3)_{12}]Cl_3$.

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[1] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1921, 119, 97.

[2] Meyer, *ibid.*, 1900, 24, 347.

[3] Renz, *Ber.*, 1902, 35, 1111.

On gradually heating the substance six different temperatures are obtained at which ammonia is rapidly evolved, indicating the existence of the following derivatives: $[Nd(NH_3)_{11}]Cl_3$, $[Nd(NH_3)_8]Cl_3$, $[Nd(NH_3)_5]Cl_3$, $[Nd(NH_3)_4]Cl_3$, $[Nd(NH_3)_2]Cl_3$, $[Nd(NH_3)]Cl_3$. These ammino-derivatives, however, have not been further investigated.[1]

Ammino-derivatives of Samarium Chloride.

Anhydrous samarium chloride when mixed with liquid ammonia in a sealed tube is converted into a bulky white powder having the composition $[Sm(NH_3)_{11\cdot5}]Cl_3$. If progressively heated it loses ammonia at eight different temperatures, indicating the formation of derivatives of composition $[Sm(NH_3)_{9\cdot5}]Cl_3$, $[Sm(NH_3)_8]Cl_3$, $[Sm(NH_3)_5]Cl_3$, $[Sm(NH_3)_4]Cl_3$, $[Sm(NH_3)_3]Cl_3$, $[Sm(NH_3)_2]Cl_3$, $[Sm(NH_3)]Cl_3$, respectively.[2]

Organic bases such as pyridine also unite with the chlorides of the rare earths. The following compounds have been obtained: *dipyridino-praesodymium chloride*, $[Pr(C_5H_5N)_2]Cl_3$; *tripyridino-neodymium chloride*, $[Nd(C_5H_5N)_3]Cl_3$; *tripyridino-yttrium chloride*, $[Y(C_5H_5N)_3]Cl_3$; *tripyridino-samarium chloride*, $[Sm(C_5H_5N)_3]Cl_3$.[3]

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[1] Matignon, *Compt. rend.*, 1906, 142, 1042; Muthman and Beck, *Annalen*, 1904, 58, 331.

[2] Matignon, *Compt. rend.*, 1905, 140, 141.

[3] Matignon, *Ann. Chim. Phys.*, 1906, [8], 8, 268, 395, 401, 416.

CHAPTER VII.

THE METAL-AMMINES OF THE ELEMENTS OF GROUP IV.

CARBON and silicon, the two typical non-metals of the group, form an enormous number of complex derivatives. Among the metallic elements of the group ammino-derivatives are known, but many of these are unstable.

Carbon. Silicon.	
Subgroup A.	*Subgroup B.*
Titanium.	Germanium.
Zirconium.	Tin.
Cerium.	Lead.
Thorium.	

Ammino-derivatives of Titanium Salts.

Titanium forms three series of salts in which the element is respectively tetra-, tri-, and mono-valent. Thus, titanium and chlorine form titanium tetrachloride, $TiCl_4$, titanium trichloride, $TiCl_3$, and titanium monochloride, TiCl. The two last are unstable and readily pass into the higher chloride. Titanium tetrachloride shows a marked resemblance to tin tetrachloride; it unites easily with hydrochloric acid in solution, with formation of the complex acid, chloro-titanic acid, $[TiCl_6]H_2$, and forms many crystalline products with other chlorides. It also unites with ammonia, forming ammines.

Two ammino-derivatives of titanic chloride, namely, *octammino-titanic chloride,* $[Ti(NH_3)_8]Cl_4$, and *hexammino-titanic chloride,* $[Ti(NH_3)_6]Cl_4$, are described.[1]

Octammino-titanic Chloride, $[Ti(NH_3)_8]Cl_4$, is obtained by passing dry ammonia gas into a suspension of titanic chloride in ether; ammonia is rapidly absorbed, and a dark yellow powder formed of composition $TiCl_4.8NH_3$. The substance loses ammonia very readily, and is immediately decomposed by moist air, but not if kept over freshly prepared anhydrous calcium chloride.

Hexammino-titanic Chloride, $[Ti(NH_3)_6]Cl_4$, is prepared by allowing a stream of dry hydrogen saturated with gaseous titanic chloride to come in contact with dry ammonia gas in a specially designed flask. A voluminous yellow powder remains, which is unaltered in dry air, and does not lose its yellow colour over freshly ignited calcium chloride in absence of air. Water decomposes the substance, with formation of titanic acid and ammonium chloride thus:

$$[Ti(NH_3)_6]Cl_4+4H_2O \longrightarrow Ti(OH)_4+4NH_4Cl+2NH_3.$$

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[1] Stähler, *Ber.*, 1905, 38, 2626. See also Rosenheim and Schütte, *Zeitsch. anorg. Chem* 1901, 26, 239.

On standing over ordinary dry calcium chloride the compound becomes white, due probably to hydrolysis caused by moisture in the calcium chloride and in the air.

Rosenheim described a tetrammino-derivative, $TiCl_4.4NH_3$, which he obtained by allowing the product from the action of dry ammonia on an ethereal suspension of titanic chloride to stand over dry calcium chloride. The substance so obtained was white, but further examination proved it to be a mixture of titanic acid and ammonium chloride produced by moisture in the air and in the imperfectly dried calcium chloride.

On treating titanic chloride with liquid ammonia a yellow powder is formed of composition $TiCl_4.8NH_3$, which seems identical with that produced by passing ammonia gas into an ethereal suspension of titanic chloride. On extracting either the octammino- or the hexammino-salt with liquid ammonia, ammonium chloride is removed and a dark yellow powder is left. This residue appears to be the tetramide of titanium, $Ti(NH_2)_4$, and corresponds to the substances obtained from aluminium chloride and boron chloride by Joannis. Additive compounds of titanic chloride with pyridine and quinoline are known, and if pyridine be added to a suspension of titanic chloride in ether, a compound is produced of composition $TiCl_4(C_5H_5N)_6$. Additive compounds of chloro-titanic acid and bromo-titanic acids with pyridine and quinoline may also be formed.

Pyridino-chloro-titanic Acid, $(C_5H_5N)_2.H_2TiCl_6$, is deposited from a solution of pyridine hydrochloride and titanic chloride in hydrochloric acid as a yellow powder which decomposes on exposure to air or when treated with water. The corresponding quinoline derivative is more stable.

Titanium tetrabromide unites with ammonia, forming *octammino-titanic bromide*, $[Ti(NH_3)_8]Br_4$, which has similar properties to the chloride.

Pyridino-bromo-titanic Acid, $(C_5H_5N)_2.H_2TiBr_6$, is formed by saturating a solution of pyridine hydrobromide and titanic acid in alcoholic hydrobromic acid with hydrogen bromide.[1]

Iodine additive products are not known.

Ammino-derivatives of Zirconium Salts.

Zirconium fluoride reacts with liquid ammonia, forming the unstable compound, ammino-zirconium tetrafluoride, $2ZrF_4 2NH_3$. Zirconium tetrachloride forms several ammines.

Diammino-zirconium Tetrachloride, $[Zr(NH_3)_2]Cl_4$, is prepared by passing dry ammonia gas over solid zirconium tetrachloride at ordinary temperature.[2] The compound is a fine white powder which readily loses ammonia in moist air, and is decomposed by water with formation of zirconium hydroxide, $Zr(OH)_4$, and ammonium chloride. At higher temperatures more ammonia is absorbed, and *tetrammino-zirconium tetrachloride*, $[Zr(NH_3)_4]Cl_4$, is formed.

Octammino-zirconium Tetrachloride, $[Zr(NH_3)_8]Cl_4$, is produced by passing ammonia gas into an ethereal suspension of zirconium chloride, or by passing dry ammonia gas over anhydrous zirconium

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[1] Rosenheim and Schütte, *Zeitsch. anorg. Chem.*, 1901, 26, 239.

[2] Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815.

tetrachloride at ordinary temperature.[1] It is a white hygroscopic powder which is easily decomposed by water, and on heating to 232° C. loses ammonia, with formation of the triammine, $[Zr(NH_3)_3]Cl_4$.

Zirconium tetrabromide unites with ammonia to form *decammino-zirconium bromide*, $[Zr(NH_3)_{10}]Br_4$, and the iodide forms a variety of derivatives according to the temperature at which absorption takes place. The following compounds are obtained: $[Zr(NH_3)_8]I_4$ at $-22°$ C., $[Zr(NH_3)_7]I_4$ at 100° C., $[Zr(NH_3)_6]I_4$ at 150° C. With liquid ammonia $[Zr(NH_3)_8]I_4$ is formed, but on washing the solid with liquid ammonia, ammonium iodide is removed in considerable quantity and the zirconium content of the solid is increased. Stähler and Denk therefore suggest that the octammino-compound is probably a mixture of zirconium amide, $Zr(NH_2)_4$, and ammonium iodide. The ammonia additive compounds of zirconium tetrachloride decompose on heating, with formation of the nitride, Zr_3N_2.[2]

Ammino-derivatives of Cerium Chloride.

Cerium trichloride very readily unites with ammonia at low temperature. Barre[3] proved the existence of five different ammines; they are all white powders which decompose in water. By studying the dissociation pressures the following compounds have been shown to exist, namely: $CeCl_3.20NH_3$, $CeCl_3.12NH_3$, $CeCl_3.8NH_3$, $CeCl_3.4NH_3$, and $CeCl_3.2NH_3$. Increase in volume and rise in temperature occur during the formation of the compounds.

Ammino-derivatives of Thorium Halides.

Thorium tetrachloride, like cerium chloride, combines readily with gaseous ammonia. The compounds known are formed by the union of gaseous or liquid ammonia with anhydrous thorium tetrachloride. All lose ammonia on standing, and on heating are transformed into thorium tetramide, $Th(NH_2)_4$. The following derivatives have been prepared: $ThCl_4.18NH_3$, $ThCl_4.12NH_3$, $ThCl_4.7NH_3$, $ThCl_4.6NH_3$, $ThCl_4.4NH_3$. Tetrammino-thorium tetrachloride is the most stable member of the series, and may be heated to 150° C. before decomposition takes place. On heating to 250° C. it decomposes into thorium tetramide, $Th(NH_2)_4$. Chauvenet[4] prepared these derivatives and examined their properties. He classifies the addition compounds into three groups. Group I. comprises those obtained by treating thorium tetrachloride with liquid ammonia at different temperatures. The compounds obtained contain 6, 7, 12, or 18 molecules of ammonia, and are decomposed by water or *in vacuo*, with loss of ammonia and formation of tetrammino-thorium tetrachloride, $ThCl_4.4NH_3$. Group II. comprises those compounds obtained by exposing the chloride to gaseous ammonia. They contain 4, 6, or 7 molecules of ammonia, are unaltered *in vacuo*, and are not decomposed by treatment with water. Group III. consists of compounds obtained by treating Group II. with liquid ammonia. They contain 6, 7, 12, or 18 molecules of ammonia. Two of the compounds

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[1] Stähler and Denk, *Ber.*, 1905, 38, 2611.

[2] Bruère and Chauvenet, *Compt. rend.*, 1918, 167, 201.

[3] M. Barre, *ibid.*, 1913, 156, 1017.

[4] Chauvenet, *ibid.*, 1910, 151, 387.

are identical with two of the first group. Tetrammino-thorium chloride is the only one of the series stable above 150° C.

Ammino-derivatives of Tin Halides.

The halogen salts of tin unite readily with ammonia, with formation of derivatives the composition of which depends on the temperature at which reaction takes place.

Ammino-derivatives of Stannic Fluoride.—Stannic fluoride unites with ammonia on heating to 43° C., forming the white solid **monammino-stannic fluoride,** $[Sn(NH_3)]F_4$. The compound is remarkably stable, and may be heated to 400° C. with little decomposition.[1]

Diammino-stannic Fluoride, $[Sn(NH_3)_2]F_4$, is formed if stannic fluoride and ammonia are heated together in a sealed tube to a temperature of 120° C. Both the monammine and the diammine are soluble in water, the solutions becoming cloudy due to decomposition. Stannic fluoride also forms addition derivatives with the bases pyridine and quinoline.

Ammino-derivatives of Stannous Chloride.—The composition of the additive compounds of stannous chloride and ammonia varies with the temperature at which the substances are caused to combine.[2]

Diammino-stannous Chloride, $[Sn(NH_3)_2]Cl_2$.—If dry ammonia gas is passed over anhydrous stannous chloride, immersed in a freezing mixture, a yellow powder is formed of composition $SnCl_2.2NH_3$. It blackens on exposure to light, and moist air attacks the substance, with formation of stannous oxide and ammonium chloride. If absorption is allowed to take place at ordinary temperature a mixture of monammino-stannous chloride, $[Sn(NH_3)]Cl_2$, and diammino-stannous chloride, $[Sn(NH_3)_2]Cl_2$, is obtained; whilst at 100° C. stannous chloride is claimed to absorb ammonia gas, with formation of a white powder of composition corresponding to **monammino-stannous chloride,** $[Sn(NH_3)]Cl_2$.

At temperatures between 120° and 300° C. a brownish-red crystalline substance, of composition $3SnCl_2.2NH_3$, is formed. This is the most stable of the compounds, and is only slowly decomposed by water.[2, 3] On examination of the temperature of dissociation of the addition products of stannous chloride and ammonia, the highest ammine obtained has composition $SnCl_2.9NH_3$; this is formed by the action of liquid ammonia on anhydrous stannous chloride at —78° C. The chloride increases greatly in volume during addition, and the temperature, at which the dissociation pressure is 100 mm., is —55° C. This compound and tetrammino-stannous chloride, $[Sn(NH_3)_4]Cl_2$, with temperature —15° C., at which the dissociation pressure is 100 mm., are the only ammines of stannous chloride and ammonia which exist with certainty.[4]

Ammino-derivatives of Stannic Chloride.—Persoz[3] found that anhydrous stannic chloride combines readily with ammonia gas, giving a white solid of composition $SnCl_4.4NH_3$, which can be sublimed without change. It may be obtained in a crystalline state by evaporating an aqueous solution of the compound over sulphuric acid, but long standing in water causes it to decompose, with formation of stannic hydroxide.

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[1] Wolter, *Chem. Zeit.*, 1912, 36, 165.

[2] Sofianopoulos, *Compt. rend.*, 1911, 152, 865.

[3] Persoz, *Ann. Chim. Phys.*, 1830, 44, 322.

[4] Biltz and Fischer, *Zeitsch. anorg. Chem.*, 1923, 129, 1.

Ammino-derivatives of Stannous Bromide.—Four compounds of stannous bromide and ammonia are known, namely, $[Sn(NH_3)_9]Br_2$, $[Sn(NH_3)_5]Br_2$, $[Sn(NH_3)_3]Br_2$, and $[Sn(NH_3)_2]Br_2$.[1]

At ordinary temperature and under atmospheric pressure stannous bromide absorbs only 0·6 molecules of ammonia for every molecule of salt, even after standing for forty hours ; on lowering the temperature, however, to 0° C. and allowing the salt to remain in contact with ammonia gas for twenty-four hours, triammino-stannous bromide, $[Sn(NH_3)_3]Br_2$, is formed as a yellow powder. At low temperatures stannous bromide and liquid ammonia react, and at $-78°$ C. ammonia is rapidly absorbed, increase in bulk takes place, and addition compounds containing nine and five molecules of ammonia are produced.

The temperatures at which the dissociation pressure of the ammines of stannous bromide is equal to 100 mm. are as follows: $[Sn(NH_3)_9]Br_2$ $-57°$ C., $[Sn(NH_3)_5]Br_2$ $-2°$ C., $[Sn(NH_3)_3]Br_2$ $+66°$ C., $[Sn(NH_3)_2]Br_2$ $+102°$ C. The substances are yellow in colour, a fact that Biltz and Fischer remark upon, as both components of the addition product are white.[1]

The same investigators describe four ammino-derivatives of stannous iodide, namely, $[Sn(NH_3)_5]I_2$, $[Sn(NH_3)_3]I_2$, $[Sn(NH_3)_2]I_2$, $[Sn(NH_3)]I_2$.

Diammino-stannous Iodide, $[Sn(NH_3)_2]I_2$, is obtained as a yellow powder by passing dry ammonia gas over anhydrous stannous iodide.[2] By dissolving stannous iodide in liquid ammonia at a temperature of $-78°$ C. a white crystalline substance separates containing ten molecules of ammonia. This, however, is not regarded as a definite compound, and from dissociation-pressure measurements it seems probable that pentammino-stannous iodide is the highest ammino-derivative which definitely exists. **Diammino-stannous iodide,** $[Sn(NH_3)_2]I_2$, and **monammino-stannous iodide,** $[Sn(NH_3)]I_2$, are coloured, the former yellow, the latter brown. The other ammines are white.

It is suggested that in the ammines of higher co-ordination number two shells of ammonia may surround the central metallic atom, and in the case of stannous bromide the co-ordination numbers are assumed to be 3+2 or 3+6, thus giving an explanation of the ammino-compounds containing nine or five molecules of ammonia.[1]

No ammino-derivatives of stannic bromide are known, but derivatives of the iodide exist.

Octammino-stannic Iodide, $[Sn(NH_3)_8]I_4$, is produced by passing dry ammonia gas into a solution of stannic iodide in carbon disulphide and then allowing the solvent to evaporate. It is white in colour and is insoluble in water.[2] It may also be prepared by treating anhydrous stannic iodide with dry ammonia gas.

The halogen salts of tin unite with aniline and pyridine bases. Stannous chloride and pyridine hydrochloride unite to form the compound $(C_5H_5N).SnCl_2.2HCl$. It crystallises in white needles which are soluble in dilute hydrochloric acid but only slightly soluble in alcohol.[3] Stannous bromide also unites with aniline hydrobromide, forming the substance $(C_6H_5NH_2).HBr.SnBr_2$, and stannic bromide

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[1] Biltz and Fischer, *Zeitsch. anorg. Chem.*, 1923, 129, 1.

[2] Ephraim and Schmidt, *Ber.*, 1909, 42, 3856.

[3] Hayes, *J. Amer. Chem. Soc.*, 1902, 24, 360.

forms dianilino-bromo-stannate, $(C_6H_5NH_2)_2.H_2SnBr_6$, and tetra-anilino-bromo-stannate, $(C_6H_5NH_2)_4.4HBr.SnBr_4$.[1]

A pyridine addition product of stannic iodide is formed by adding a solution of pyridine hydriodide in alcohol to a solution of stannic iodide in alcoholic hydrogen iodide. Pyridino-iodo-stannate, $(C_5H_5N)_2.H_2SnI_6$, separates in bluish-black needles which decompose on standing with liberation of iodine. The corresponding quinoline addition compound, $(C_9H_7N)_2.H_2SnI_6$, crystallises in bluish-black crystals which break down on keeping.[2]

Ammino-derivatives of Lead Halides.

Several additive compounds of ammonia and lead halides have been described.

At ordinary temperatures lead chloride does not absorb ammonia, but if cooled to −78° C. and saturated with liquid ammonia, the salt increases to about five times its volume, yielding a white powder of composition $PbCl_2.8NH_3$. On raising the temperature loss of ammonia occurs, with the production of lower ammines.

In 1830 Rose[3] obtained a compound of lead chloride and ammonia to which he gave the formula $PbCl_2.1{\cdot}5NH_3$. In 1913 Ephraim[4] described diammino-lead chloride, $[Pb(NH_3)_2]Cl_2$, and suggested the possible existence of the octammino-derivative. This was confirmed by Biltz and Fischer,[5] who also prepared the monammine, $[Pb(NH_3)]Cl_2$, the sesquiammine, $PbCl_21{\cdot}5NH_3$ or $[Pb_2(NH_3)_3]Cl_4$, and a body of composition $PbCl_2.3{\cdot}25NH_3$ or $4PbCl_2.13NH_3$. This last-named substance is probably a mixture of three ammines, namely, $PbCl_2.8NH_3$, $PbCl_2.2NH_3$, and $2PbCl_2.3NH_3$.

Ammino-lead Tetrachlorides.—Lead tetrachloride absorbs ammonia more readily than does the dichloride. If dry ammonia gas is passed into a suspension of anhydrous lead tetrachloride in chloroform, tetrammino-lead tetrachloride, $[Pb(NH_3)_4]Cl_4$, or diammino-lead tetrachloride, $[Pb(NH_3)_2]Cl_4$, is produced, according to the concentration of the solution. The former crystallises in orange-yellow needles and the latter separates as a white powder. Both compounds are stable in air.[6]

Lead tetrachloride forms additive compounds with the bases pyridine and aniline, as, for example, dipyridino-lead tetrachloride, $[Pb(C_5H_5N)_2]Cl_4$, and trianilino-lead tetrachloride, $[Pb(C_6H_5NH_2)_3]Cl_4$. These compounds are prepared by adding the base to solutions of the chloride in chloroform. They decompose in moist air and on heating. Two pyridino-derivatives of lead dichloride are known: a compound of composition $3PbCl_2.4(C_5H_5N)$, which crystallises in colourless needles,[7] and dipyridino-lead dichloride, which corresponds to the diammine. Dipyridino-lead dichloride, $[Pb(C_5H_5N)_2]Cl_2$, crystallises in colourless needles and readily loses pyridine on exposure to air.[8]

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[1] Richardson and Adams, *Amer. Chem. J.*, 1899, 22, 446.

[2] Rosenheim and Aron, *Zeitsch. anorg. Chem.*, 1904, 39, 170.

[3] Rose, *Pogg. Annalen*, 1830, 20, 157.

[4] Ephraim, *Zeitsch. physikal. Chem.*, 1913, 83, 196.

[5] Biltz and Fischer, *Zeitsch. anorg. Chem.*, 1922, 124, 230.

[6] Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 825.

[7] Classen and Zahorski, *Zeitsch. anorg. Chem.*, 1893, 4, 100.

[8] Heise, *J. Physical Chem.*, 1912, 16, 373.

Ammino-lead Dibromides.—By saturating lead dibromide with liquid ammonia at low temperatures and allowing the temperature to rise, several additive compounds are obtained. Thus, for example, the following derivatives are known: $[Pb(NH_3)]Br_2$, $[Pb(NH_3)_2]Br_2$, $[Pb(NH_3)_3]Br_2$, $PbBr_2.5{\cdot}5NH_3$ or $2PbBr_2.11NH_3$.[1, 2] The last-named compound may be regarded as a mixed substance made up of octammino-lead dibromide, $[Pb(NH_3)_8]Br_2$, and triammino-lead dibromide, $[Pb(NH_3)_3]Br_2$.

Ammino-lead Iodides.—Diammino-lead iodide, $[Pb(NH_3)_2]I_2$, was prepared by Rammelsberg[3] by treating lead iodide with gaseous ammonia, whilst Ephraim[1] prepared monammino-lead iodide, $[Pb(NH_3)]I_2$, and tetrammino-lead iodide, $[Pb(NH_3)_4]I_2$. Biltz and Fischer prepared, in addition, the derivatives, $PbI_2.0{\cdot}5NH_3$ and $PbI_2.5NH_3$. The former, they suggest, is a mixed compound of monammino-lead iodide with ammonia-free lead iodide, and may have the composition $PbI_2.PbI_2.NH_3$; the latter, a mixed derivative of the type already mentioned, being a mixture of octammino-lead iodide, $[Pb(NH_3)_8]I_2$, and the diammine.

The iodide also forms additive compound with pyridine, such as dipyridino-lead iodide, $[Pb(C_5H_5N)_2]I_2$, and tripyridino-lead iodide, $[Pb(C_5H_5N)_3]I_2$.[4]

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[1] Ephraim, *Zeitsch. physikal. Chem.*, 1913, 83, 196.

[2] Biltz and Fischer, *Zeitsch. anorg. Chem.*, 1922, 124, 230.

[3] Rammelsberg, *Pogg. Annalen*, 1839, 48, 166.

[4] Heise, *J. Physical Chem.*, 1912, 16, 373.

CHAPTER VIII.

METAL-AMMINES OF THE ELEMENTS OF GROUP V.

In this group there is gradation from non-metal to metal. The element arsenic has some of the characteristics of a metal ; the metallic character becomes more marked in the element antimony, and bismuth is a true metal. All three elements form ammino-salts.

Ammino-derivatives of Arsenic Salts.

In 1830 Persoz [1] obtained a solid body of composition $AsCl_3.3NH_3$ by acting upon arsenic trichloride with ammonia gas. Rose,[2] in 1841, described a compound obtained from arsenic trichloride to which he gave the formula $2AsCl_3.7NH_3$. Arsenic trichloride absorbs ammonia gas fairly rapidly at first, but the reaction slows down before completion, and the substance must be powdered several times and exposed to more gas before absorption is at an end. The substance formed was described as **tetrammino-arsenic trichloride**, $AsCl_3.4NH_3$, and appears to be identical with the derivatives prepared by Persoz and Rose. It is a yellowish-white powder which, on heating, loses ammonia, whilst ammonium chloride and some unchanged tetrammine volatilise. It dissolves gradually in water with increase in temperature and loss of ammonia.[3]

Hugot [4] claims that the substance is most probably a mixture of ammonium chloride and arsenic triamide, $As(NH_2)_3$, and not the ammine, for if ammonia gas is allowed to act upon arsenic trichloride at $-30°$ to $-40°$ C., arsenic triamide, $As(NH_2)_3$, is formed according to the equation

$$AsCl_3+6NH_3 \longrightarrow As(NH_2)_3+3NH_4Cl.$$

The amide is a greyish-white powder which is stable below 0° C. out of contact with air, and decomposes in water with liberation of ammonia. If heated above 0° C. the amide decomposes slowly into the imide, $As_2(NH)_3$, decomposition being complete at 60° C. The reaction may be expressed by the equation

$$2As(NH_2)_3 \longrightarrow As_2(NH)_3+3NH_3.$$

The imide is a stable amorphous substance, yellow in colour, is not

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[1] Persoz, *Ann. Chim. Phys.*, 1830, 44, 320.
[2] Rose, *Pogg. Annalen*, 1841, 52, 62.
[3] Besson, *Compt. rend.*, 1890, 110, 1258.
[4] Hugot, *ibid.*, 1904, 139, 54.

decomposed if heated to 100° C. *in vacuo*, and is less easily decomposed by water than the amide.

Ammino-arsenic Trifluoride.—A substance, of composition $[As_2(NH_3)_5]F_6$, is formed by acting upon arsenic trifluoride vapour with ammonia. It is a light white powder which is decomposed by water, with formation of an acid solution.[1]

Ammino-arsenic Bromides.—Arsenic bromide also absorbs ammonia. By passing dry ammonia gas into a solution of arsenic tribromide in benzene, a white powdery substance, of composition $[As_2(NH_3)_7]Br_6$, is produced which is slightly soluble in cold water, decomposed by hot water, and may be recrystallised without decomposition from alcohol.[2] Triammino-arsenic bromide, $AsBr_3.3NH_3$, is stated to be formed by passing ammonia gas over arsenic tribromide.[1] The triammine is pale yellow in colour, and decomposes on heating in a sealed tube to 300° C. As in the case of the tetrammino-arsenic chloride, it is probable that it is the amide of arsenic and not the ammino-salt which is formed.[3]

Ammino-arsenic Tri-iodides.—Several compounds of arsenic tri-iodide have been prepared. Bamberger and Philipp [4] obtained a compound, $[As_2(NH_3)_9]I_3$, by passing dry ammonia gas into arsenic tri-iodide in ether, when a bulky white precipitate was produced. On heating to 50° C. it loses ammonia, and is completely decomposed at higher temperatures. Arsenic tri-iodide absorbs ammonia, slowly at first, and then more rapidly towards the point of saturation. The compound produced is a tetrammino-derivative.[1]

The substance described as tetrammino-arsenic iodide, $[As(NH_3)_4]I_3$, is a yellow powder which loses ammonia on heating above 50° C., and at 300° C. decomposes into arsenic, nitrogen, and ammonium iodide. If the compound be cooled to 0° C. and ammonia again passed over it, a pale yellow liquid, of composition $[As(NH_3)_{12}]I_3$, is formed. Hugot again obtained only the amide, $As(NH_2)_3$, on treating the iodide with ammonia gas.

The ammonia additive compounds of arsenic trihalides all react energetically on addition of cold concentrated sulphuric acid with formation of arsenic trihalides, a fact which Besson regards as evidence that the ammonia derivatives are true additive compounds.

Ammino-derivatives of organic bases are known, such as tetraethylamino-arsenic tribromide, $AsBr_3.4(C_2H_5NH_2).H_2O$, and trianilino-arsenic tribromide, $AsBr_33(C_6H_5NH_2).H_2O$.[2]

Ammino-derivatives of Antimony Salts.

Antimony trichloride absorbs ammonia with formation of the following compounds: *monammino-antimony trichloride*, $[Sb(NH_3)]Cl_3$; *diammino-antimony trichloride*, $[Sb(NH_3)_2]Cl_3$; and *triammino-antimony trichloride*, $[Sb(NH_3)_3]Cl_3$.

Monammino-antimony Trichloride, $[Sb(NH_3)]Cl_3$, was obtained by Déherain [5] by allowing molten antimony trichloride to cool in an atmosphere of ammonia. A hard mass is formed, which loses ammonia

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[1] Besson, *Compt. rend.*, 1890, 110, 1258.
[2] Landau, *Chem. Zentr.*, 1888, 1354.
[3] Hugot, *Compt. rend.*, 1904, 139, 54.
[4] Bamberger and Philipp, *Ber.*, 1881, 14, 2643.
[5] Déherain, *Compt. rend.*, 1861, 52, 734.

readily on heating, leaving pure antimony trichloride. It volatilises more slowly in air than antimony chloride. In the solid state antimony trichloride absorbs ammonia very slowly.

Diammino-antimony Trichloride, $[Sb(NH_3)_2]Cl_3$.—This derivative is prepared by passing ammonia gas over molten antimony trichloride or warm antimony pentachloride.[1] It is a yellowish-white semi-crystalline substance, which is volatile without decomposition and is attacked by hydrochloric acid, with formation of the compound $NH_4Cl.SbCl_3$.

Triammino-antimony Trichloride, $[Sb(NH_3)_3]Cl_3$, is produced when dry ammonia is passed through a solution of antimony trichloride in acetone.[2] A mixture of compounds is apparently formed of which the triammine is the chief. It is a white powdery substance which is stable in air but loses ammonia on heating.

Antimony pentachloride also unites with ammonia. Two products are formed by passing ammonia gas into cold antimony pentachloride, namely, triammino-antimony pentachloride, $[Sb(NH_3)_3]Cl_5$, and tetrammino-antimony pentachloride, $[Sb(NH_3)_4]Cl_5$.[1] Triammino-antimony pentachloride is a red substance which decomposes on heating, with formation of a sublimate of composition $3NH_4Cl.SbCl_5$. Tetrammino-antimony pentachloride is a white volatile substance which decomposes into antimony ammonium chloride. $NH_4Cl.SbCl_5$, on treatment with hydrochloric acid.

A hexammino-derivative, $[Sb(NH_3)_6]Cl_5$, is obtained by passing ammonia gas over antimony pentachloride and then gently heating the brown substance formed. On heating the colour changes to white, and the hexammine may be sublimed out of contact with air without decomposition. Water, however, decomposes it.[3]

Rosenheim and Jacobsohn [4] obtained a white crystalline addition compound on treating the monohydrate of antimony pentachloride with liquid ammonia, but the exact composition is doubtful.

Antimony trifluoride also unites with ammonia. **Diammino-antimony trifluoride,** $[Sb(NH_3)_2]F_3$, is produced by allowing liquid ammonia and the fluoride to react. Increase in volume and rise in temperature take place, but the reaction is only complete after several weeks. The ammine is a yellow powder which is sparingly soluble in liquid ammonia. It loses ammonia in moist air without deliquescence and becomes colourless, and is almost completely dissociated at 100° C.[5] Additive compounds of antimony trichloride and organic bases are known; for example, quinolino-antimony trichloride, $[Sb(C_9H_7N)]Cl_3$,[6] and trianilino-antimony trichloride, $[Sb(C_6H_5NH_2)_3]Cl_3$.[7] These are prepared by mixing the salt and the base and allowing them to stand for some time. Trianilino-antimony trichloride crystallises in colourless needles from benzene, is decomposed by water, and transformed into the hydrochloride on treatment with hydrochloric acid. Antimony tri-iodide forms trianilino-antimony iodide, $[Sb(C_6H_5NH_2)_3]I_3$, crystallising in small yellow needle-shaped crystals.[7]

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[1] Déherain, *loc. cit.*

[2] Naumann, *Ber.*, 1904, 37, 4332.

[3] Rose, *Pogg. Annalen*, 1831, 24, 165.

[4] Rosenheim and Jacobsohn, *Zeitsch. anorg. Chem.*, 1906, 50, 307.

[5] Ruff, *Ber.*, 1906, 39, 4326.

[6] Schiff, *Ann. Chim. Phys.*, 1864, 131, 161; *Compt. rend.*, 1863, 56, 1905.

[7] Schiff, *Ber.*, 1901, 34, 805.

Ammino-derivatives of Bismuth Salts.

Bismuth trichloride absorbs ammonia gas on slight warming, forming a volatile additive compound, $BiCl_3.3NH_3$.[1]

Triammino-bismuth Chloride, $[Bi(NH_3)_3]Cl_3$, is a colourless solid which is stable in ammonia gas and reacts with hydrochloric acid, forming the compound $3NH_4Cl.BiCl_3$. Along with the triammine are produced two other non-volatile substances, $2BiCl_3.NH_3$ and $BiCl_3.2NH_3$. The former is a red, fairly stable substance, which melts on heating and is decomposed by moisture, whilst hydrochloric acid attacks it with formation of the ammonium salt, $2BiCl_3.NH_4Cl$; the latter is greenish in appearance, but cannot be obtained free from $2BiCl_3.NH_3$.

A mixture of diammino- and triammino-bismuth trichloride is produced by passing dry ammonia gas into a solution of bismuth chloride in acetone.[2] A white powder is formed, which becomes slightly yellow in air and loses ammonia on heating.

Bismuth trichloride also unites with quinoline and pyridine. Quinolino-bismuth chloride, $[Bi(C_9H_7N)]Cl_3$, is obtained as a white crystalline mass on mixing the chloride with the base. This derivative is only slowly decomposed by water and is not deliquescent.[3] Bismuth chloride and pyridine form a white compound of composition $BiCl_3.1{\cdot}5(C_5H_5N)$ or $2BiCl_3.3(C_5H_5N)$ on adding pyridine to an ethereal solution of bismuth chloride,[4] or it may be formed from an acetone solution of the chloride and excess of pyridine.[3] It is a white crystalline powder, fairly stable towards water, and only attacked slowly by hydrochloric acid. Aqueous sodium hydroxide quickly decomposes the additive compound.

Ammino-bismuth Bromides.—Bismuth tribromide, on warming in an atmosphere of ammonia, melts, becomes gradually darker in colour, and volatilises as a yellowish-white powder of composition, corresponding to triammino-bismuth tribromide, $[Bi(NH_3)_3]Br_3$. The powder absorbs moisture from the air and is decomposed, forming bismuth oxy-bromide. It is, however, difficult to obtain the triammine free from diammino-bismuth bromide, $[Bi(NH_3)_2]Br_3$, which is formed at a higher temperature. On heating the residue more strongly, after volatilisation of the triammine, diammino-bismuth bromide, $[Bi(NH_3)_2]Br_3$, distils as a dark red liquid, solidifying on cooling as an olive-green powder. It deliquesces in air and decomposes in contact with water.[5] Still another derivative is obtained by heating the remaining residue until no more gas is evolved, when a grey, infusible, crystalline substance remains, of composition $[Bi_2(NH_3)_5]Br_6$. A green solid of the same composition as the last-mentioned substance may be prepared by heating bismuth oxy-bromide in ammonia gas. It decomposes on heating in air, but is not deliquescent and is not decomposed by water.[5]

Ammino-bismuth Iodides.—Bismuth triodide absorbs ammonia gas on heating, forming a red crystalline mass of triammino-bismuth tri-iodide, $[Bi(NH_3)_3]I_3$.[6] From this, water abstracts ammonium iodide without change of colour of the substance.

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[1] Persoz, *Ann. Chim. Phys.*, 1830, 44, 315.
[2] Naumann, *Ber.*, 1904, 37, 4333.
[3] Vanino and Hauser, *ibid.*, 1901, 34, 416 ; 1903, 36, 3682.
[4] Montemartini, *Gazzetta*, 1900, 30, 493 ; 1902, 32, 178.
[5] Muir, *Trans. Chem. Soc.*, 1876, 29, 147 ; 1877, 31, 27.
[6] Rammelsberg, *Pogg. Annalen*, 1839, 48, 168.

Pyridino-bismuth Iodide, $[Bi(C_5H_5N)]I_3$, is formed by treating a cold mixture of bismuth trichloride in pyridine with potassium iodide, when the pyridino-iodide separates as a dark red powder.[1] The substance is soluble in alcohol and in aqueous potassium iodide, and separates from a saturated solution in red needle-shaped crystals which decompose on heating. The corresponding quinoline derivative, $[Bi(C_9H_7N)]I_3$, is also a red crystalline substance, and is produced by boiling quinolino-bismuth chloride with an aqueous solution of potassium iodide.

Ephraim and Mosimann[2] obtained several interesting compounds of bismuth tri-iodide by combining it with cobalt-ammines. Hexammino-cobaltic iodide unites with bismuth iodide on mixing solutions of the compounds with formation of hexammino-cobalti-bismuth iodide, $[Co(NH_3)_6]I_3.BiI_3$. The compound separates in dark red crystals. Chloro-pentammino-cobalti-bismuth iodide, $[Co(NH_3)_5Cl]I_2.2BiI_3$, separates as a red crystalline powder, and dinitro-tetrammino-cobalti-bismuth iodide, $[Co(NH_3)_4(NO_2)_2]I.BiI_3$, in red hexagonal crystals. The compounds are sparingly soluble in water, and are formed when aqueous solutions of the complex ammine and bismuth salt, dissolved in potassium iodide, are mixed.

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[1] Vanino and Hauser, *Ber.*, 1901, 34, 416.

[2] Ephraim and Mosimann, *ibid.*, 1921, 54, 396.

CHAPTER IX.

METAL-AMMINES OF THE ELEMENTS OF GROUP VI.

Subgroup A—Chromium, Molybdenum, Tungsten, Uranium.

THESE elements constitute the metallic elements of Group VI. They are characterised by the complexity of their compounds, especially the oxy-compounds. For example, the elements all form important complex oxides, and from these are derived highly complex oxy-salts and acids.

Chromium, the first member, forms complex oxy-salts, cyanides, and ammines. The ammino-derivatives constitute nearly as large a class as those of cobalt, and many of them are remarkably stable.

AMMINO-DERIVATIVES OF CHROMIUM SALTS.

Chromium forms two series of salts, known as chromous and chromic, where the metal is divalent and trivalent respectively. The chromous salts, which are unstable and readily pass into the stable chromic salts, form several crystalline hydrates. For example, chromous chloride may be obtained of composition $CrCl_2.6H_6O$, $CrCl_2.4H_2O$, $CrCl_2.3H_2O$, or $CrCl_2.2H_2O$. No ammonia additive compounds of the salts have been prepared, although a hydrazine derivative, $CrCl_2.2N_2H_4$, is known. Hydrazino-chromous chloride is very stable in air, only slightly soluble in water, and dissolves in aqueous ammonia with formation of a deep blue solution.[1]

Chromium in the trivalent state forms a variety of salts, the most important and the simplest being the violet salts, which liberate in aqueous solution chromium cation $Cr^{\cdots}$. A green series of chromic salts, isomeric with the violet salts, liberate in aqueous solution some chromium cation, whilst part of the chromium is present as a complex ion. With weak acids, sulphurous, hydrocyanic, or thiocyanic acids, the chromic ion forms complex ions of great stability. Finally, a very large group of salts exists where chromium associated with ammonia forms the complex ion, the chromi-ammines.

The first well-characterised ammonia additive derivative of chromium was prepared by Frémy in 1858.[2] Shortly after, in 1862, the compound was examined by Clève,[3] who prepared a number of compounds of chromic salts and ammonia. He proved the composition of these substances and endeavoured, in so far as the knowledge of that time allowed, to explain their constitution.

Clève gave descriptions of the aquo-tetrammino-chromic halogen

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[1] Traube and Passarge, *Ber.*, 1913, 46, 1505.

[2] Frémy, *Compt. rend.*, 1858, 47, 883.

[3] Clève, *J. prakt. Chem.*, 1862, 86, 47.

salts, and showed the existence of additive compounds containing less ammonia in the molecule. In 1861 Morland [1] obtained a salt containing ammonia by melting together ammonium thiocyanate and ammonium dichromate, and from the melt Reinecke,[2] in 1863, isolated an ammonium salt of composition $[Cr(NH_3)_2(SCN)_4]NH_4$, to which was given the name "Reinecke salt." Reinecke prepared analogous compounds, and his work was further investigated by Nördenskjöld [3] and Christensen [4] in 1892.

The research of Jörgensen [5] on the chromi-ammines is important; he prepared a large number of compounds, and proved that the compounds richest in ammonia contained six molecules of ammonia for every molecule of chromic salt ; that a series of salts could be formed containing five molecules of ammonia, the acido-pentammino-salts ; and that other derivatives could be prepared containing more than one atom of chromium in the molecule. He also examined Clève's aquo-tetrammino-chromic halogen salts, and proved that they may be regarded as acido-pentammino-salts where one molecule of ammonia is replaced by a molecule of water, the pentammino-salt, $[Cr(NH_3)_5R]R_2$, becoming the acido-aquo-tetrammino-salt, $[Cr(NH_3)_4R(H_2O)]R_2$. He compared the chromi-ammines with the cobalt-ammines, and found that the properties of the two classes correspond generally, and therefore the two series must be given the same constitutional formulæ.

In 1893 Werner founded his new constitutional formula for inorganic compounds, applied the theory to the systematic classification of the chromi-ammines, and found that all the chromi-ammines which had been investigated could be fitted in to his system of classification. Since then the chemistry of the chromi-ammines has been further developed by Werner, Pfeiffer, and many others ; relationships have been traced between chromi-ammines, complex salts, and chromic salt hydrates, and numerous cases of isomerism have been discovered in this series of ammines.

The chromic salts readily combine with ammonia or substituted ammonia molecules, forming ammines. They contain a complex ion made up of one atom of chromium and six molecules of ammonia, or corresponding basic groups for every molecule of ammine. This cation is trivalent, and remains trivalent even if ammonia is replaced by neutral groups. If, however, acidic groups replace ammonia the valency is correspondingly modified, and each monovalent acidic group entering the complex reduces the valency by one. Hence the complex ion in the chromi-ammines may be trivalent, divalent, monovalent, or if more acidic groups are present than ammonia the complex may become anionic in character. The salts are capable of undergoing double decomposition where the complex acts as a whole, giving rise, therefore, to a large number of derivatives. Like other complex substances they do not give the ordinary ionic reactions of the metal, and acidic groups in the complex, being un-ionised, do not give the usual acidic reactions. For example, hexammino-chromic chloride, $[Cr(NH_3)_6]Cl_3$, is ionised in aqueous solution, each molecule yielding four ions, namely, $[Cr(NH_3)_6]^{\cdot\cdot\cdot}$, and three chlorine ions, whereas each molecule of chloro-

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[1] Morland, *Quart. J. Chem. Soc.*, 1861, 13, 252.
[2] Reinecke, *Annalen*, 1863, 126, 113.
[3] Nördenskjöld, *Zeitsch. anorg. Chem.*, 1892, 1, 126.
[4] Christensen, *J. prakt. Chem.*, 1892, [2], 45, 213.
[5] Jörgensen, *ibid.*, 1891, 44, 63 ; 1892, 45, 274.

pentammino-chromic chloride, $[Cr(NH_3)_5Cl]Cl_2$, gives, in solution, only three ions, namely, $[Cr(NH_3)_5Cl]^{\cdot\cdot}$, and two chlorine ions.

As the various theories of the constitution of the metal-ammines have been discussed,[1] only the constitutional formulæ for these compounds, adopted at the present time, will be used.

Chromium has a maximum co-ordination number of six; the chromium atom, therefore, may combine with, at most, six monovalent atoms or groups, over and above its ordinary valency value, with formation of a complex radicle. Hence chromic chloride is capable of associating with, or adding on, six molecules of ammonia with formation of the derivative, $[Cr(NH_3)_6]Cl_3$. Ammonia may be replaced by a substituted ammonia group or some other basic group, such as alkylamine, pyridine, or ethylenediamine.

The chromi-ammines containing one atom of chromium in the molecule form by far the largest class of these additive compounds.

The following scheme serves as a convenient method of classification, and is based on the one adopted by Abegg.[2]

CLASS I. CHROMOUS SALT AMMINES.

No ammonia additive compounds of chromous salts are known, but certain salts unite with hydrazine, forming complex salts of the same type as the ammines.

CLASS II. CHROMIC SALT AMMINES, THE CHROMI-AMMINES.

These comprise a very large number of compounds, and are subdivided into three groups.

A. Mononuclear Chromi-ammines containing One Atom of Chromium in the Molecule.

This class is by far the largest, and is further subdivided according to the number of ammonia molecules and acidic, or other, radicles in the complex, in the following manner:—

1. *Compounds containing Trivalent Cation.*

General Formula $[CrA_6]R_3$

(where $A = NH_3$ or substituted ammonia
and $R =$ monovalent acidic radicle).

(*a*) Hexammino-chromic salts, luteo-salts, $[Cr(NH_3)_6]R_3$.
(*b*) Triethylenediamino-chromic salts, $[Cr\,en_3]R_3$ (where en = ethylenediamine).
(*c*) Diethylenediamino-propylenediamino-chromic salts, $[Cr\,en_2pr]R_3$.
(*d*) Aquo-pentammino-chromic salts, roseo salts, $[Cr(NH_3)_5H_2O]R_3$.
(*e*) Diaquo-tetrammino-chromic salts, $[Cr(NH_3)_4(H_2O)_2]R_3$.
(*f*) Triaquo-triammino-chromic salts, $[Cr(NH_3)_3(H_2O)_3]R_3$.
(*g*) Tetraquo-diammino-chromic salts, $[Cr(NH_3)_2(H_2O)_4]R_3$.
(*h*) Hexaquo-chromic salts, $[Cr(H_2O)_6]R_3$.

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[1] See Chapter III.

[2] Abegg, *Handbuch der anorganischen Chemie*, Band iv. (Hirzel, Leipzig, 1921).

2. *Ammines containing Divalent Cation.*
General Formula $[CrA_5R]R_2$.

(*a*) Hydroxo-pentammino-chromic salts, $[Cr(NH_3)_5OH]R_2$.
(*b*) Hydroxo-aquo-tetrammino-chromic salts, $[Cr(NH_3)_4.H_2O.OH]R_2$.
(*c*) Hydroxo-diaquo-triammino-chromic salts, $[Cr(NH_3)_3(H_2O)_2OH]R_2$.
(*d*) Hydroxo-triaquo-diammino-chromic salts, $[Cr(NH_3)_2(H_2O)_3OH]R_2$.
(*e*) Acido-pentammino-chromic salts, $[Cr(NH_3)_5R]R_2$.
(*f*) Acido-aquo-tetrammino-chromic salts, $[Cr(NH_3)_4H_2O.R]R_2$.

3. *Ammines containing Monovalent Cation.*
General Formula $[CrA_4R_2]R$.

(*a*) Dihydroxo-diaquo-diammino-chromic salts, $[Cr(NH_3)_2(H_2O)_2(OH)_2]R$.
(*b*) Diacido-tetrammino-chromic salts, $[Cr(NH_3)_4R_2]R$.
(*c*) Diacido-aquo-triammino-chromic salts, $[Cr(NH_3)_3H_2O.R_2]R$.
(*d*) Diacido-diaquo-diammino-chromic salts, $[Cr(NH_3)_2(H_2O)_2R_2]R$.
(*e*) Diacido-tetraquo-chromic salts, $[CrR_2(H_2O)_4]R$.

4. *Ammines containing Non-dissociable Complex.*
General Formula $[CrA_3R_3]$.

(*a*) Triacido-triammino-chromium, $[Cr(NH_3)_3R_3]$.
(*b*) Trihydroxo-aquo-diammino-chromium, $[Cr(NH_3)_2(OH)_3(H_2O)]$.
(*c*) Triacido-triaquo-chromium, $[CrR_3(H_2O)_3]$.

5. *Ammines containing Monovalent Anion.*
General Formula $[CrA_2R_4]M$

(where M=monovalent metal).

(*a*) Dioxalato-diammino-chromium derivative, $[Cr(NH_3)_2(C_2O_4)_2]M$.
(*b*) Dichloro-dibromo-diammino-chromium derivative, $[Cr(NH_3)_2Cl_2Br_2]M$.

6. *Salts with Trivalent Anion.*
General Formula $[CrR_6]M_3$.

These are regarded as comparable with the ammines in structure.

B. Polynuclear Chromi-ammines containing Two or more Chromium Atoms in the Molecule.

C. Chromi-ammines of Unknown Constitution.

The chromi-ammines show very clearly the parallelism between hydrated salts and ammino-salts. It has been proved that water may be gradually substituted for ammonia in the metal-ammines, and in the hexammino-salts of chromium all degrees of substitution, with the exception of one, have been obtained. Thus, from hexammino-chromic chloride, $[Cr(NH_3)_6]Cl_3$, six derivatives are theoretically possible;[1] five of these are known, the only one missing being the monammine, which is so unstable that it has not been prepared. The following series of compounds are therefore known:—

$[Cr(NH_3)_6]Cl_3$;	$[Cr(NH_3)_5H_2O]Cl_3$; Aquo.	$[Cr(NH_3)_4(H_2O)_2]Cl_3$; Diaquo.
$[Cr(NH_3)_3(H_2O)_3]Cl_3$; Triaquo.	$[Cr(NH_3)_2(H_2O)_4]Cl_3$; Tetraquo.	$[Cr(NH_3)(H_2O)_5]Cl_3$; Pentaquo (unknown).

$[Cr(H_2O)_6]Cl_3$.
Hexaquo
(blue hexahydrate of chromic chloride).

The last three derivatives lose two molecules of water very readily, and chlorine enters the complex, giving compounds with only one ionisable chlorine atom in the molecule.

Water and ammonia, therefore, behave similarly in the formation of substitution compounds, and there is gradation from ammino-salt through aquo-ammino- to purely aquo- or hydrated salt; further, the entrance of water in place of ammonia does not alter the ionic nature of the acidic radicles outside the complex.

When aquo-pentammino-salts lose water the acid residue enters the complex, just as in the case of loss of ammonia from the complex. For example, aquo-pentammino-chromic chloride, $[Cr(NH_3)_5(H_2O)]Cl_3$, on loss of water becomes chloro-pentammino-chromic chloride, $[Cr(NH_3)_5Cl]Cl_2$. Other aquo-salts behave similarly, and almost any acidic radicle attached to the complex as a whole may in this way be caused to enter the complex itself.

The entrance or elimination of water in the chromi-ammines causes a change in the ionic properties of the acidic radicles. Thus, the compound trichloro-triammino-chromium, $[Cr(NH_3)_3Cl_3]$, has no ionic properties, but if water be introduced, the compound becomes dichloro-aquo-triammino-chromic chloride, $[Cr(NH_3)_3Cl_2H_2O]Cl$, and an acid radicle being thrown out of the complex becomes ionic in function. Further entrance of water causes elimination of another acid radicle, with the result that chloro-diaquo-triammino-chromic chloride, $[Cr(NH_3)_3Cl(H_2O)_2]Cl_2$, is formed, two acid radicles becoming ionic. Finally, three molecules of water enter the complex, when all the acid radicles become ionic, the substance having the formula $[Cr(NH_3)_3(H_2O)_3]Cl_3$.[2] A reverse set of changes occurs if water be eliminated, and with complete elimination all three radicles, having now entered the complex, become non-ionic.

The chromi-ammines are produced by the action of ammonia and ammonium salts on chromic salts, or by the action of ammonia in presence of ammonium salts on chromous salts and subsequent oxidation. The second method is analogous to that for the formation of cobalt-ammines. The chromi-ammines form a group of coloured substances, and comprise unstable and stable derivatives, some of which are very complex.

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[1] Werner, *Ber.*, 1906, 39, 2656.

[2] Frowein, *Zeitsch. anorg. Chem.*, 1920, 110, 107.

Isomerism in the Chromi-ammines.

Numerous cases of isomerism occur, the isomerism being of the following types:—

1. *Polymerisation Isomerism.*—The complex ammines, $[Cr(NH_3)_3(SCN)_3][Cr(NH_3)_3(SCN)_3]$ and $[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$, may be regarded as polymeric with trithiocyanato-triammino-chromium, $[Cr(NH_3)_3(SCN)_3]$.[1] The same type of isomerism occurs in the compounds $[Cr\,en_3][Cr(SCN)_6]$ and $[Cr(SCN)_2en_2]_3[Cr(SCN)_6]$.[2]

2. *Co-ordination Isomerism.*—As examples of this type of isomerism, triethylenediamino-chromi-hexacyano-cobalt, $[Cr\,en_3][Co(CN)_6]$, is isomeric with triethylenediamino-cobalti-hexacyano-chromium, $[Co\,en_3][Cr(CN)_6]$; and hexammino-chromi-trioxalato-chromium, $[Cr(NH_3)_6][Cr(C_2O_4)_3]$, is isomeric with oxalato-tetrammino-chromi-dioxalato-diammino-chromium, $[Cr(NH_3)_4(C_2O_4)][Cr(NH_3)_2(C_2O_4)_2]$.[2]

3. *Hydrate Isomerism.*—Chromic chloride hexahydrate, $CrCl_3.6H_2O$, itself occurs in isomeric forms. Three isomers are known, a greenish-blue form and two green forms. The greenish-blue form contains chlorine, which functions ionically in aqueous solution, and has the formula $[Cr(H_2O)_6]Cl_6$, where water is represented as forming part of the co-ordination complex.[3] The other two forms behave differently in aqueous solution, for, in the one case, it is only possible to precipitate two-thirds of the chlorine with silver nitrate when it is added to a freshly prepared solution acidified with nitric acid, and in the other case only one chlorine atom is precipitated with silver nitrate from a fresh solution. The former has the formula $[Cr(H_2O)_5Cl]Cl_2.H_2O$,[3] the latter, which is green in colour, has the formula $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.[4] The water outside is very easily removed, and its removal does not affect the properties of the complex. The same type of isomerism is observed in the ammines; for example, dichloro-diaquo-dipyridino-chromic chloride, $[Cr\,py_2Cl_2(H_2O)_2]Cl$, is isomeric with trichloro-aquo-dipyridino-chromium monohydrate, $[Cr\,py_2Cl_3(H_2O)].H_2O$.[5]

4. *Ionisation Isomerism.*—This is shown in the chromic hydrates, chloro-pentaquo-chromic sulphate, $[Cr(H_2O)_5Cl]SO_4$, and sulphato-pentaquo-chromic chloride, $[Cr(H_2O)_5SO_4]Cl$.[6]

5. *Stereo-isomerism.*—Two isomeric dichloro-diethylenediamino-chromic chlorides, $[Cr\,en_2Cl_2]Cl$, are known, a violet modification and a green modification. Dibromo-diethylenediamino-chromic chloride exists also in two forms, and many other examples of this type of isomerism are known. The configuration of these isomers was determined by showing that from oxalato-diethylenediamino-chromic salts, $[Cr\,en_2(C_2O_4)]R$, only chloro- and bromo-salts of violet colour could be obtained, and as these oxalato-salts form ring compounds, and only violo salts are obtained from them by replacement of the (C_2O_4) group by chlorine or bromine, these chloro and bromo salts are regarded as *cis*-salts. The *trans*-salts isomeric with them are not obtained in

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[1] Werner, *New Ideas on Inorganic Chemistry.* Translated by E. P. Hedley (Longmans, 1911), p. 232.

[2] Pfeiffer, *Annalen*, 1906, 346, 28.

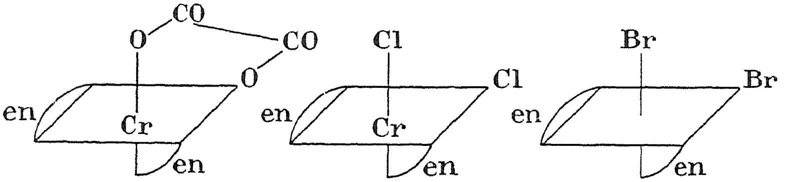
[3] Gubser, *Ber.*, 1901, 34, 1601.

[4] Bjerrum, *ibid.*, 1906, 39, 1599.

[5] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 322.

[6] Weinland and Schumann, *Ber.*, 1907, 40, 3091; *Zeitsch. anorg. Chem.*, 1908, 58, 176.

this way. The formation of *cis*-salts is represented in the following manner:—[1]

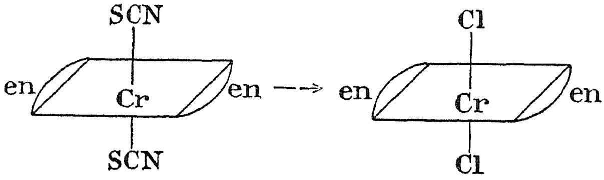


Oxalato-diethylenediamino-chromic complex. *Cis.*

Dichloro-diethylenediamino-chromic complex. *Cis.*

Dibromo-diethylenediamino-chromic complex. *Cis.*

The green *trans*-compounds are formed from 1, 6-dithiocyanato-diethylenediamino-chromic salts by replacement of thiocyanato radicles thus:



Trans-dichloro-diethylenediamino-chromic complex.

6. *Valency Isomerism.*—Finally, in the polynuclear compounds occur cases of valency isomerism. For example, the decammino-ol-dichromic salts or rhodo-chromium salts, $[(NH_3)_5Cr.OH.Cr(NH_3)_5]R_5$, are isomeric with the decammino-hydroxonium chromic salts or erythro-chromic salts, $[(NH_3)_5Cr.\underset{\substack{\dot{H}\\ \dot{R}}}{O}.Cr(NH_3)_5]R_4$. The rhodo-salts are red and neutral in reaction, the isomeric erythro-salts have strongly acid reaction, and may be transformed into the rhodo-salts by the action of heat.

Class II. (A).—Mononuclear Chromi-ammines containing One Atom of Chromium in the Molecule.

1. *Chromic Salts with Trivalent Cation,* $[CrA_6]^{\cdots}$.

(*a*) Hexammino-chromic Salts, Luteo-salts.

This series of salts is yellow or brown in colour, and consists of the true hexammino-compounds, and also compounds where all, or part, of the ammonia is replaced by ethylenediamine or propylenediamine. Every molecule of ethylenediamine or propylenediamine replaces two molecules of ammonia, and thus occupies two co-ordination positions in the complex. A few compounds are known where urea replaces ammonia in the complex, and in this case one molecule of urea replaces one molecule of ammonia, and occupies one co-ordination position only.

The hexammino-chromic salts are formed by reducing potassium dichromate in acid solution with alcohol. Zinc is added so that reduction

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[1] Pfeiffer, *Ber.*, 1904, 37, 4255.

takes place in an atmosphere of hydrogen, and the reduced solution is then run into a mixture of ammonium chloride and concentrated aqueous ammonia. The blue solution obtained is then placed in a cooled flask and the hydrogen allowed to escape. With removal of hydrogen the liquid begins to oxidise, and when oxidation is complete ammonium chloride and hexammino-chromic chloride are precipitated. The salt is washed free from admixed ammonium chloride by treating the mixture with cold water, in which hexammino-chromic chloride is easily soluble, and from the solution hexammino-chromic nitrate is precipitated by the addition of concentrated nitric acid.

The salts may also be prepared by oxidising a solution of chromous salt in an aqueous solution of ammonium sulphate by means of iodine. The nitrate or the chloride is usually prepared first, and the other salts obtained from them by double decomposition.

The salts are stable in air in absence of light, and are decomposed on heating to 100° C. The chloride, nitrate, and sulphate are fairly soluble in water, the other salts are sparingly soluble. They form many double salts.

Hexammino-chromic Nitrate, $[Cr(NH_3)_6](NO_3)_3$, is obtained by the method described above.[1] It crystallises in brilliant orange-yellow plates or prisms, is insoluble in alcohol and soluble in cold water, one part dissolving in forty parts of water; the addition of soluble sulphates to the solution causes the precipitation of the less soluble *nitrate-sulphate*, $[Cr(NH_3)_6](NO_3)(SO_4)$, which crystallises in glistening yellow octahedra. Sodium chloroplatinate added to an aqueous solution of the nitrate precipitates the *nitrate-chloroplatinate*, $[Cr(NH_3)_6](NO_3).(PtCl_6).H_2O$.

The *acid nitrate*, $[Cr(NH_3)_6](NO_3).HNO_3$, is produced by dissolving the normal salt in water and adding concentrated nitric acid.[2]

Hexammino-chromic Chloride, $[Cr(NH_3)_6]Cl_3.H_2O$, is produced by the addition of concentrated hydrochloric acid to a solution of the nitrate, or, better, by the decomposition of the mercury double salt, $[Cr(NH_3)_6]Cl_3.(HgCl_2)$, with hydrogen sulphide, when a purer chloride is obtained.[3] It is formed as one of the products of the action of liquid ammonia on anhydrous violet chromic chloride.[4]

The salt crystallises in large, efflorescent, yellow leaflets, which are soluble in water and decompose on treatment with concentrated hydrochloric acid, with formation of chloro-pentammino-chromic chloride, $[Cr(NH_3)_5Cl]Cl_2$.

The double salt, $[Cr(NH_3)_6]Cl_3.HgCl_2$, mentioned above, is prepared from crude hexammino-chromic nitrate by dissolving it in cold water and adding concentrated hydrochloric acid and a solution of mercuric chloride in acid. It forms yellow octahedral plates and is decomposed by water. By adding the salt to a boiling aqueous solution of mercuric chloride, acidifying with dilute hydrochloric acid and filtering the hot solution, glittering yellow needles of composition $[Cr(NH_3)_6]Cl_3.3HgCl_2$ separate.

Hexammino-chromic Chloroplatinate, $[Cr(NH_3)_6]_2(PtCl_6)_3.6H_2O$, is formed by the addition of sodium chloroplatinate to a neutral solution of hexammino-chromic chloride. It is very sparingly soluble

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[1] Jörgensen, *J. prakt. Chem.*, 1884, 30, 1.

[2] Jörgensen, *ibid.*, 1891, 44, 63.

[3] Jörgensen, *ibid.*, 1884, 30, 12.

[4] Christensen, *Zeitsch. anorg. Chem.*, 1893, 4, 229.

in water and crystallises in orange-yellow prisms. In acid solution a substance of composition $[Cr(NH_3)_6]_2Cl_2.(PtCl_6)_2.5H_2O$, crystallising in orange-yellow needles, is formed, and on further addition of acid it becomes dark orange in colour, and has the composition $[Cr(NH_3)_6]Cl_4.(PtCl_6).2H_2O$. The two latter compounds are decomposed by water into the normal salt.

Hexammino-chromic Bromide, $[Cr(NH_3)_6]Br_3$, is precipitated from a concentrated solution of the nitrate of the series by decomposing it with concentrated hydrobromic acid. The orange-yellow plates which separate are decanted from the solution, washed with dilute hydrobromic acid and then with water. It is easily soluble in pure water but sparingly so in presence of hydrobromic acid. The transformation of the salt into bromo-pentammino-chromic bromide on heating with acid takes place more slowly than the analogous reaction with the chloride of the series.

The bromoplatinate, $[Cr(NH_3)_6]PtBr_6.6H_2O$, is obtained in the same way as the chloroplatinate, and crystallises in orange-red prisms.

Hexammino-chromic Iodide, $[Cr(NH_3)_6]I_3$, is also formed by the decomposition of the nitrate. A solution of hexammino-chromic nitrate is shaken with solid potassium iodide, the precipitate formed is washed with hydriodic acid, dissolved in cold water, and reprecipitated with dilute acid. It separates in yellow rhombic plates and is sparingly soluble in cold water. On warming with hydriodic acid iodo-pentammino-iodide is not produced.[1]

Hexammino-chromic Oxalate, $[Cr(NH_3)_6]_2(C_2O_4)_3.4H_2O$, is prepared by decomposing a solution of the nitrate with aqueous ammonia and a saturated solution of ammonium oxalate. The salt, being difficultly soluble in hot water, is almost completely precipitated in crystalline aggregates. It is decomposed on prolonged heating at 100° C., and loses water if left to stand over sulphuric acid.

A double oxalate, the **chromi-oxalate,** $[Cr(NH_3)_6][Cr(C_2O_4)_3].3H_2O$, is produced by treating a solution of hexammino-chromic nitrate with aqueous blue potassium chromi-oxalate. A grey precipitate is first obtained, and on allowing the liquid to stand, dark green leaflets separate which are collected, well washed with cold water, and dried.[2] Other double salts are produced in similar manner from the nitrate. For example, the chromi-cyanide, $[Cr(NH_3)_6]Cr(CN)_6$, formed by adding potassium chromi-cyanide, $[Cr(CN)_6]K_3$, to a solution of the nitrate, crystallises in long orange-yellow needles; [3] the ferricyanide, $[Cr(NH_3)_6]Fe(CN)_6$, obtained by decomposing the nitrate with potassium ferricyanide, is sparingly soluble, and is a brownish-yellow crystalline substance.

(*b*) Triethylenediamino-chromic Salts, $[Cr\ en_3]R_3$.

This series, which corresponds to the hexammino-chromic salts, was discovered by Pfeiffer in 1900.[4]

Triethylenediamino-chromic Chloride, $[Cr\ en_3]Cl_3.3\frac{1}{2}H_2O$, is formed by adding gradually the theoretical quantity of trichloro-tri pyridino-chromium, $[Cr\ py_3Cl_3]$, to ethylenediamine monohydrate; on

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[1] Jörgensen, *J. prakt. Chem.*, 1884, 30, 22.
[2] Pfeiffer and Basci, *Annalen*, 1906, 346, 46.
[3] Jörgensen, *Zeitsch. anorg. Chem.*, 1900, 24, 274.
[4] Pfeiffer, *ibid.*, 1900, 24, 279.

warming, the mixture becomes green, and most of it passes into solution. The pyridine liberated is removed, and the reaction product dissolved in water and precipitated from it with alcohol. The compound may also be prepared from chromic alum. Dehydrated chromic alum is warmed on a water-bath with ethylenediamine monohydrate, a yellow mass is formed, which is then treated with a small quantity of water; the triethylenediamino-salt goes into solution, leaving a red powder consisting of a complex salt, $[Cr_4(OH)_6en_6](SO_4)_3$, undissolved. From the solution triethylenediamino-chromic chloride is precipitated as a yellow powder on the addition of ammonium chloride, and the crude product is recrystallised from a little warm water.[1] The same product is formed by the action of ethylenediamine on *cis*- or *trans*-dichloro-diethylenediamino-chromic chloride.[2] The salt crystallises in orange-yellow prisms, is easily soluble in water, yielding a neutral solution, and decomposes on exposure to sunlight, or when its aqueous solution is warmed. On treatment with moist silver oxide a strongly alkaline, unstable solution is obtained, which precipitates the hydroxides of many of the metallic salts and behaves as the base, $[Cr(en)_3](OH)_3$.[3]

Triethylenediamino-chromic Nitrate, $[Cr(en)_3](NO_3)_3$, is prepared from the chloride by treating the aqueous solution with the calculated quantity of silver nitrate; the precipitated silver chloride is removed by filtration, and, on the addition of alcohol to the filtrate, the nitrate separates and is then recrystallised from water. It crystallises in yellow transparent clusters, which become reddish in colour on warming, but on cooling regain their original colour.

Triethylenediamino-chromic Bromide, $[Cr\,en_3]Br_3.xH_2O$ (x may be 5 or 3), is formed from the chloride by the addition of hydrobromic acid, when the bromide is almost quantitatively precipitated. The crude product is recrystallised from water at 30° to 40° C. It crystallises in long, clear yellow prisms, which are less soluble than the chloride.

Triethylenediamino-chromic Iodide, $[Cr\,en_3]I_3.H_2O$, is obtained from the chloride by decomposing it with hydriodic acid and recrystallising the product from water. It crystallises in yellow leaflets, which are less soluble in water than either the chloride or the bromide.

Triethylenediamino-chromic Thiocyanate, $[Cr\,en_3](SCN)_3.H_2O$, is obtained in compact, yellow crystals by decomposing the chloride with ammonium thiocyanate and recrystallising the crude product from water. It is stable towards light, and decomposes on heating to 120° C., with loss of one molecule of ethylenediamine and formation of *trans*-dithiocyanato-diethylenediamino-chromic thiocyanate,[4] $[Cr\,en_2(SCN)_2]SCN$.

(*c*) Diethylenediamino-propylenediamino-chromic Salts, $[Cr\,en_2pn]R_3$.

A series of salts is known of the above type where ethylenediamine and propylenediamine enter the chromic complex, giving rise to mixed salts. This series was described by Pfeiffer in 1908.[5]

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[1] Pfeiffer, *Ber.*, 1904, 37, 4277.

[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 311.

[3] Pfeiffer, *ibid.*, 1900, 24, 278.

[4] Pfeiffer, *ibid.*, 1900, 24, 294; 1901, 29, 113.

[5] Pfeiffer, *ibid.*, 1908, 58, 297.

Diethylenediamino-propylenediamino-chromic Thiocyanate, $[Cr\,en_2pn](SCN)_3.\frac{1}{2}H_2O$, is prepared by heating *cis*-dichloro-diethylenediamino-chromic chloride, $[Cr\,en_2Cl_2]Cl$, with propylenediamine monohydrate on a water-bath for some time until the mass becomes yellow. It is then cooled, treated with a little water, filtered, and a concentrated aqueous solution of ammonium thiocyanate added to the filtrate. Small yellow crystals separate, which are recrystallised from warm water. They are soluble in water and insoluble in alcohol.[1]

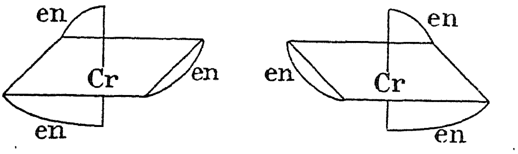
From this salt the *bromide*, $[Cr\,en_2pn]Br_3.3H_2O$, is prepared by decomposing it with concentrated aqueous hydrobromic acid. A finely crystalline precipitate separates, which is recrystallised from water and alcohol in glistening yellow clusters.

The *iodide*, $[Cr\,en_2pn]I_3.2H_2O$, is obtained in lustrous yellow needles by decomposition of the thiocyanate with potassium iodide. The iodide is more soluble in water than triethylenediamino-chromic iodide, and is insoluble in alcohol and ether. The aqueous solution is decomposed by moist silver oxide, giving a strongly alkaline solution containing the base, $[Cr\,en_2pn](OH)_3$.

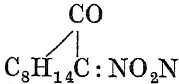
Tripropylenediamino-chromic salts are prepared in a similar manner to triethylenediamino-salts, and have the same general properties.[2]

Tripropylenediamino-chromic Iodide, $[Cr\,pn_3]I_3.H_2O$, may be prepared, for instance, by the decomposition of trichloro-tripyridino-chromium with propylenediamine monohydrate. It crystallises in small yellow needles, soluble in water, and is decomposed by moist silver oxide with liberation of the base, $[Cr\,pn_3](OH)_3$.

Isomerism in the Triethylenediamine Series.—Two configurations for these salts are possible, the one being the mirror image of the other, thus :



Each of the compounds mentioned, therefore, should exist in a racemic form and two optically active forms. After Werner had succeeded in isolating optically active forms of the corresponding cobalt compound, he attempted to isolate, by the same means, isomers of the chromic series. Optically active tartaric acid, chloro- or bromo-tartaric acid, camphor-sulphonic acid, and brom-camphor-sulphonic acid proved unsatisfactory, since the aqueous solutions change on evaporation; but sodium d-camphor nitronate, $C_8H_{14}\overset{\overset{CO}{|}}{C}:NO_2Na$, proved a useful reagent, and by its means triethylenediamino-chromic iodide and triethylenediamino-chromic thiocyanate were resolved.[3]



Resolution of Triethylenediamino-chromic Iodide.—Triethylenediamino-chromic chloride in aqueous solution was mixed with sodium d-camphor nitronate, when the sparingly soluble d-triethylenedi-

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[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 297.

[2] Pfeiffer and Haimann, *Ber.*, 1903, 36, 1064.

[3] Werner, *ibid.*, 1912, 45, 865.

amino-chromic d-camphor nitronate immediately separates as a yellow powdery precipitate. This is collected, and after salting out the remaining d-salt, l-triethylenediamino-chromic d-camphor nitronate remains in the mother-liquor.

d-Triethylenediamino-chromic Iodide, $[\mathrm{Cr\,en_3}]\mathrm{I_3.H_2O}$, results on treating the d-camphor nitronate, in presence of water, with solid sodium iodide in sufficient quantity to cause the mixture to set to a solid yellow mass. It is washed with a little water, then with alcohol and ether, and purified by reprecipitation from a concentrated aqueous solution by means of sodium iodide. It forms flat golden-yellow crystals, and has rotation :

$$[\alpha]_D = +60^\circ \, ; \qquad [M]_D = +378 \cdot 67^\circ.$$

l-Triethylenediamino - chromic Iodide, $[\mathrm{Cr\,en_3}]\mathrm{I_3.H_2O}$, is obtained from the mother-liquor from the action of sodium d-camphor nitronate and racemic triethylenediamino-chromic chloride by adding sodium iodide, filtering off the precipitate of inactive $[\mathrm{Cr\,en_3}]\mathrm{I_3}$ formed, and adding solid sodium iodide to the filtrate when the l-modification separates. In appearance it resembles the d-salt, and has rotation :

$$[\alpha]_D = -60^\circ \, ; \qquad [M]_D = -378 \cdot 67^\circ.$$

d-Triethylenediamino-chromic Thiocyanate, $[\mathrm{Cr\,en_3}](\mathrm{SCN})_3.\mathrm{H_2O}$, is obtained when a concentrated solution of d-iodide is treated with solid potassium thiocyanate. The d-salt separates as a yellow crystalline powder with rotation :

$$[\alpha]_D = +78^\circ \, ; \qquad [M]_D = 330 \cdot 72^\circ.$$

The l-salt is formed similarly from l-iodide, and has rotation :

$$[\alpha]_D = -80^\circ \, ; \qquad [M]_D = -339 \cdot 2^\circ.$$

From these results it is therefore assumed that all members of the series are racemic salts, which may be resolved into optically active forms.

(*d*) Aquo-pentammino-chromic Salts, Roseo-salts, $[\mathrm{Cr(NH_3)_5H_2O}]\mathrm{R_3}$.

The series was discovered by Jörgensen in 1879,[1] and in 1881 Christensen[2] established the constitution of the substances. The salts are prepared by the decomposition of the chloro-purpureo-chromic salts. They are orange-yellow in colour and less stable than the luteo-salts. They form double salts like the luteo-salts, the most characteristic of these being the sparingly soluble ferricyanide and the sulphato-chloroplatinate.

Aquo-pentammino-chromic Hydroxide, $[\mathrm{Cr(NH_3)_5H_2O}](\mathrm{OH})_3$, is known only in solution, and is formed when dry chloro-pentammino-chromic chloride, $[\mathrm{Cr(NH_3)_5Cl}]\mathrm{Cl_2}$, is rubbed, in absence of light, with moist silver oxide and water ; on filtering a deep red solution, which is strongly alkaline in reaction, is left, which contains the base, $\mathrm{Cr}[(\mathrm{NH_3})_5\mathrm{H_2O}](\mathrm{OH})_3$. The solution is unstable and decomposes on

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[1] Jörgensen, *J. prakt. Chem.*, 1879, 20, 105.

[2] Christensen, *ibid.*, 1881, 23, 26.

standing, and even more quickly on warming with formation of $Cr(OH)_3$ and NH_3. If acid be added to the cold, freshly prepared solution, aquo-pentammino-chromic salt is produced.[1]

Aquo-pentammino-chromic Sulphate, $[Cr(NH_3)_5H_2O]_2(SO_4)_3.3H_2O$, is produced from a solution of aquo-pentammino-chromic base by neutralising it with dilute sulphuric acid, adding half its volume of 90 per cent. alcohol, and allowing the oil which is precipitated to stand until it becomes solid. The salt crystallises in short quadratic prisms which are soluble in water and decompose on standing even in the dark. On heating to 100° C. four molecules of water are removed, and, on addition of sodium chloroplatinate to a dilute solution of the salt, the very sparingly soluble sulphate chloroplatinate, $[Cr(NH_3)_5H_2O]_2SO_4.PtCl_6.2H_2O$, is precipitated in glistening yellow crystals. This salt and the corresponding bromoplatinate, $[Cr(NH_3)_5H_2O]_2SO_4.PtBr_6$, on account of their sparing solubility, are precipitated from all the aquo-pentammino-chromic salts on addition of soluble chloro- or bromoplatinate and magnesium sulphate.

Aquo-pentammino-chromic Chloride, $[Cr(NH_3)_5H_2O]Cl_3$, is formed by filtering an aqueous solution of the corresponding base into dilute hydrochloric acid, or, together with chloro-pentammino-chromic chloride, by precipitation of a concentrated aqueous solution of the base with concentrated acid. It crystallises as an orange-coloured salt, easily dissolves in water, and the neutral solution decomposes on heating.

On heating with hydrochloric acid the salt changes to chloro-pentammino-chromic chloride, $[Cr(NH_3)_5Cl]Cl_2$. A concentrated solution gives with mercuric chloride a yellowish-red, sparingly soluble double salt, $[Cr(NH_3)_5H_2O]Cl_3.(HgCl_2)_3.H_2O$.

Aquo-pentammino-chromic Bromide, $[Cr(NH_3)_5H_2O]Br_3$, is prepared from the chloride by treating an aqueous solution of the salt with hydrobromic acid. The solution is evaporated to dryness and the residue taken up in water, filtered to remove any bromo-pentammino-chromic bromide formed, and the filtrate treated with concentrated hydrobromic acid to precipitate the aquo-salt, which is then washed with alcohol. It forms a yellow crystalline powder, easily soluble in water, and much more stable than the corresponding chloride. At 100° C. it loses water, and is transformed into bromo-pentammino-chromic bromide.

Aquo-pentammino-chromic Iodide, $[Cr(NH_3)_5H_2O]I_3$, is produced in the same way as the bromide or the chloride. It is a crystalline powder, easily soluble in water, and more stable in acid than the bromide, and on strongly heating with hydriodic acid it is transformed in the same way as the other salts into the iodo-pentammino-iodide.

Aquo-pentammino-chromic Nitrate, $[Cr(NH_3)_5H_2O](NO_3)_3$, may be formed by a method similar to that for the bromide, or it may be produced by treating chloro-pentammino-chromic chloride in aqueous solution with 1·4 nitric acid and allowing the mixture to stand at 0° C. The solution is filtered and treated with a further portion of nitric acid and allowed to stand at 0° C., when the aquo-salt crystallises out.[2] It is a yellowish-red crystalline salt, easily soluble in water, and decomposes if heated to 100° C.

An *acid nitrate*, $[Cr(NH_3)_5H_2O](NO_3)_3.HNO_3$, is formed by dis-

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[1] Christensen, *J. prakt. Chem.*, 1881, 23, 27.

[2] Werner and Surber, *Annalen*, 1914, 405, 212.

solving the normal salt in water and adding concentrated nitric acid. It is rather more yellow in colour than the normal salt.[1]

Oxalic acid converts the nitrate into oxalato-tetrammino-chromic nitrate, $[Cr(NH_3)_5(C_2O_4)](NO_3)_3$.[2]

The double compound, $[Cr(NH_3)_5H_2O][Cr(CN)_6]$, is precipitated from the aquo-pentammino-chloride on addition of potassium chromicyanide; it separates as a sparingly soluble yellow crystalline powder, and on heating with concentrated hydrochloric acid decomposes with formation of chloro-pentammino-chloride. The ferricyanide, $[Cr(NH_3)_5H_2O][Fe(CN)_6]$, is precipitated from a dilute solution of the aquo-pentammino-chloride on addition of potassium ferricyanide, and crystallises in yellowish-brown prisms. The cobalti-cyanide, $[Cr(NH_3)_5H_2O][Co(CN)_6]$, obtained, by the addition of potassium cobalti-cyanide, in yellowish-brown crystals, is isomeric with the chromi-cyanide of aquo-pentammino-cobalt, $[Co(NH_3)_5H_2O][Cr(CN)_6]$.

(*e*) **Diaquo-tetrammino-chromic Salts, $[Cr(NH_3)_4(H_2O)_2]R_3$.**

This series of salts, resembling in their constitution and properties the aquo-pentammino-salts, was prepared in 1907.[3] The salts may be obtained by the action of acid on hydroxo-aquo-tetrammino-chromic salts. They are orange to red in colour, easily soluble in water, giving an orange-coloured solution, and are acid in reaction.

Diaquo-tetrammino-chromic Acid Nitrate, $[Cr(NH_3)_4(H_2O)_2](NO_3)_4.H$, is formed when hydroxo-aquo-tetrammino-chromic dithionate, $[Cr(NH_3)_4(H_2O)(HO)]S_2O_6$, is treated with fuming nitric acid. It forms light orange-coloured prismatic needles, which decompose in a desiccator over sodium hydroxide, or, on heating, being transformed into red nitrato-aquo-tetrammino-chromic nitrate, $[Cr(NH_3)_4H_2O(NO_3)](NO_3)_2$.[4]

Diaquo-tetrammino-chromic Chloride,. $[Cr(NH_3)_4(H_2O)_2]Cl_3$, is obtained as a scarlet crystalline powder by decomposing hydroxo-tetrammino-chromic dithionate with hydrochloric acid. It is soluble in water, acid in reaction, and yields with potassium cobalticyanide orange-red crystals of $[Cr(NH_3)_4(H_2O)_2][Co(CN)_6]$. If the solution at 0° C. be treated with pyridine in aqueous solution, the hydroxo-compound, $[Cr(NH_3)_4H_2O(HO)]Cl_2$, is formed, and on slowly evaporating a solution of the salt containing hydrochloric acid, it is converted into chloro-aquo-tetrammino-chromic chloride, $[Cr(NH_3)_4H_2O.Cl]Cl_2$.

The *bromide*, $[Cr(NH_3)_4(H_2O)_2]Br_3$, obtained by the same method as the chloride, crystallises in orange-red plates, is soluble in water with acid reaction, and changes slowly into the reddish-violet bromo-aquo-compound. Pyridine changes the aqueous solution into the hydroxo-aquo-tetrammino-chromic bromide, $[Cr(NH_3)_4H_2O(HO)]Br_2$, which crystallises from an aqueous solution in red leaflets. Mineral acids decompose the compound, forming the diaquo-salt.

Diaquo-diethylenediamino-chromic Salts, $[Cr\ en_2(H_2O)_2]R_3$.—This series, corresponding to the diaquo-tetrammino-salts, is interesting, as the isomeric *cis*- and *trans*-forms have been isolated. In this parti-

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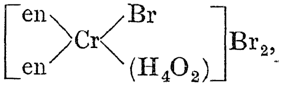
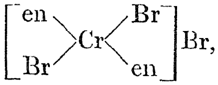
[1] Jörgensen, *J. prakt. Chem.*, 1891, 44, 66.
[2] Werner and Surber, *Annalen*, 1914, 405, 212.
[3] Pfeiffer, *Ber.*, 1907, 40, 3126.
[4] Pfeiffer, *ibid.*, 1907, 40, 3133.

cular series, however, the *cis*- and *trans*-salts, with one exception, are not strictly isomeric, for they differ in water content. In the *trans*-series most of the salts contain two molecules of water in the complex cation, whereas in the *cis*-series the salts contain four molecules of water in the complex, arranged as double water molecules or dimolecular water, (H_4O_2), each occupying one co-ordinate position. That these double water molecules occupy one co-ordinate position is proved by the fact that, on replacement of water by halogen in the nucleus, one atom of halogen eliminates two molecules of water. The salts containing dimolecular water are designated the *bisaquo-salts*.[1]

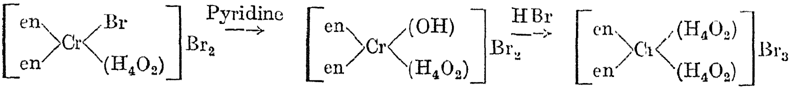
Diaquo-diethylenediamino-chromic Salts are prepared from *cis*-bisaquo-bromo-diethylenediamino-chromic bromide,



and *trans*-dibromo-diethylenediamino-chromic bromide,

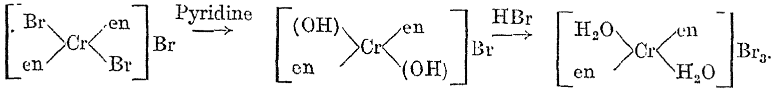


by treating these salts with pyridine and then with mineral acids, when the hydroxo-salt is first formed, and then the aquo-salt according to the scheme :



Cis-dibisaquo.

and



Trans-diaquo.

Cis-dibisaquo-diethylenediamino-chromic Bromide, $[Cr\,en_2(H_4O_2)_2]Br_3$, is prepared from bromo-bisaquo-diethylenediamino-chromic bromide, $[Cr\,en_2Br(H_4O_2)]Br_2$, by treating it, in aqueous solution, with pyridine, when *cis*-hydroxo-bisaquo-diethylenediamino-chromic bromide, $[Cr\,en_2(H_4O_2)(OH)]Br_2$, separates in compact crystals. On treating these crystals with concentrated hydrobromic acid, the dibisaquo-salt is formed in small yellowish-red crystals. The salt crystallises in shining orange plates, which are soluble in water, giving an acid solution, from which it may be precipitated by means of concentrated hydrobromic acid. If, however, it is left to stand in contact with the acid the colour gradually changes to violet, and violet-red leaflets of bromo-bisaquo-salt are deposited. Pyridine also acts upon the compound, forming the hydroxo-bisaquo-bromide again. A concentrated aqueous solution of the salt yields, with solid potassium oxalate, small, brilliant orange leaflets of the oxalate. Heating to 120° C., or evaporating with hydrobromic acid on the water-bath, causes the salt to lose water, *cis*-dibromo-diethylenediamino-chromic bromide being produced.

Cis - dibisaquo - diethylenediamino - chromic Chloride,

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[1] Pfeiffer, *Ber.*, 1907, 40, 3828.

$[Cr\,en_2(H_4O_2)_2]Cl_3$, is prepared by an analogous method to that for the bromide,[1] *cis*-hydroxo-aquo-diethylenediamino-chromic dithionate being treated with hydrochloric acid, when lustrous orange-red plates separate. This salt and also the bromide are considerably hydrolysed in aqueous solution, and react with pyridine to form the basic salts, $[Cr\,en_2(H_4O_2)(HO)]Br_2$ and $[Cr\,en_2(H_4O_2)(HO)]Cl_2$, from which the dibisaquo-salt is regenerated by mineral acids. The reaction may be represented thus :

$$[Cr\,en_2(H_4O_2)_2]Cl_3 \rightleftharpoons [Cr\,en_2(H_4O_2)(OH)]Cl_2+H_2O+HCl.$$

Cis-diaquo salts, namely, those with two simple water molecules in the complex, have not been prepared.

Trans - diaquo - diethylenediamino - chromic Bromide, $[Cr\,en_2(H_2O)_2]Br_3$, is obtained in a manner much like that for the *cis*-salt; the green *trans*-dibromo-diethylenediamino-chromic bromide, $[Cr\,en_2Br_2]Br$, is treated in solution with potassium bromide and pyridine, when the basic salt, *trans*-hydroxo-aquo-diethylenediamino-chromic bromide, $[Cr\,en_2(H_2O)(HO)]Br_2$, is formed, and on acidifying it with hydrobromic acid the diaquo-compound is obtained. It crystallises in brownish-yellow prismatic needles, soluble in water, and behaves towards heat and acid like the *cis*-compound.[1] Pyridine gives an almost quantitative yield of *trans*-hydroxo-aquo-bromide ; potassium iodide added to a solution of the salt yields flesh-coloured leaflets of hydroxo-aquo-iodide, $[Cr\,en_2H_2O(HO)]I_2$.

Trans - dibisaquo - diethylenediamino - chromic Bromide, $[Cr\,en_2(H_4O_2)_2]Br_3$, is known, but unlike the *cis*-isomer it loses two molecules of water very easily, being converted into the normal diaquo-bromide, $[Cr\,en_2(H_2O)_2]Br_3$. It crystallises in brownish-orange needles, and is the only representative of the *trans*-dibisaquo-salts, the true isomers of the *cis*-dibisaquo-salts.

The *cis*-dibisaquo-diethylenediamino-chromic halides on loss of water yield violet *cis*-diacido-salts; the *trans*-salts, on the same treatment, green *trans*-diacido-salts.

(*f*) Triaquo-triammino-chromic Salts, $[Cr(NH_3)_3(H_2O)_3]R_3$.

These salts are purple in colour, and yield a purple solution when dissolved in water. They may be prepared from hydroxo-diaquo-triammino-chromic iodide, $[Cr(NH_3)_3(H_2O)_2(HO)]I_2.H_2O$,[2] or from chromium tetroxo-triammine, $CrO_4.3NH_3$.[3]

Triaquo-triammino-chromic Chloride, $[Cr(NH_3)_3(H_2O)_3]Cl_3$, is obtained by dissolving chromium tetroxo-triammine in cold dilute hydrochloric acid and passing hydrogen chloride through the solution. After a time red needle-shaped crystals of the triaquo-salt are formed. Care has to be taken not to pass in the gas in excess, otherwise the solution becomes green in colour and crystals of the monacido- or diacido-salt are formed. The salt is recrystallised from water containing a few drops of concentrated acid. The same substance may be produced from dichloro-aquo-triammino-chromic chloride by treating it in aqueous solution with pyridine to form the hydroxo-compound, which is transformed by means of solid potassium iodide into the sparingly soluble hydroxo-

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[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 228.

[2] Werner, *Ber.*, 1910, 43, 2290.

[3] Riesenfeld and Seemann, *ibid.*, 1909, 42, 4222.

iodide, $[Cr(NH_3)_3(H_2O)_2(HO)]I_2.H_2O$; this is rubbed with a small quantity of concentrated hydrochloric acid, dissolved in water, and saturated with hydrogen chloride at 0° C. The crystalline chloride precipitated is then washed with alcohol and dried over phosphorus pentoxide.[1]

If an aqueous solution of the chloride be treated with concentrated nitric acid, deep red crystals of triaquo-triammino-chromic chloride nitrate, $[Cr(NH_3)_3(H_2O)_3]Cl_2(NO_3)$, are produced.[2]

Triaquo-triammino-chromic Bromide, $[Cr(NH_3)_3(H_2O)_3]Br_3$, is prepared by treating hydroxo-diaquo-triammino-iodide in aqueous solution at low temperature with concentrated hydrobromic acid; after a short time a brownish-red crystalline precipitate is formed. The salt is very soluble in water, giving a blue-red solution.[3]

The triaquo-salts tend to decompose in solution on standing, with precipitation, finally, of chromic hydroxide.[4]

(*g*) Tetraquo-diammino-chromic Salts, $[Cr(NH_3)_2(H_2O)_4]R_3$.

The high water content of these salts make them approach the chromic salt hydrates in properties.

Tetraquo-diammino-chromic Bromide, $[Cr(NH_3)_2(H_2O)_4]Br_3$, is produced by rubbing the basic bromide, $[Cr(NH_3)_2(H_2O)_2(OH)_2]Br$, with concentrated hydrobromic acid at low temperature; the crude product obtained is dissolved in the least possible quantity of water, and the pure neutral bromide precipitated by hydrobromic acid. It forms large bluish-red crystals which are very hygroscopic, soluble in water and in dilute alcohol. On keeping it is transformed into green dibromo-diaquo salt.[5]

Tetraquo-diammino-chromic Chloride, $[Cr(NH_3)_2(H_2O)_4]Cl_3$, is prepared in the same manner as the bromide by decomposing the basic salt. It forms light red monoclinic prisms which are very soluble in water, insoluble in alcohol, and on warming the aqueous solution with a little acid is transformed into the dichloro-diaquo-salt.

From the basic bromide by treatment with hydrobromic acid and then concentrated sulphuric acid, the *sulphate*, $[Cr(NH_3)_2(H_2O)_4]_2(SO_4)_3$, is formed. It crystallises in red leaflets and is hygroscopic.

A series of tetraquo-derivatives containing two molecules of pyridine is also known. These have formula $[Cr\,py_2(H_2O)_4]R_3$, and correspond in general properties to the diammino series. They are prepared from green hydrated chromic chloride, $[CrCl_2(H_2O)_4]Cl.2H_2O$, by treatment with pyridine, when it is transformed into the dihydroxo-diaquo-dipyridino-chloride, $[Cr\,py_2(H_2O)_2(OH)_2]Cl$, and this on treatment with mineral acid changes into the tetraquo-salt.[6]

The salts may also be prepared from tetrathiocyanato-dipyridino-chromium compounds, $[Cr\,py_2(SCN)_4]M$, by oxidising with chlorine.[7]

Tetraquo-dipyridino-chromic Chloride, $[Cr\,py_2(H_2O)_4]Cl_3.2H_2O$,[8] formed by acting upon dihydroxo-diaquo-dipyridino-chromic

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[1] Werner, *Ber.*, 1910, 43, 2290.
[2] Riesenfeld and Seemann, *ibid.*, 1909, 42, 4222.
[3] Werner, *ibid.*, 1906, 39, 2667.
[4] F. Frowein, *Zeitsch. anorg. Chem.*, 1920, 110, 107.
[5] Werner and Klien, *Ber.*, 1902, 35, 287.
[6] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, 31, 401.
[7] Pfeiffer and Osann, *Ber.*, 1906, 39, 2122.
[8] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, 31, 418; *Ber.*, 1906, 39, 1874.

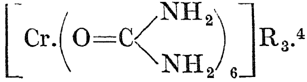
chloride, $[\mathrm{Cr\,py_2(H_2O)_2(OH)_2}]\mathrm{Cl}$, with concentrated hydrochloric acid, crystallises in brownish-red leaflets which are easily soluble in water and in alcohol. If the aqueous liquid is left to stand for some time, greyish-green crystals of dihydroxo-diaquo-dipyridino-chromic chloride separate, and on heating in a closed tube the dichloro-chloride, $[\mathrm{Cr\,py_2(H_2O)_2Cl_2}]\mathrm{Cl}$, is formed.

The *bromide*, $[\mathrm{Cr\,py_2(H_2O)_4}]\mathrm{Br_3.2H_2O}$,[1] crystallises in red transparent rhombic prisms, and resembles the chloride in general reactions; the *sulphate*, $[\mathrm{Cr\,py_2(H_2O)_4}]_2\mathrm{(SO_4)_3.3H_2O}$, and the *nitrate*, $[\mathrm{Cr\,py_2(H_2O)_4}]\mathrm{(NO_3)_3}$,[2] are red crystalline solids and are soluble in water. The *chromi-cyanide*, $[\mathrm{Cr\,py_2(H_2O)_4}][\mathrm{Cr(CN)_6}]\mathrm{.2H_2O}$, crystallises in red leaflets and is insoluble in water.[3]

Salts containing one molecule of ammonia, the **pentaquo-salts**, are unknown.

Of the **hexaquo-salts**, hexaquo-chromic chloride, $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$, has been most thoroughly examined; it is isomeric with chloropentaquo-chromic chloride, $[\mathrm{Cr(H_2O)_5Cl}]\mathrm{Cl_2.H_2O}$, and dichloro-tetraquo-chromic chloride, $[\mathrm{Cr(H_2O)_4Cl_2}]\mathrm{Cl.2H_2O}$. The salts differ in colour and in ionisable acidic radicle.

Compounds where urea takes the place of ammonia are known which correspond to the hexaquo-chromic salts; these contain six molecules of urea bound to the central chromium atom through oxygen, and are prepared by the action of chromyl chloride on urea. The formula for the salts is



$$\left[\mathrm{Cr.}\left(\mathrm{O{=}C}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{matrix}\right)_6\right]\mathrm{R_3}.^{4}$$

Class II. (A)—*continued.*

2. *Chromi-ammines containing Divalent Cation*, $[\mathrm{CrA_5R'}]^{\cdot\cdot}$

(R′ being either acid radicle or hydroxyl).

(*a*) Hydroxo-pentammino-chromic Salts, $[\mathrm{Cr(NH_3)_5.OH}]\mathrm{R_2}$.

This series is represented by the **dithionate**, $[\mathrm{Cr(NH_3)_5(OH)}]\mathrm{S_2O_6.2H_2O}$, which is prepared from aquo-pentammino-chromic bromide by treating it with dilute aqueous ammonia till the colour changes from yellow to deep red; a concentrated aqueous solution of sodium dithionate is then added, the liquid stirred and left to stand, when carmine-red crystals separate. These are washed with dilute alcohol and dried in air. The dithionate is slightly soluble in water, and is decomposed by dilute hydrochloric acid with formation of aquo-pentammino-chromic chloride, $[\mathrm{Cr(NH_3)_5H_2O}]\mathrm{Cl_3}$.

(*b*) Hydroxo-aquo-tetrammino-chromic Salts, $[\mathrm{Cr(NH_3)_4H_2O.OH}]\mathrm{R_2}$.

Hydroxo-aquo-tetrammino-chromic dithionate, $[\mathrm{Cr(NH_3)_4(H_2O).OH}]\mathrm{S_2O_6}$, is produced by the action of pyridine and sodium

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[1] Pfeiffer, *loc. cit.*

[2] Pfeiffer and Osann, *Ber.*, 1907, 40, 4035.

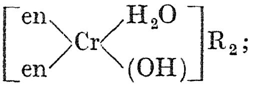
[3] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, 31, 435.

[4] Werner and Kalkmann, *Annalen*, 1902, 322, 296; Pfeiffer, *Ber.*, 1903, 36, 1926.

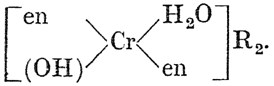
dithionate on chloro-aquo-tetrammino-chromic chloride, $[Cr(NH_3)_4Cl.H_2O]Cl_2$; it forms compact, deep red crystals which are soluble in water with neutral reaction. This salt is the starting-point in the preparation of the diaquo-tetrammino-salts [1] (see p. 87).

The *bromide*, $[Cr(NH_3)_4(H_2O)(OH)]Br_2$, crystallises in red glistening leaflets and is soluble in water.

Hydroxo-aquo-diethylenediamino-chromic Salts, $[Cr\,en_2(H_2O)(OH)]R_2$.—These salts exist in two isomeric forms, the *cis*-, or 1-, 2-series, and the *trans*-, or 1-, 6-series, thus :

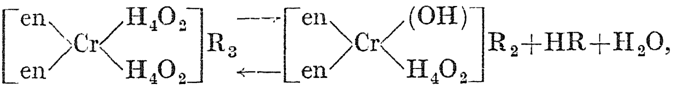


Cis.



Trans.

They are produced by the removal of acid from the corresponding diaquo-salts, thus :



and may be hydrated again, giving the diaquo-salts by the action of mineral acids [2] (see p. 88).

Cis-dithionate has the formula $[Cr\,en_2(H_2O)(OH)]S_2O_6$, where the salt contains simple water molecules ; the *cis*-halogen salts, like the corresponding diaquo-salts, contain dimolecular water and are therefore bisaquo-salts.

The *trans*-salts contain simple water molecules, and on hydration yield true diaquo-salts. The behaviour of the two isomeric series towards heat is characteristic, for the *cis*-salts lose water and give compounds containing two chromium atoms in the nucleus, thus :

$$2[Cr\,en_2(H_4O_2)(OH)]R_2 \longrightarrow [Cr_2en_4(OH)_2]R_4+4H_2O,$$

whilst the members of the *trans*-series remain unchanged.

Cis-salts.

Hydroxo - aquo - diethylenediamino - chromic Dithionate, $[Cr\,en_2(H_2O)(OH)]S_2O_6$, is prepared by treating bromo-bisaquo-diethylenediamino-chromic bromide, $[Cr\,en_2(H_4O_2)Br]Br_2$, with an aqueous solution of pyridine until the salt is dissolved and the liquid acquires a red colour. Solid sodium dithionate is then added, and within an hour a precipitate of hydroxo-dithionate separates, which is washed free from sodium dithionate and dried in air. It may also be prepared from the *cis*-dichloro-chloride, $[Cr\,en_2Cl_2]Cl.H_2O$, by warming with water till the solution becomes orange-yellow and adding pyridine and excess of crystalline sodium dithionate. It forms small deep-red needles, soluble in water; on rubbing with mineral acids the colour changes to orange, and the *cis*-dibisaquo salt, $[Cr\,en_2(H_4O_2)_2]R_3$, is formed.[3]

Cis-hydroxo-bisaquo-diethylenediamino-chromic Chloride, $[Cr\,en_2(H_4O_2)(OH)]Cl_2$, is produced from a concentrated aqueous

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[1] Pfeiffer, *Ber.*, 1907, 40, 3129.

[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 228.

[3] Pfeiffer and Stern, *ibid.*, 1908, 58, 245.

solution of the *cis*-dibisaquo-chloride, $[Cr\ en_2(H_4O_2)_2]Cl_3$, by treating it with excess of pyridine. It separates in small red crystals, soluble in water, and decomposes on treatment with mineral acids, giving the dibisaquo-salt. The *bromide*, $[Cr\ en_2(H_4O_2)(OH)]Br_2$, and the *iodide* are prepared by the same method as the chloride and have the same general properties. Both salts crystallise in glistening, compact red crystals.

Trans-salts.

Trans-hydroxo-aquo-diethylenediamino-chromic Bromide, $[Cr\ en_2(H_2O)(OH)]Br_2$, is derived from the green *trans*-dibromo-bromide, $[Cr\ en_2Br_2]Br$, by allowing an aqueous solution of the salt to stand for some time at ordinary temperature, when the colour changes to brownish red. The liquid is then saturated with potassium bromide, an equal volume of pyridine added, when a flesh-coloured precipitate forms which consists of a mixture of potassium bromide and basic bromide. The precipitate is washed with alcohol and water till the potassium bromide is removed, and the residue dried in air. It may be obtained from *trans*-diaquo-bromide, $[Cr\ en_2(H_2O)_2]Br_3$, by adding to a solution of the salt excess of pyridine when the hydroxo-aquo-salt separates. It crystallises in small, glistening, flesh-coloured leaflets, soluble in water, giving a red solution which is neutral in reaction ; it is decomposed by mineral acids with formation of the *trans*-diaquo-salt, and if rubbed with concentrated hydrobromic acid, solid brownish-orange *trans*-dibisaquo-bromide, $[Cr\ en_2(H_4O_2)_2]Br_3$, is produced. Contrary to the behaviour of the *cis*-salt, on heating it remains unaltered.[1]

Trans - hydroxo - aquo - diethylenediamino - chromic Iodide, $[Cr\ en_2(H_2O)(OH)]I_2$, is formed by the decomposition of the bromide with potassium iodide. It crystallises in silky, flesh-coloured leaflets.

Trans-hydroxo-aquo-diethylenediamino-chromic Dithionate, $[Cr\ en_2(H_2O)(OH)]S_2O_6$, is also formed from the bromide by treating it in concentrated aqueous solution with sodium dithionate ; it is slightly less red in colour than the bromide or iodide, but otherwise behaves similarly.

(*c*) Hydroxo-diaquo-triammino-chromic Salts, $[Cr(NH_3)_3(H_2O)_2OH]R_2$.

A few of these salts are known. For example, the iodide, $[Cr(NH_3)_3(H_2O)_2(OH)]I_2.H_2O$, which is prepared from dichloro-aquo-triammino-chromic chloride, $[Cr(NH_3)_3(H_2O)Cl_2]Cl$, by treating it with pyridine and solid potassium iodide. It crystallises in purple leaflets, soluble in water, and is transformed into triaquo-triammino-chromic bromide by hydrobromic acid.[2]

(*d*) Hydroxo-triaquo-diammino-chromic Salts and Hydroxo-triaquo-dipyridino-chromic Salts.

Salts such as hydroxo - triaquo - diammino - chromic sulphate, $[Cr(NH_3)_2(H_2O)_3.OH]SO_4.H_2O$, and the corresponding dipyridino-salt, $[Cr\ py_2(H_2O)_3(OH)]SO_4$, have been prepared, the former from dihydroxo-diaquo-diammino-chromic bromide by treatment with sulphuric acid,[3]

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[1] Pfeiffer and Prade, *Zeitsch. anorg. Chem.*, 1908, 58, 253.

[2] Werner, *Ber.*, 1906, 39, 2666.

[3] Werner and Klien, *Ibid.*, 1902, 35, 288.

and the latter from tetraquo-dipyridino-chromic sulphate by treatment with pyridine or by the addition of sulphuric acid to the dihydroxo-sulphate, $[Cr\,py_2(H_2O)_2(OH)_2]_2SO_4$.[1]

The hydroxo-triaquo-dipyridino-chromic salts are decomposed by mineral acids with formation of tetraquo-dipyridino-salts; the aqueous solution is acid in reaction and the salts are violet-grey in colour.[2]

(*e*) Acido-pentammino-chromic Salts, $[Cr(NH_3)_5R]R_2$.

Nitro-pentammino-chromic Salts, Xantho-chromic Salts, $[Cr(NH_3)_5(NO_2)]R_2$.—These salts were discovered by Christensen in 1881. It is still doubtful whether the salts are true nitrito-salts with the group O—NO in the nucleus, or whether they are nitro-compounds; they are yellow in colour, which points to the possibility that they are nitro-compounds. Only one series is known, whereas in the cobalt-ammino-compounds both nitro- and nitrito-salts have been isolated (see p. 144).

Nitro-pentammino-chromic Chloride, $[Cr(NH_3)_5NO_2]Cl_2$, is prepared from chloro-pentammino-chromic chloride by heating it for a short time with water acidified with nitric acid, allowing the mixture to cool slowly, and filtering off the undissolved chloro-pentammino-salt. The filtrate, which contains aquo-pentammino-chromic salt, is decomposed with sodium nitrite and a 12 per cent. solution of hydrochloric acid; after a few minutes the precipitate formed is collected, washed with water, dissolved in water, and filtered into a strong solution of ammonium chloride. The precipitated crystals are collected, washed with water and alcohol, and obtained as yellow octahedral prisms. The salt, which is soluble in water, decomposes on heating with hydrochloric acid, giving chloro-pentammino-salt.[3]

The *bromide*, $[Cr(NH_3)_5NO_2]Br_2$, and the *iodide*, $[Cr(NH_3)_5NO_2]I_2$, are prepared by methods analogous to those for the chloride. The former crystallises in yellow octahedra, the latter in red octahedra.

Nitro-pentammino-chromic Nitrate, $[Cr(NH_3)_5NO_2](NO_3)_2$, is obtained from the chloride by precipitation of a solution of the chloride with concentrated aqueous ammonium nitrate, or by decomposing a solution of aquo-pentammino-salt with half its volume of dilute nitric acid and addition of sodium nitrite. It crystallises in yellow octahedra, is less soluble in water than the corresponding chloride, and decomposes explosively on heating.

Nitro-pentammino-chromic Sulphate, $[Cr(NH_3)_5NO_2]SO_4$, is formed by rubbing the chloride with water and the calculated quantity of silver sulphate, filtering off silver chloride and precipitating the salt from the filtrate with alcohol.

Nitrato-pentammino-chromic Nitrate, $[Cr(NH_3)_5NO_3](NO_3)_2$, is obtained from thiocyanato-pentammino-chromic nitrate, $[Cr(NH_3)_5(SCN)](NO_3)_2$, by treating it with well-cooled fuming nitric acid until it has dissolved to a clear brownish-red liquid; ice is then added slowly to the solution until the volume is double, when the nitrato-salt is precipitated as a fine, powdery, pale pink solid. It is sparingly soluble in water, and the solution is very easily decomposed. If warmed with

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[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, 31, 434; *Ber.*, 1906, 39, 1874.

[2] Pfeiffer and Osann, *Ibid.*, 1907, 40, 4032.

[3] Christensen, *J. prakt. Chem.*, 1881, 24, 75.

concentrated hydrochloric acid it quickly passes into chloro-pentammino-chromic chloride.[1]

The *nitrato-iodide*, $[Cr(NH_3)_5NO_3]I_2$, is formed by treating the nitrate with potassium iodide.

Chloro-pentammino-chromic Salts, Purpureo-chromic Salts, $[Cr(NH_3)_5Cl]R_2$.—These salts were first prepared by Jörgensen in 1879;[2] they correspond exactly to the chloro-pentammino-cobalti-salts.

Chloro-pentammino-chromic Chloride, $[Cr(NH_3)_5Cl]Cl_2$, the most important member, is the starting-point for the preparation of the other salts of the series. It is prepared, according to Jörgensen[2] and Christensen,[3] in the following way. Chromous chloride, obtained from chromic chloride reduced with hydrogen, or potassium dichromate and concentrated hydrochloric acid reduced first with alcohol and then with zinc, is dissolved in an aqueous solution of ammonium chloride containing ammonia, and the blue solution so obtained oxidised by passing air through it for some time until the colour of the solution is carmine red. After adding the red solution to concentrated hydrochloric acid and boiling the mixture for a little, carmine octahedral crystals of the chloride separate. They may be purified by dissolving in water slightly acidified with sulphuric acid, and reprecipitating with concentrated hydrochloric acid in which the salt is insoluble. The same salt is produced when liquid ammonia acts upon chromic chloride.[4] The salt is soluble in water, neutral in reaction, and decomposes in a short time with formation of aquo-pentammino-chromic chloride; prolonged heating with sodium hydroxide decomposes the salt, forming chromic hydroxide. With mercuric chloride a cold aqueous solution forms the sparingly soluble double salt, $[Cr(NH_3)_5Cl]Cl_2.3HgCl_2$. It crystallises in rose-coloured needles, is decomposed slowly on exposure to light, and splits up into its components on treatment with dilute hydrochloric acid.

Chloro-pentammino-chromic Bromide, $[Cr(NH_3)_5Cl]Br_2$, has similar properties, and is prepared by addition of concentrated hydrobromic acid to a cold aqueous solution of the chloride.

Chloro-pentammino-chromic Sulphate, $[Cr(NH_3)_5Cl]SO_4.2H_2O$, is prepared by treating the chloride with silver carbonate, removing the precipitated silver chloride and cautiously adding to the liquid dilute sulphuric acid; a little silver chloride is thereby precipitated, it is removed by filtration, and the sulphate is precipitated from the filtrate by means of alcohol in carmine-red prisms. It is fairly soluble in water, and loses water if left over sulphuric acid or on heating to 100° C.

Chloro-pentammino-chromic Nitrate, $[Cr(NH_3)_5Cl](NO_3)_2$, is precipitated by the addition of excess of nitric acid at 0° C. to a solution of the chloride. It may be crystallised from water acidified with nitric acid, and obtained in red octahedral crystals which are more soluble in water than the chloride. The chloro-pentammino-salts react in aqueous solution with chloroplatinic acid, with precipitation of the very sparingly soluble chloroplatinate, $[Cr(NH_3)_5Cl](PtCl_6)$, which crystallises in yellow prisms. The oxalate, $[Cr(NH_3)_5Cl]C_2O_4$, and the ferrocyanide, $[Cr(NH_3)_5Cl]_2[Fe(CN)_6].4H_2O$, are precipitated by the

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[1] Werner and Halban, *Ber.*, 1906, 39, 3671.

[2] Jörgensen, *J. prakt. Chem.*, 1879, 20, 130.

[3] Christensen, *ibid.*, 1881, 23, 54.

[4] Christensen, *Zeitsch. anorg. Chem.*, 1893, 4, 229.

addition of ammonium oxalate and potassium ferrocyanide respectively to solutions of the chloride; both salts are sparingly soluble in cold water.

Bromo-pentammino-chromic Salts, $[Cr(NH_3)_5Br]R_2$.—These salts resemble in appearance and reactions the chloro-pentammino-salts, and the methods of formation are somewhat similar.

Bromo-pentammino-chromic Bromide, $[Cr(NH_3)_5Br]Br_2$, is prepared by transforming chloro-pentammino-chloride into aquo-pentammino-chromic hydroxide, $[Cr(NH_3)_5H_2O](OH)_3$, by means of silver oxide, treating the mixture with dilute hydrobromic acid, filtering off silver bromide formed, and allowing the filtrate to evaporate to small bulk. It is then heated with an equal volume of concentrated acid, the precipitate formed, collected, washed with dilute acid and alcohol.[1] It crystallises in violet-red octahedra, and in solution the salt decomposes like the chloro-pentammino-salt; warming with water and a little acid transforms the salt into aquo-pentammino-bromide; silver oxide and water convert it into aquo-pentammino-hydroxide.

The *chloride*, $[Cr(NH_3)_5Br]Cl_2$, is formed from the bromide, and crystallises in violet octahedra, which are more easily soluble in water than the bromide, and on treatment with silver nitrate in the cold, silver chloride only is precipitated.

The *nitrate*, $[Cr(NH_3)_5Br](NO_3)_2$, crystallises in violet microscopic octahedra. A sparingly soluble *bromoplatinate*, $[Cr(NH_3)_5Br][PtBr_6]$, is formed when a freshly prepared solution of the nitrate is mixed with excess of sodium chloroplatinate. It separates in dark orange-red crystals.[2]

Iodo-pentammino-chromic Salts, $[Cr(NH_3)_5I]R_2$, resemble the chloro- and bromo-pentammino-salts. The *iodide*, $[Cr(NH_3)_5I]I_2$, crystallises in bluish-violet octahedra, sparingly soluble in water and insoluble in alcohol; the *nitrate*, $[Cr(NH_3)_5I](NO_3)_2$, is a reddish-violet crystalline powder; and the *chloride*, $[Cr(NH_3)_5I]Cl_2$, is also a reddish-violet crystalline powder, fairly soluble in cold water, the solution of which is easily affected by light. All are prepared from the aquo-pentammino-chromic salts on treatment with hydriodic acid.[3]

Thiocyanato-pentammino-chromic Salts, $[Cr(NH_3)_5(SCN)]R_2$, are prepared by replacing chlorine in chloro-pentammino-chloride with (SCN) by treating a concentrated aqueous solution containing acetic acid with excess of potassium thiocyanate, warming the solution, and thus obtaining the thiocyanate, $[Cr(NH_3)_5(SCN)](SCN)_2$. From this the other salts are prepared by double decomposition. The thiocyanate, which has not been obtained pure, is reddish brown in colour and does not crystallise easily; it is soluble in cold water, and the aqueous solution gives with hydrochloric acid, potassium bromide, potassium nitrate, potassium iodide, and potassium dichromate, the corresponding salts.

The *chloride*, $[Cr(NH_3)_5(SCN)]Cl_2$, is very stable towards concentrated hydrochloric acid; the *bromide*, $[Cr(NH_3)_5(SCN)]Br_2$, separates in deep orange crystals; and the *nitrate*, $[Cr(NH_3)_5(SCN)](NO_3)_2$, crystallises from acetic acid in orange-yellow crystals. The *dichromate*, $[Cr(NH_3)_5(SCN)]Cr_2O_7$, crystallises in bronze-coloured needles, which are sparingly soluble in water and decomposed by light.[4]

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[1] Jörgensen, *J. prakt. Chem.*, 1879, 20, 126.

[2] Jörgensen, *ibid.*, 1882, 25, 88.

[3] Jörgensen, *ibid.*, 1882, 25, 91.

[4] Werner and Halban, *Ber.*, 1906, 39, 2668.

(*f*) Acido-aquo-tetrammino-chromic Salts, Roseo-purpureo-salts, $[Cr(NH_3)_4H_2O.R]R_2$.

Chloro-aquo-tetrammino-chromic Salts, $[Cr(NH_3)_4H_2O.Cl]R$.—The salts of this series are interesting historically, as they were the first chromi-ammines prepared. Frémy, in 1858,[1] discovered the series; in 1862[2] Clève established their constitution; and Jörgensen, in 1890, showed their relationship with the chloro-pentammino-salts.[3]

Chloro-aquo-tetrammino-chromic Chloride, $[Cr(NH_3)_4H_2O.Cl]Cl_2$, was originally prepared by dissolving chromic hydroxide in an ammoniacal solution of ammonium chloride, precipitating the salt with alcohol, and recrystallising the crude product from hydrochloric acid. It is formed along with the chloro-pentammino-salt by heating ammonium dichromate with hydrochloric acid, ammonium chloride, and alcohol, evaporating to dryness, dissolving the residue in concentrated aqueous ammonia and precipitating with hydrochloric acid. The solid obtained is washed free from ammonium chloride with acid and the chloro-aquo-tetrammino-salt separated from chloro-pentammino-salt by treatment with water, when the aquo-salt goes into solution and is precipitated by the addition of a concentrated solution of ammonium sulphate. The sulphate is transformed into the chloride by digesting with hydrochloric acid.[4] It may also be prepared from dihydroxo-diaquo-dipyridino-chromic chloride, $[Cr\,py_2(H_2O)_2(OH)_2]Cl$,[5] by heating it to 45° to 48° C. with 25 per cent. aqueous ammonia and treating the solution formed with concentrated hydrochloric acid; on standing, deep red crystals separate.[6] The salt crystallises in dark red rhombic prisms which are stable in air but decompose on exposure to light; the solution in water decomposes on heating but is stable in presence of acid.

Chloro-aquo-tetrammino-chromic Bromide, $[Cr(NH_3)_4(H_2O)Cl]Br_2$, is precipitated from a solution of the chloride on the addition of hydrobromic acid; it forms violet-red octahedral crystals which are soluble in water, giving a red solution.

Chloro-aquo-tetrammino-chromic Iodide, $[Cr(NH_3)_4(H_2O)Cl]I_2$, is best prepared by decomposition of the sulphate with excess of barium iodide; it is easily soluble in water and crystallises in red prisms.

Chloro-aquo-tetrammino-chromic Nitrate, $[Cr(NH_3)(H_2O)Cl](NO_3)_2$, is formed when the chloride is mixed with nitric acid, filtered and allowed to stand. It separates in purple rhombic crystals.

Chloro-aquo-tetrammino-chromic Sulphate, $[Cr(NH_3)_4(H_2O)Cl]SO_4$, may be obtained from the chloride by decomposing it with concentrated sulphuric acid, or by treating an aqueous solution of the chloride with a concentrated aqueous solution of ammonium sulphate. The salt is very sparingly soluble in water, and crystallises in small rose-red plates.

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[1] Frémy, *Compt. rend.*, 1858, 47, 883.

[2] Clève, *J. prakt. Chem.*, 1862, 86, 47.

[3] Jörgensen, *ibid.*, 1890, 42, 206.

[4] Jörgensen, *ibid.*, 1879, 20, 105; 1890, 42, 206.

[5] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, 31, 416; Pfeiffer and Osann, *Ber.*, 1907, 40, 4032.

[6] Pfeiffer and Basci, *ibid.*, 1905, 38, 3594.

The **oxalate**, $[Cr(NH_3)_4H_2O.Cl]C_2O_4$, separates in violet-red crystals on the addition of potassium oxalate to a solution of the chloride. It is sparingly soluble in water, and the solution gives a precipitate of calcium oxalate with calcium chloride. A freshly prepared solution of the salt in nitric acid gives no precipitate with silver nitrate. The chlorine atom in the chloro-aquo-salts is within the complex, and hence silver chloride is not at first precipitated by silver nitrate; on boiling with nitric acid and silver nitrate, however, chlorine is precipitated as silver chloride.

Bromo-aquo-tetrammino-chromic Salts, $[Cr(NH_3)_4H_2O.Br]R_2$.—These salts are similar in properties to the chloro-aquo-tetrammino-salts, and are prepared in the same manner.

Bromo-aquo-tetrammino-chromic Bromide, $[Cr(NH_3)_4H_2O.Br]Br_2$, is produced by heating dihydroxo-diaquo-dipyridino-chromic bromide with a 25 per cent. aqueous solution of ammonia and mixing the resulting solution with concentrated hydrobromic acid; it forms glistening violet rhombic prisms which are easily soluble in water. From this salt and potassium oxalate is obtained the sparingly soluble oxalate, $[Cr(NH_3)_4H_2O.Br]C_2O_4$.[1]

Bromo-aquo-tetrammino-chromic Chloride, $[Cr(NH_3)_4H_2O.Br]Cl_2$, is prepared from the bromide by dropping a solution of the salt into fuming hydrochloric acid, when a bright red crystalline powder is formed.

The **sulphate**, $[Cr(NH_3)_4(H_2O)Br]SO_4$, is also obtained from the bromide by decomposing it, in aqueous solution, with sodium sulphate and sulphuric acid. It is a red crystalline powder, easily soluble in water, and on heating the solution it decomposes into ammonia and chromic hydroxide.

Corresponding to the aquo-tetrammino-derivatives a series of compounds are known containing two molecules of ethylenediamine in place of ammonia.

Bromo-aquo-diethylenediamino-chromic Salts, $[Cr\ en_2(H_2O)Br]R_2$.—The best known member of this series is the bromide, which belongs to the "bisaquo" series.

Bromo-bisaquo-diethylenediamino-chromic Bromide, $[Cr\ en_2(H_4O_2)Br]Br_2$, is prepared from dihydroxo-diaquo-dipyridino-chromic chloride by evaporating it almost to dryness with a solution of ethylenediamine and then adding concentrated hydrobromic acid; the mixture is allowed to stand for some days at ordinary temperature, when a crystalline precipitate is formed; the product is dissolved in water and an equal volume of concentrated hydrobromic acid added. It forms beautiful violet-red crystalline leaflets which are soluble in water.[2] The aqueous solution on standing, or if warmed, changes colour, due to formation of dibisaquo-diethylenediamino-chromic bromide, and this may be reconverted into the bromo-bisaquo-salt by the addition of hydrobromic acid. On addition of pyridine to the moist salt *cis*-hydroxo-bisaquo-bromide, $[Cr\ en_2(H_4O_2)(OH)]Br_2$, is precipitated, and on evaporation with hydrobromic acid violet *cis*-dibromo-diethylenediamino-chromic bromide is formed. If, however, mercuric bromide is added to the solution before evaporation with hydrobromic acid, the green *trans*-dibromo-bromide mercuric bromide double salt,

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[1] Pfeiffer and Basci, *Ber.*, 1905, 38, 3596.
[2] Pfeiffer, *ibid.*, 1907, 40, 3828.

$[Cr\,en_2Br_2]Br.HgBr_2$, is obtained in sparingly soluble green leaflets; with mercuric iodide and hydriodic acid a similar *trans*-iodide, $[Cr\,en_2I_2]I.HgI_2$, is formed.[1]

An orange-coloured precipitate of *cis*-dithiocyanato-diethylene-diamino-chromic thiocyanate, $[Cr\,en_2(SCN)_2](SCN)$, is produced on warming an aqueous solution of the salt with potassium thiocyanate, and a sparingly soluble chromithiocyanate, $[Cr\,en_2(H_4O_2)Br]_3[Cr(SCN)_6].2H_2O$, is precipitated on mixing a freshly prepared aqueous solution of the bromide with potassium chromithiocyanate. It crystallises in violet-red transparent needles which are almost insoluble in water and decompose on exposure to light.[2]

The bromo-aquo-salts belong to the *cis*-series, as on treatment with potassium thiocyanate only *cis*-dithiocyanato-chromic thiocyanate is obtained and no *trans*-salt.[3]

Class II. (A)—*continued.*

3. *Chromi-ammines containing Monovalent Cation,* $[Cr(NH_3)_4R_2]^{\cdot}$ (R being either (OH) or an acidic group).

(*a*) Dihydroxo-diaquo-diammino-chromic Salts, $[Cr(NH_3)_2(H_2O)_2(OH)_2]R$.

These are derived from tetraquo-diammino-salts by the removal of two molecules of acid, and they revert again to the diaquo-salts on treatment with mineral acids.

Dihydroxo-diaquo-diammino-chromic Bromide, $[Cr(NH_3)_2(H_2O)_2(OH)_2]Br$, is obtained by treating dibromo-diaquo-diammino-chromic bromide in water with pyridine; the colour changes and a light violet precipitate of the dihydroxo-salt is produced. It is unstable, and loses two molecules of water at 60° C. The salt is insoluble in acetic acid but dissolves in water containing acetic acid, giving a red solution. From this solution the corresponding salts are formed by treating it with the respective alkali salts of the acids. The presence of hydroxyl groups may be proved, as it is possible to acetylate the salts by means of acetic anhydride.[4]

Dihydroxo-diaquo-diammino-chromic Chloride, $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$, is formed by the addition of ammonia or pyridine to an aqueous solution of tetraquo-diammino-chloride,[5] or saturating an aqueous acetic acid solution with rubidium chloride.[6] It forms light red violet crystals which are insoluble in water. The iodide is obtained from the bromide on addition of potassium iodide to a dilute acetic acid solution of the salt as a light red violet precipitate. The thiocyanate, $[Cr(NH_3)_2(H_2O)_2(OH)_2]SCN$, is amorphous, and is prepared from the bromide by dissolving in aqueous acetic acid and adding potassium thiocyanate.

Dihydroxo-diaquo-dipyridino-chromic Salts, $[Cr\,py_2(H_2O)_2(OH)_2]R$.—These salts, like the diammino-salts, are derived from tetraquo-dipyridino-salts by removal of acid, thus:

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[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1907, 56, 281.

[2] Pfeiffer and Stern, *Ber.*, 1907, 40, 3828.

[3] Pfeiffer, *ibid.*, 1904, 37, 4266.

[4] Werner and Dubsky, *ibid.*, 1907, 40, 4090.

[5] Werner and Klien, *ibid.*, 1902, 35, 287.

[6] Werner and Dubsky, *ibid.*, 1907, 40, 4091.

$$[\mathrm{Cr\,py_2(H_2O)_4}]\mathrm{R_3} \longrightarrow [\mathrm{Cr\,py_2(H_2O)_3(OH)}]\mathrm{R_2}+\mathrm{HR};$$
$$[\mathrm{Cr\,py_2(H_2O)_3(OH)}]\mathrm{R_2} \longrightarrow [\mathrm{Cr\,py_2(H_2O)_2(OH)_2}]\mathrm{R}+\mathrm{HR}.$$

Dihydroxo-diaquo-dipyridino-chromic Chloride, $[\mathrm{Cr\,py_2(H_2O)_2(OH)_2}]\mathrm{Cl}$, is prepared from green chromic chloride hydrate by dissolving in pyridine and mixing with water, when the impure dihydroxo-diaquo-dipyridino-chromic chloride is precipitated, collected, treated with hydrochloric acid to convert to the tetraquo-dipyridino-chloride, and re-treated with pyridine to obtain the pure salt.[1] It crystallises in small greyish-green leaflets which are sparingly soluble in water, and give a deep red colour in aqueous acetic acid. On evaporating a solution of the salt in 50 per cent. acetic acid the dihydroxo-chloride crystallises unchanged, and on addition of sodium chloride, potassium bromide, or potassium iodide to the liquid, the corresponding dihydroxo-salt crystallises out. Ammonium thiocyanate and ammonium sulphate give the thiocyanate and the sulphate of the monohydroxo-salt. Mineral acids cause formation of the tetraquo-salt.

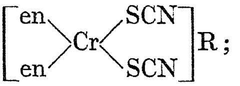
Dihydroxo - diaquo - dipyridino - chromic Sulphate, $[\mathrm{Cr\,py_2(H_2O)_2(OH)_2}]\mathrm{SO_4.15}$ or $14\mathrm{H_2O}$, is obtained by carefully treating an aqueous solution of acid tetraquo-dipyridino-sulphate with ammonia; the monohydroxo-compound is first formed and then the dihydroxo-sulphate as a fine, greyish-violet crystalline powder. It is soluble in water, giving a greyish-green solution, and mineral acids change the colour of the solution to red with formation of tetraquo-salt.[2]

All salts of the series are greyish green in colour and are easily converted into tetraquo-salts by mineral acids. The chloride is the least soluble of the series.

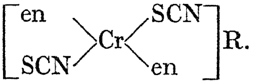
(*b*) Diacido-tetrammino-chromic Salts, $[\mathrm{Cr(NH_3)_4R_2}]\mathrm{R}$.

This series is represented by the diethylenediamino-salts, $[\mathrm{Cr\,en_2R_2}]\mathrm{R}$, which exist in two isomeric forms, the *cis*-series and the *trans*-series. The former are violet in colour, the latter green in colour.

The *cis*-salts are formed by the action of chlorine on the *cis*-dithiocyanato-chromic salts,



the *trans*-salts in an analogous manner from the *trans*-dithiocyanato-chromic salts,



The isomeric dichloro-chlorides on hydration pass into the diaquo-salts, $[\mathrm{Cr\,en_2(H_2O)_2}]\mathrm{R_3}$, and by the removal of water from these the corresponding dichloro-chlorides remain. The configuration is established by the behaviour of the salts towards potassium oxalate. The *cis*-salts react easily with potassium oxalate, giving the oxalato-derivative, $[\mathrm{Cr\,en_2C_2O_4}]\mathrm{R}$, whereas *trans*-salts are not acted upon by the oxalate. Further, the oxalato-salt formed gives, on treatment with

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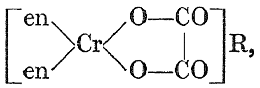
[1] Pfeiffer and Osann, *Ber.*, 1907, 40, 4032.
[2] Pfeiffer and Tapuach, *ibid.*, 1906, 39, 1875.

hydrochloric acid, only the violet salt. The oxalate on account of ring formation must have the formula



and thus the derivatives from it are the *cis*-salts.[1]

The *cis*-salts may be made to pass into the *trans*-salts. Dichloro-salts are most easily transformed, whilst the transformation of the thiocyanato-derivatives can only be accomplished indirectly. Both series of salts are remarkably stable, and an aqueous solution may be repeatedly evaporated in presence of hydrochloric acid or heated in the dry state to 160° C. without change.

If an aqueous solution of green *trans*-dichloro-chloride is left to stand for one or two days the colour changes to red, and on evaporation, after addition of acetic acid, a residue is obtained from which a considerable quantity of isomeric violet *cis*-dichloro-chloride may be obtained. The change from *cis*- into *trans*-salt is accomplished by evaporating several times an aqueous solution of the violet isomer after addition of hydrochloric acid and mercuric chloride.

On taking up the residue with water a green crystalline powder remains, which is the double salt of *trans*-dichloro-chloride, and from this the simple salt is easily obtained (see p. 105).

Indirectly the change from *trans*- into *cis*-salt may be brought about by warming *trans*-dichloro-diethylenediamino-chromic chloride with ethylenediamine; triethylenediamino-chromic chloride is produced, and this on heating to 150° C. loses one molecule of ethylenediamine, giving the violet *cis*-salt, thus :

$$[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl} \xrightarrow{\text{en}} [\mathrm{Cr\ en_3}]\mathrm{Cl_3} \xrightarrow[150^{\circ}]{\text{heat}} [\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl}.$$

Trans- (green salt). Luteo-. *Cis*- (violet salt).

Cis- and *trans*-dithiocyanato-salts are transformed one into the other through the dichloro-salts, according to the following scheme :—

$$\begin{tikzcd}
\underset{\alpha}{\textit{Trans}\text{-dithiocyanato-salt}} \arrow[r, "\mathrm{Cl_2}"] & \textit{trans}\text{-dichloro-salt,} \arrow[d] \\
\underset{\beta}{\textit{cis}\text{-dithiocyanato-salt}} & \textit{cis}\text{-dichloro-salt.} \arrow[l, "\text{KSCN}"']
\end{tikzcd}$$

$$\begin{tikzcd}
\underset{\beta}{\textit{Cis}\text{-dithiocyanato-salt}} \arrow[r, "\mathrm{Cl_2}"] & \textit{cis}\text{-dichloro-salt,} \arrow[d, "\text{en}"] \\
 & \text{triethylenediamino-chloride} \arrow[d, "\text{KSCN}"] \\
\textit{trans}\text{-thiocyanato-salt} & \text{triethylenediamino-thiocyanate.} \arrow[l, "\text{heat}"']
\end{tikzcd}$$

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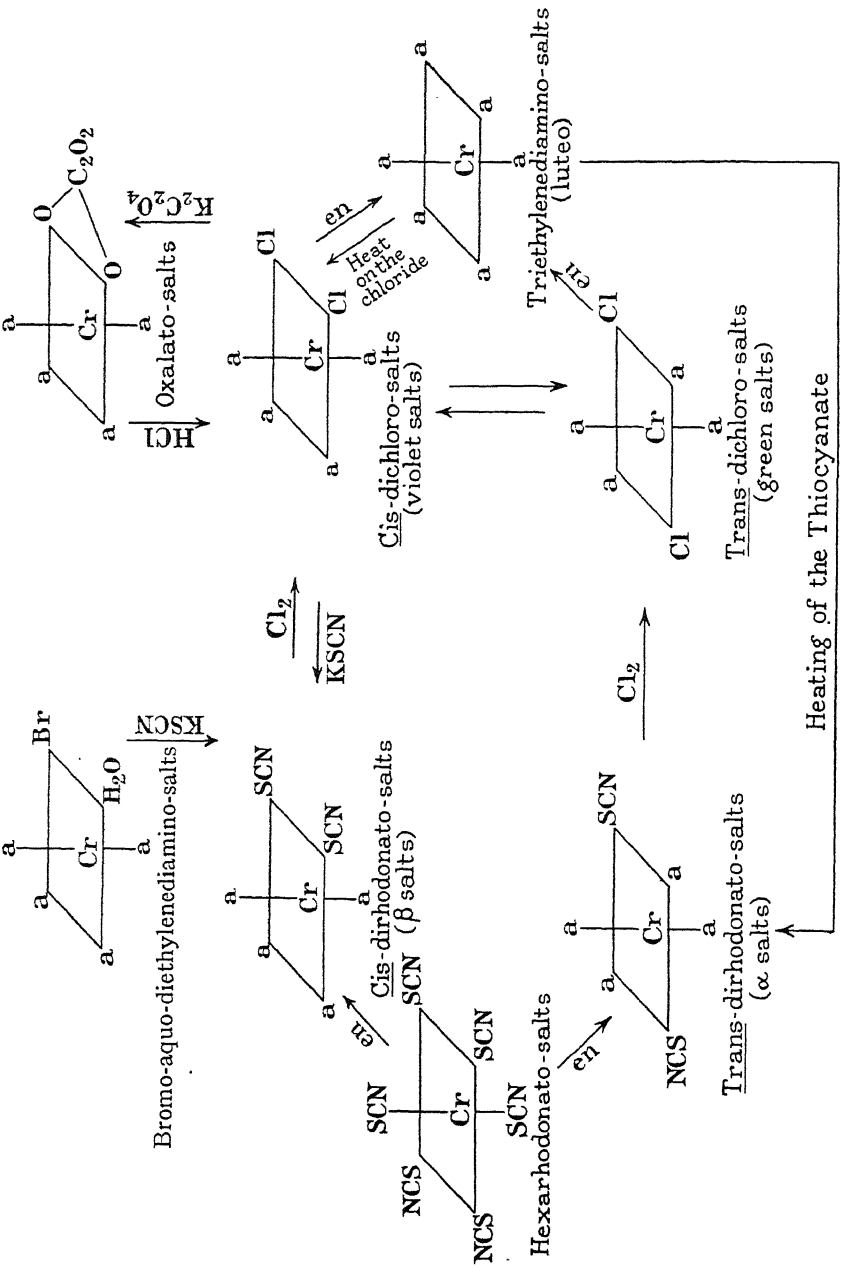
[1] Pfeiffer, *Ber.*, 1904, **37**, 4255.

The following scheme, given by Pfeiffer,[1] shows the relationship between acido-aquo-salts, oxalato-salts, and diacido-salts :—



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[1] Pfeiffer, *Ber.*, 1904, 37, 4266.

Cis-series, or 1-, 2-*salts.*

Dichloro-diethylenediamino-chromic Chloride, $[Cr\,en_2Cl_2]Cl.H_2O$, may be produced from dihydroxo-diaquo-dipyridino-chromic chloride (see p. 100) by evaporating it with a 10 per cent. aqueous solution of ethylenediamine. In a few days the dichloro-chloride is precipitated, mixed with ethylenediamine hydrochloride, which, on rubbing the mixture with 50 per cent. methyl alcohol, is dissolved away.[1] It may be formed by heating *cis*-dibisaquo-chloride to 100° C., or by evaporating the solution acidified with hydrochloric acid; or it may be prepared from potassium chromioxalate, $[Cr(C_2O_4)_3]K_3$, by heating it with ethylenediamine and decomposing the double salt, $[Cr\,en_2C_2O_4][Cr\,en(C_2O_4)_2]$, with hydrochloric acid.[2] It crystallises in red-violet needles which are soluble in water. On allowing the solution to stand, or, more quickly, on warming, it is gradually transformed into *cis*-dibisaquo-chloride, $[Cr\,en_2(H_4O_2)_2]Cl_3$. It passes into triethylenediamino-chromic chloride on heating with ethylenediamine,[3] and forms the double salt, $[Cr\,en_2C_2O_4][Cr\,en(C_2O_4)_2$, with potassium oxalate.[4]

The *bromide*, $[Cr\,en_2Cl_2]Br.H_2O$, is obtained from the chloride by adding concentrated hydrobromic acid to a concentrated aqueous solution of the *cis*-dichloro-chloride. It crystallises in violet needles which are less soluble in water than the chloride, and lose water at 100° C. without change of colour.

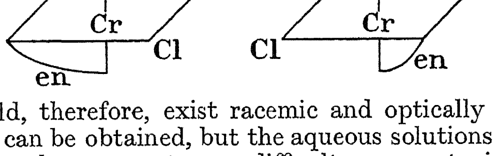
The *iodide*, $[Cr\,en_2Cl_2]I$, may be prepared from the chloride or from the sulphate by decomposition with potassium iodide.[1] It crystallises in violet needles and is the least soluble of the halogen salts.

The *nitrate*, $[Cr\,en_2Cl_2]NO_3$, is precipitated from the chloride solution, on treatment with concentrated nitric acid, in violet-red needles.

The *sulphate*, $[Cr\,en_2Cl_2]SO_4H$, is obtained by decomposing *cis*-dichloro-diethylenediamino-chromic thiocyanate with sulphuric acid, when the acid sulphate crystallises in violet needles.

The *chloroplatinate*, $[Cr\,en_2Cl_2]_2PtCl_6.12H_2O$, is a violet crystalline powder and is almost insoluble in alcohol and water.

Optical Activity in the Series.—Another type of isomerism is possible in the series, for the *cis*-dichloro-salts present a case of molecular asymmetry similar to that observed in 1-, 2-dinitro-diethylenediamino-cobalt salts. Two configurations are possible, the one being the mirror image of the other, thus:



There should, therefore, exist racemic and optically active d- and l-salts. These can be obtained, but the aqueous solutions are somewhat unstable, and on that account some difficulty was met with in resolving the racemic form. The resolution was successfully accomplished by means of the ammonium salt of optically active α-bromo-camphor sul-

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[1] Pfeiffer and Lando, *Ber.*, 1904, 37, 4278.
[2] Werner, *ibid.*, 1911, 44, 3135.
[3] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 311.
[4] Pfeiffer and Trieschmann, *Ber.*, 1904, 37, 4288; *Annalen*, 1905, 342, 285.

phonic acid, $C_{10}H_{14}OBrSO_3(NH_4)_2$, in the following manner. A freshly prepared saturated solution of racemic 1-, 2-dichloro-diethylenediamino-chromic chloride is mixed with d-ammonium α-bromo-camphor sulphonate; in a short time the sparingly soluble l-dichloro-diethylene-diamino-chromic d-bromo-camphor sulphonate separates in violet crystals. From the mother-liquor any remaining racemate may be precipitated as the dithionate, and on the addition of potassium chloroplatinite the d-isomer separates as the chloroplatinite. The nitrate is obtained from this by decomposition with silver nitrate. Similar results are obtained with l-ammonium α-bromo-camphor sulphonate, d-dichloro-diethylenediamino-chromic l-α-bromo-camphor sulphonate separating first.

The l-dichloro-d-bromo-camphor sulphonic salts are the least soluble. The colour of these optically active derivatives is the same as that of the racemic salts. l-Dichloro-diethylenediamino-chromic d-α-bromo-camphor sulphonate, $[Cr\,en_2Cl_2]SO_3C_{10}H_{14}OBr$, forms small, shining violet crystals, and has specific rotation $[\alpha]_D - 35°$, molecular $[M]_D$ rotation $-193·55°$. The corresponding d-l-salt shows specific $[\alpha]_D$ rotation of $+32°$, and a molecular rotation of $[M]_D + 176·9°$. Solutions of both isomers are rapidly racemised.

The dichloro-salts are obtained from the camphor sulphonate by the action of hydrochloric acid.

l-Dichloro-diethylenediamino-chromic d-bromo-camphor sulphonate is treated with concentrated hydrochloric acid, quickly filtered, and mixed with alcohol. On rubbing the mixture the chloride crystallises and is quickly separated from the mother-liquor. The crystalline substance is purified by dissolving in a little cold water and adding to the liquid concentrated hydrochloric acid. From this violet needles of the l-salt separate. It is easily soluble in water and has a rotation in water, $[\alpha]_D - 140°$, $[M]_D - 415·1°$.

d-Dichloro-diethylenediamino-chromic chloride has rotation of $[\alpha]_D + 140°$, $[M]_D + 415·1°$.

The optically active bromides are obtained from the chlorides by treating in aqueous solution with concentrated hydrobromic acid. They crystallise in small reddish-violet needles and are soluble in water. l-Bromide has rotation $[\alpha] - 130°$, $[M] - 419·9°$. d-Bromide has rotation $[\alpha]_D + 124°$, $[M]_D + 400·52°$.

The nitrates are prepared in the same way by treating with concentrated nitric acid. Rotation: d-Nitrate, $[\alpha] + 122°$, $[M] + 372°$; l-Nitrate, $[\alpha] - 120°$, $[M] - 366°$.

The salts are easily racemised in aqueous solution, racemisation being complete at 0° C. in a 0·5 per cent. solution after three hours. In hydrochloric acid the speed of racemisation is slower and the rotation of the chloride is less.[1] The colour of the isomers is the same as the racemic form, but the solubility of the active chloride in water is greater than that of the racemic form.

The following table shows the rotation of the chromic salts described and of the corresponding optically active dichloro-cobalt salts,[2] showing that the optical activity depends on the central atom as well as the surrounding groups in the complex.[3]

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[1] Werner, *Ber.*, 1911, 44, 3132.

[2] Werner, *ibid.*, 1911, 44, 3279.

[3] The author does not state the wave-length of the light employed.

Chloride.		Bromide.		Nitrate.	
Cr.	Co.	Cr.	Co.	Cr.	Co.
−140° +140° } [α]	−182° +184°	−130° +124°	−176° +168°	−120° +122°	−164° +164°
−415·1° +415·1° } [M]	−552·4° +558°	−419·9° +400·52°	−571° +554°	−366° +372°	−511° +511°

Trans-salts.—The *trans*-salts being symmetrical in configuration can exist only in one form.

Trans-dichloro-diethylenediamino-chromic Chloride, $[\mathrm{Cr\,en_2Cl_2}]\mathrm{Cl}$, is prepared by leading chlorine gas into an aqueous suspension of *trans*-dithiocyanato-chromic thiocyanate, the mixture being kept cool. A green crystalline compound separates consisting of the acid sulphate and *trans*-dichloro-chloride. This is transformed into the chloride by treatment with concentrated hydrochloric acid, an acid chloride being first formed.

Three chlorides have been isolated: an anhydrous form, $[\mathrm{Cr\,en_2Cl_2}]\mathrm{Cl}$; a monohydrate, $[\mathrm{Cr\,en_2Cl_2}]\mathrm{Cl.H_2O}$; and an acid chloride, $[\mathrm{Cr\,en_2Cl_2}]\mathrm{Cl.HCl.2H_2O}$. All are green in colour.[1]

The *nitrate*, $[\mathrm{Cr\,en_2Cl_2}]\mathrm{NO_3}$, is precipitated from a concentrated solution of *trans*-dichloro-chloride with concentrated nitric acid. It crystallises in greyish-green needles and is less soluble in water than the chloride.[2]

The bromide and the iodide are prepared from the chloride; the former crystallises in small green rhombic plates, the latter in greyish-green needles.

Dibromo-diethylenediamino-chromic Salts, $[\mathrm{Cr\,en_2Br_2}]\mathrm{R}$.—These, like the dichloro-salts, exist in isomeric forms, namely, violet *cis*-salts and green *trans*-salts. There should also exist, reasoning from analogy with dichloro-diethylenediamino-chromic salts, two optically active modifications corresponding to the d- and l-dichloro-compounds of the *cis*-series, but so far they have not been prepared.

Cis-salts.

Cis-dibromo-diethylenediamino-chromic Bromide, $[\mathrm{Cr\,en_2Br_2}]\mathrm{Br.H_2O}$, is obtained by evaporating a solution of bromo-bisaquo-bromide with a little hydrobromic acid on a water-bath and treating the residue, which is mainly water-free dibromide, with a small quantity of water, when it yields a finely crystalline violet powder. The anhydrous dibromide is formed as a violet powder by heating bromo-bisaquo-chromic bromide and *cis*-dibisaquo-chromic bromide to 100° to 120° C.

The substance crystallises as a fine violet powder and contains one molecule of water; it is soluble in water, forming a violet liquid, and on heating, or on allowing it to stand for some time, the solution change

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[1] Pfeiffer, *Ber.*, 1904, 37, 4283; *Zeitsch. anorg. Chem.*, 1907, 56, 293.

[2] Pfeiffer, *Ber.*, 1904, 37, 4255.

to orange-yellow with formation of *cis*-dibisaquo-bromide, $[Cr\,en_2(H_4O_2)_2]Br_3$.

The *iodide* is produced by treating an aqueous solution of the bromide with potassium iodide. It crystallises in shining violet leaflets.

The *dithionate*, $[Cr\,en_2Br_2]_2S_2O_6$, crystallises in bluish-violet needles on the addition of sodium dithionate to an aqueous solution of the bromide.

The *nitrate* is obtained by treating the bromide with concentrated nitric acid.[1]

Trans-series.

Trans-dibromo-diethylenediamino-chromic Bromide, $[Cr\,en_2Br_2]Br.H_2O$, crystallises in microscopic green plates, and is prepared by evaporating an aqueous solution of the dibisaquo-salt, $[Cr\,en_2(H_4O_2)_2Br]Br_2$, with hydrobromic acid in presence of mercuric bromide. A double salt, $[Cr\,en_2Br_2]HgBr_3$, separates as a green lustrous powder which is practically insoluble in water, and on removal of mercury by means of hydrogen sulphide a green solution of the *trans*-salt remains. On treating this with potassium bromide the simple salt is obtained.[2] With concentrated hydrobromic acid the bromide forms an acid salt, $[Cr\,en_2Br_2]Br.HBr.2H_2O$, which crystallises in transparent plates and is unstable, easily losing hydrobromic acid.

Trans-dithionate, $[Cr\,en_2Br_2]_2S_2O_6$, crystallises in lustrous, flat green needles.

The *trans*-series are green crystalline substances which are soluble in water, the iodide and the dithionate being the least soluble.

Di-iodo-diethylenediamino-chromic Salts are derived from di-iodo-diethylenediamino-chromic iodide mercuric iodide, $[Cr\,en_2I_2]I.HgI_2$, which is prepared by decomposing bromo-bisaquo-salts with hydriodic acid and mercuric iodide. It crystallises in very green leaflets, and is almost insoluble in water. The double salt is decomposed by hydrogen sulphide. The iodide is unstable, and in solution very readily decomposes.[3]

Dithiocyanato-tetrammino-chromic Salts, $[Cr(NH_3)_4(SCN)_2]R$. —This series is the only representative of the true diacido-tetrammino-salts. Attempts to prepare compounds containing chlorine or bromine instead of thiocyanate in the nucleus have been unsuccessful.

Dithiocyanato-tetrammino-chromic Thiocyanate, $[Cr(NH_3)_4(SCN)_2]SCN$, is prepared by warming an aqueous solution of chloro-aquo-tetrammino chromic chloride, $[Cr(NH_3)_4H_2O.Cl]Cl_2$, with excess of potassium thiocyanate, when dark orange-red crystals separate. The crystals are soluble in water, and by the addition of concentrated hydrochloric or hydrobromic acid the corresponding chloride or bromide is produced. These also are orange-red in colour. The nitrate is formed from the chloride by precipitation with nitric acid, and the sulphate by rubbing the chloride with sulphuric acid.[4]

Dithiocyanato-diethylenediamino-chromic Salts.—These compounds occur in two stereo-isomeric forms, namely, the *cis*- and the *trans*-salts. The *cis*-series, corresponding to the violet dichloro-salts,

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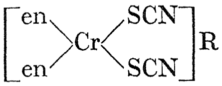
[1] Pfeiffer, *Ber.*, 1907, 40, 3837.

[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1907, 56, 285.

[3] Pfeiffer and Lando, *ibid.*, 1907, 56, 292.

[4] Werner and Halban, *Ber.*, 1906, 39, 2668; Pfeiffer and Tilgner, *Zeitsch. anorg. Chem.*, 1907, 56, 367.

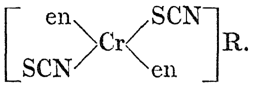
is reddish orange in colour and the *trans*-series yellowish orange. Their constitution is established by the behaviour of the compounds with chlorine. *Trans*-dithiocyanato-salts give green *trans*-dichloro-salts, and *cis*-dithiocyanato-salts, violet *cis*-dichloro-derivatives. The solubility of the series differs, the *cis*-salts being less soluble than the *trans*-salts. The configuration of the two series may be represented by the formulæ



$$\left[\begin{matrix}en & & SCN\\ & Cr & \\ en & & SCN\end{matrix}\right]R$$

1, 2-*cis*.

and



$$\left[\begin{matrix}en & & SCN\\ & Cr & \\ SCN & & en\end{matrix}\right]R.$$

1, 6-*trans*.

Cis-salts.

Dithiocyanato - diethylenediamino - chromic Thiocyanate, $[Cr\,en_2(SCN)_2]SCN$, is formed by dissolving bromo-bisaquo-diethylenediamino-chromic bromide in warm water and adding to the solution potassium thiocyanate. The mixture is filtered, and from the filtrate, on standing for some time, small brick-red crystals separate. These are purified by recrystallisation from warm water.

Dithiocyanato-diethylenediamino-chromic Chloride, $[Cr\,en_2(SCN)_2]Cl.HCl$, is prepared from the thiocyanate on treatment with concentrated hydrochloric acid, filtering off undissolved substance, and cooling the filtrate, when a crystalline powder separates. This is recrystallised from water and obtained in ruby-red glistening needles. From a solution of this salt may be precipitated the nitrate, sulphate, bromide, or dichromate by means of the corresponding acid or potassium dichromate.

The bromide separates in prismatic needles which are reddish in colour and less soluble than the chloride. The mercury double salt with mercuric iodide is produced by mixing the chloride with mercuric iodide and hydriodic acid. The salt is very sparingly soluble in water and separates as an orange-coloured powder.[1]

Trans-salts.

Dithiocyanato - diethylenediamino - chromic Thiocyanate, $[Cr\,en_2(SCN)_2]SCN.xH_2O$, is produced from triethylenediamino-chromic thiocyanate, $[Cr\,en_3](SCN)_3.H_2O$, on heating it to 130° C., when it loses a molecule of ethylenediamine and a molecule of water. The mass is extracted with water and allowed to crystallise. It crystallises in orange-yellow prisms which are soluble in alcohol, pyridine, and water, but a solution in the latter decomposes on heating. Chlorine transforms it into green *trans*-dichloro-salt.[2, 3]

The *chloride*, $[Cr\,en_2(SCN)_2]Cl.H_2O$, is formed by gently warming the thiocyanate with concentrated hydrochloric acid, filtering, and allowing the acid chloride to crystallise from the filtrate. The substance is transformed into the neutral chloride by washing repeatedly with alcohol, recrystallising from warm water, when it separates in compact orange-yellow needles.

The *sulphate*, $[Cr\,en_2(SCN)_2](SO_4H).1\frac{1}{2}H_2O$, is formed by rubbing

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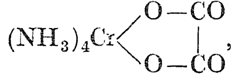
[1] Pfeiffer and Koch, *Ber.*, 1904, 37, 4274.
[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1901, 29, 107.
[3] Pfeiffer and Koch, *Ber.*, 1904, 37, 4282.

the thiocyanate with sulphuric acid. It crystallises in prisms which are soluble in water with acid reaction. The *nitrate*, $[Cr\,en_2(SCN)_2]NO_3.H_2O$, and the *bromide*, $[Cr\,en_2(SCN)_2]Br.\frac{1}{2}H_2O$, are prepared in the same manner by treating the thiocyanate with the corresponding acid. All are soluble in water, giving an orange-coloured solution. The *trans*-salts generally are more soluble in water than the *cis*-salts, and the change from *cis*- into *trans*-salt is brought about by forming triethylenediamino-chromic thiocyanate, which on heating gives the *trans*-salt.[1]

Oxalato-tetrammino-chromic Salts, $[Cr(NH_3)_4(C_2O_4)]R$.—In the oxalato-salts the oxalate radicle occupies two co-ordinate positions in the complex, so that the substances have formula  $(NH_3)_4Cr\left\langle\begin{array}{l}O-CO\\ \quad\ \ |\\ O-CO\end{array}\right.$, the oxalate group forming a ring. The compounds are derived from chloro-aquo-tetrammino-chromic chloride.

Oxalato-tetrammino-chromic Nitrate, $[Cr(NH_3)_4(C_2O_4)](NO_3).H_2O$, is prepared by dissolving chloro-aquo-tetrammino-chromic chloride in water and adding to the solution ammonium oxalate. The mixture is then heated till an orange-red liquid is obtained; it is thereafter cooled and solid potassium nitrate is added. The precipitated oxalato-nitrate is dissolved in water and reprecipitated with concentrated nitric acid. The substance forms glistening, orange-red, needle-shaped crystals which are soluble in water, and on warming with concentrated hydrochloric or hydrobromic acid yield chloro-aquo- or bromo-aquo-tetrammino-salts.

The *bromide*, $[Cr(NH_3)_4(C_2O_4)]Br.\frac{1}{2}H_2O$, and the *chloride*, $[Cr(NH_3)_4(C_2O_4)]Cl$, are obtained from the nitrate by treating with concentrated hydrobromic and hydrochloric acid respectively. They crystallise in orange-coloured leaflets. If chloro-aquo-tetrammino-chromic chloride be treated with ammonium oxalate and hydrobromic acid successively, Clève's triammino-chromium oxalate is formed and not oxalato-tetrammino-salt.[2]

The *iodide*, $[Cr(NH_3)_4(C_2O_4)]I.H_2O$, is obtained by the successive action of ammonium oxalate and potassium iodide on chloro-aquo-tetrammino-chromic chloride. It crystallises in short orange-red prisms, loses water over phosphorus pentoxide, and gradually decomposes at 100° C.[2]

The corresponding **diethylenediamino-series,** $[Cr\,en_2(C_2O_4)]X$, are of interest, as through these the *cis*- and *trans*-diacido-diethylenediamino-chromic salts are distinguished. Pfeiffer showed that only those salts with acidic groups in the *cis*-position were likely to form ring compounds when replaced by one oxalato-radicle; hence the diacido-salts formed from the oxalato-salts by treatment with halogen acids are *cis*-salts.

The series is prepared by treating blue potassium chromi-oxalate, $[Cr(C_2O_4)_3]K_3$, with aqueous 10 per cent. ethylenediamine until a red salt begins to separate from the dark violet solution. On cooling the mixture the double salt, oxalato-diethylenediamino-chromium dioxalato-ethylenediamino-chromate, $[Cr\,en_2C_2O_4][Cr\,en(C_2O_4)_2]$, is obtained in

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[1] Pfeiffer and Koch, *Ber.*, 1904, 37, 4282.

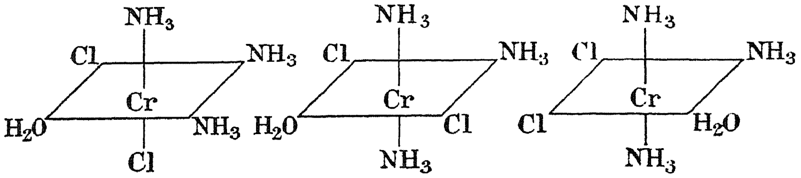
[2] Pfeiffer and Basci, *ibid.*, 1905, 38, 3598.

dark red crystals. The double compound, on treatment with concentrated hydrochloric acid, is transformed into oxalato-diethylenediamino-chromic chloride, $[Cr\,en_2(C_2O_4)]Cl.H_2O$, which is a yellowish-red crystalline body. If treated with concentrated hydrochloric acid and solid potassium iodide the iodide separates in yellowish-red needles. The bromide crystallises with one molecule of water in glistening yellowish-red leaflets. The salts are sparingly soluble in cold water, and all on warming with halogen acids yield violet *cis*-dihalogeno-salts.[1] In this respect chromium compounds are not so stable as the corresponding cobalt compounds.

(*c*) **Diacido-aquo-triammino-chromic Salts, $[Cr(NH_3)_3.H_2OR_2]R$.**

These salts are represented by the following derivatives :—

Dichloro - aquo - triammino - chromic Chloride, $[Cr(NH_3)_3H_2O.Cl_2]Cl$, forms the starting-point for the preparation of the other salts of the series. It is formed by dissolving triammino-chromium tetroxide at 0° C. in dilute hydrochloric acid, and from the red solution obtained addition of concentrated hydrochloric acid produces, on standing, reddish-violet crystals. These are soluble in water, yielding a blue solution, and are recrystallised from a concentrated aqueous solution, containing acid, by addition of alcohol and ether. The salt is stated by Riesenfeld and Seemann [2] to exist in different modifications, for if concentrated hydrochloric acid is used instead of dilute, a light green liquid is obtained from which grey needle-shaped crystals separate. This salt is scarcely soluble in cold water, but dissolves in hot water, giving a red solution. A third modification is produced by heating an acid solution of the first chloride to 60° C. The solution gradually becomes green in colour, and on evaporation in a desiccator dark green crystals separate which are soluble in water, yielding a green solution. None of the three salts lose water readily, so that it is probably in the complex. The investigators suggest that the salts are most likely stereoisomerides, for which they give the following configurations :—



It has not been possible, however, to decide which of these formulæ represents each modification.

Frowein [3] shows by conductivity measurements and by change of colour of the first isomer that the monaquo-salt gradually passes over into the diaquo-salt, and this in turn into the triaquo-salt. The colour of the solution changes from blue to reddish violet and then to red. In all three cases the change is accompanied by increase in conductivity, and the conclusion is that the compounds contain no water outside the inner sphere—that is, they are purely co-ordinated compounds.

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[1] Werner, *Annalen*, 1914, 405, 212 ; *Ber.*, 1911, 44, 3132 ; Pfeiffer and Stern, *Zeitsch. anorg. Chem.*, 1907, 56, 284 ; 1908, 58, 244.

[2] Riesenfeld and Seemann, *Ber.*, 1909, 42, 4229.

[3] Frowein, *Zeitsch. anorg. Chem.*, 1920, 110, 107.

The *nitrate*, $[Cr(NH_3)_3H_2O.Cl_2](NO_3)$, the *sulphate*, $[Cr(NH_3)_3H_2O.Cl_2]_2SO_4$, and the *iodide*, $[Cr(NH_3)_3H_2O.Cl_2]I$, are prepared from the chloride by treating it with concentrated nitric acid, concentrated sulphuric acid, or potassium iodide respectively. They are bluish-grey crystalline compounds which are soluble in water.[1]

Dibromo-aquo-triammino-chromic Salts, $[Cr(NH_3)_3H_2OBr_2]R$, are crystalline, intensely green substances which are somewhat soluble in water, giving a green liquid which soon changes to bluish red. They are assumed to belong to the *trans*-series, because they correspond completely in colour with the *trans*-dichloro- and *trans*-dibromo-diethylenediamino-chromic salts.[2]

(*d*) Diacido-diaquo-diammino-chromic Salts, $[Cr(NH_3)_2(H_2O)_2R_2]R$.

Dichloro - diaquo - diammino - chromic Chloride, $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$, is produced by passing chlorine into a 25 per cent. aqueous solution of potassium tetrathiocyanato-diammino-chromium, Reinecke's salt, $[Cr(NH_3)_2(SCN)_4]K$, and precipitating the salt with hydrochloric acid. It crystallises in light green leaflets which are soluble in water, and on treatment with silver nitrate give a deposit of silver chloride corresponding to one atom of chlorine in the molecule.[3]

The *bromide*, $[Cr(NH_3)_2(H_2O)_2Br_2]Br$, is obtained as an intensely green crystalline powder from Reinecke's salt by oxidation with bromine; from trithiocyanato-diammino-aquo-chromium, $[Cr(NH_3)_2H_2O(SCN)_3]$; or from diammino-tetraquo-chromic bromide.[4] It resembles the dichloro-derivative in reactions.

The corresponding *dipyridino-salts*, $[Cr\,py_2(H_2O)_2R_2]R$, are prepared from hydroxo-diacido-aquo-dipyridino-chromium, $[Cr\,py_2H_2O(OH)R_2]$, by treatment with acids. They are green in colour, and crystallise in green needles or leaflets.[5]

The *dibromo-bromide*, $[Cr\,py_2(H_2O)_2Br_2]Br.4H_2O$, crystallises in green plates; the *iodide*, $[Cr\,py_2(H_2O)_2Br_2]I$, in dark green short needles; and the *nitrate*, $[Cr\,py_2(H_2O)_2Br_2]NO_3.1H_2O$, in green needles.

(*e*) Diacido-tetraquo-chromic Salts, $[CrR_2(H_2O)_4]R$.

These are not ammino-derivatives, but have a complex radicle comparable with the radicle in the chromi-ammines, and are merely mentioned here to complete the scheme.[6]

Class II. (A)—*continued.*

4. *Compounds with Non-dissociable Complex Ion*, $[Cr(NH_3)_3R_3]$.

These derivatives contain in the complex three molecules of ammonia or some equivalent base, along with three monovalent acidic groups or three hydroxyl groups.

Trichloro-triammino-chromium, $[Cr(NH_3)_3Cl_3]$, is prepared

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[1] Werner, *Ber.*, 1906, 39, 2665.

[2] Werner, *ibid.*, 1910, 43, 2286.

[3] Werner and Klien, *ibid.*, 1902, 35, 289.

[4] Werner and Klien, *ibid.*, 1902, 35, 283; Werner and Dubsky, *ibid.*, 1907, 40, 4089.

[5] Pfeiffer and Tapuach, *ibid.*, 1906, 39, 1895.

[6] See this series, Vol. VII., Part III.

from triammino-chromium tetroxide, $CrO_4.3NH_3$, by dissolving in well-cooled concentrated hydrochloric acid, filtering off the greyish-green precipitate of impure trichloro-triammino-chromium and dichloro-aquo-triammino-chloride, leaving the filtrate to stand for one to two days, when an intensely blue crystalline powder separates. It is insoluble in water.[1]

The corresponding tripyridino-compound, $[Cr\,py_3Cl_3]$, has also been prepared.[2]

Trithiocyanato-triammino-chromium, $[Cr(NH_3)_3(SCN)_3]$, is formed by heating thiocyanato-pentammino-chromic thiocyanate, $[Cr(NH_3)_5SCN](SCN)_2$, at 130° to 140° C. till the odour of ammonia disappears. The residue is rubbed with water, any unchanged pentammino-salt dissolves, and treatment is continued until the filtrate is only very feebly coloured; trithiocyanato-triammino-chromium is thereby left as a light red powder. It is almost insoluble in cold water, sparingly soluble in hot water, and soluble in pyridine.[3]

Trihydroxo-aquo-diammino-chromium, $[Cr(NH_3)_2H_2O(OH)_3]$, is formed from tetraquo-diammino-chromic sulphate, $[Cr(NH_3)_2(H_2O)_4]_2(SO_4)_3$, by decomposing it in aqueous solution with excess of ammonia or pyridine. It crystallises as a violet-coloured powder, insoluble in water but easily soluble in mineral acids.[4]

The corresponding pyridino-compound, $[Cr\,py_2(H_2O)(OH)_3]$, is obtained by suspending dihydroxo-aquo-dipyridino-chromic sulphate, $[Cr\,py_2(OH)_2(H_2O)_2]_2SO_4.12H_2O$, in water and adding concentrated aqueous ammonia. The whole goes into solution, and then crystallises in pale violet leaflets which are insoluble in water and decompose on treatment with mineral acids.[5]

Class II. (A)—*continued.*

5. *Chromi-ammines containing Monovalent Anion,* $[Cr(NH_3)_2R_4]M$.

The best known of the series are the thiocyanato-compounds represented by the formula $[Cr(NH_3)_2(SCN)_4]M$, where M represents monovalent metal.

In 1861 Morland, in examining the action of ammonium thiocyanate on ammonium dichromate, obtained a thiocyanate containing ammonia, and from this Reinecke isolated the salt, $[Cr(NH_3)_2(SCN)_4]NH_4$, to which the name **Reinecke salt** was given. The free acid corresponding to this salt, $[Cr(NH_3)_2(SCN)_4]H.H_2O$, may be obtained in solution on decomposing the mercury salt, $[Cr(NH_3)_2(SCN)_4]Hg$, with hydrogen sulphide. The filtrate from the sulphide precipitate is red in colour and strongly acid, and on evaporation of the cold solution the acid is precipitated. The crude product is recrystallised from water, when it forms red glistening leaflets which decompose on heating to 80° C. It gives the potassium salt of the series on treatment with potassium hydroxide.[6]

The *ammonium salt,* $[Cr(NH_3)_2(SCN)_4]NH_4.H_2O$, is the oldest of

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[1] Werner, *Ber.*, 1910, 43, 2290.
[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1900, 24, 278; 1907, 55, 97.
[3] Werner and Halban, *Ber.*, 1906, 39, 2672.
[4] Werner and Klien, *ibid.*, 1902, 35, 289.
[5] Pfeiffer, *ibid.*, 1906, 39, 1864.
[6] Nordenskjöld, *Zeitsch. anorg. Chem.*, 1892, 1, 136.

the salts of the series. It may be formed by the method described, or by fusing chromic thiocyanate and ammonium thiocyanate and decomposing the mass with 25 per cent. aqueous ammonia. The salt crystallises from water in red, glistening, rectangular plates which are soluble in alcohol and in water and stable towards mineral acids. Prolonged treatment with water transforms it into aquo-diammino-trithiocyanato-chromium, $[Cr(NH_3)_2(H_2O)(SCN)_3]H_2O$, and with bromine it yields diaquo-diammino-dibromo-chromic bromide, $[Cr(NH_3)_2(H_2O)_2Br_2]Br$.[1] The salts of the heavy metals are red or yellowish red in colour, and many are sparingly soluble in water, notably those which form insoluble sulphides in acid solution. They are either crystalline or amorphous, and are prepared by the addition of the calculated quantity of a soluble salt of the metal to a solution of the ammonium salt. Salts of organic bases such as quinoline, ethylamine, and the alkaloids are also known. These are red crystalline bodies which are sparingly soluble in water.[2]

No aquo-salts of this series are known, and only the ammino- and pyridino-derivatives have been prepared.

The *potassium salt*, $[Cr(NH_3)_2(SCN)_4]K$, crystallises in red cubes which are easily soluble in water, and if treated with iodine in potassium iodide it forms the addition derivative, $[Cr(NH_3)_2(SCN)_4]K.I$.[3]

The *cuprous salt*, $[Cr(NH_3)_2(SCN)_4]Cu$, is precipitated from the ammonium salt by the addition of cupric sulphate and sulphur dioxide as a yellow powder.

The *cadmium salt*, $[Cr(NH_3)_2(SCN)_4]_2Cd.H_2O$, is a red, sparingly soluble, crystalline powder, and the ferric salt crystallises in golden-yellow leaflets. Double salts may also be formed; for example, the *hexammino-cobaltic salt*, $[Cr(NH_3)_2(SCN)_4]_3[Co(NH_3)_6]$, on addition of hexammino-cobaltic chloride to ammonium tetrathiocyanato-diammino-chromium, crystallises in very sparingly soluble plates. Other salts of this type have been prepared.[4]

Tetrathiocyanato-dipyridino-chromium Salts, $[Cr\,py_2(SCN)_4]M$, are obtained by heating a mixture of potassium chromithiocyanate, $[Cr(SCN)_6]K_3$, with pyridine for some time.[5]

Potassium Tetrathiocyanato-dipyridino-chromium, $[Cr\,py_2(SCN)_4]K.2H_2O$, is prepared by heating potassium chromithiocyanate with anhydrous pyridine. The melt is recrystallised from a little water, and on cooling a stable red powder separates. The thiocyanato-groups are all within the complex, and the salt in solution therefore gives no coloration with ferric chloride. It is decomposed by chlorine in presence of cold water with formation of tetraquo-dipyridino-chromic chloride. If crystallised in the dry state from pyridine it forms transparent red crystals of the addition compound, $[Cr\,py_2(SCN)_4]K.4py$, which quickly effloresce in air.

Sodium chromithiocyanate treated in the same way yields the sodium salt, $[Cr\,py_2(SCN)_4]Na.3H_2O$, and this also if crystallised from pyridine gives an addition compound, $[Cr\,py_2(SCN)_4]Na.4py$. The pyridine outside the bracket is assumed to be in combination with the alkali metal.

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[1] Werner and Klien, *Ber.*, 1902, 35, 283.

[2] Christensen, *J. prakt. Chem.*, 1892, 45, 365.

[3] Nordenskjöld, *Zeitsch. anorg. Chem.*, 1892, 1, 126; Pfeiffer, *ibid.*, 1908, 58, 439.

[4] Christensen, *J. prakt. Chem.*, 1892, 45, 213, 356.

[5] Pfeiffer and Osann, *Ber.*, 1906, 39, 2122.

Dioxalato-diammino-chromium Salts, $[Cr(NH_3)_2(C_2O_4)_2]M$.—In the investigation of dioxalato-compounds Werner [1] described two series of compounds. In the first type one oxalato-group occupies two co-ordination positions, the other one co-ordinate position, giving rise to salts of the type $[Cr(NH_3)_3(C_2O_4)_2]M$. In the second series each oxalato-group occupies two co-ordinate positions, yielding therefore salts which correspond to the tetrathiocyanato-salts just described.

Ammonium Dioxalato - diammino - chromium, $[Cr(NH_3)_2(C_2O_4)_2]NH_4.2H_2O$, is obtained in red needles by acting upon dibromo-diaquo-diammino-chromic bromide with aqueous oxalic acid at a temperature of 60° C. The colour changes in solution to dark red and the salt separates. From the ammonium salt other salts may be prepared by treating an aqueous solution with metallic halide. The potassium salt crystallises in red needles containing two molecules of water; the sodium salt crystallises in dark red prisms; the lithium salt in red needles or leaflets and the cæsium salt in dark red needles. These salts are very stable and may be recrystallised from water.

Dioxalato-ethylenediamino-chromium Salts, $[Cr\ en\ (C_2O_4)_2]M$.—This series was examined by Pfeiffer,[2] who prepared salts of this type in his examination of the properties of *cis*- and *trans*-dichloro-diethylenediamino-chromic salts, for, on heating *cis*- and *trans*-dichloro-diethylenediamino-chromic chlorides with potassium oxalate, the *cis*-salt yields red crystals of the double oxalate, $[Cr\ en_2C_2O_4][Cr\ en(C_2O_4)_2]$, whilst the *trans*-salt gives a violet double oxalate, $[Cr\ en_2Cl_2][Cr\ en(C_2O_4)_2]$. On treating the former compound with potassium iodide insoluble oxalato-diethylenediamino-chromic iodide, $[Cr\ en_2C_2O_4]I$, separates, and the soluble potassium dioxalato-ethylenediamino-chromium goes into solution and is precipitated as the double salt, $[Cr\ en(C_2O_4)_2]K.KI.2H_2O$. The same double salt may be prepared by heating a mixture of red or blue potassium chromium oxalate and 10 per cent. ethylenediamine to boiling-point, removing the precipitated by-product, and saturating the filtrate with solid potassium iodide.

By treating the product with aqueous silver nitrate at about 70° C., the potassium salt, $[Cr\ en(C_2O_4)_2]K.H_2O$, is obtained in dark red prisms. A series of salts have been prepared from the potassium salt. They are red crystalline substances, which on treatment with hydrobromic acid are converted into monoxalato-compounds, $[Cr\ enC_2O_4(H_2O)_2]Br$.[1]

Several double salts of this type exist. For example, *trans*-dichloro-diethylenediamino-chromic salt, $[Cr\ en(C_2O_4)_2][Cr\ en_2Cl_2]$, a violet crystalline powder; the oxalato-diethylenediamino-chromic salt, $[Cr\ en(C_2O_4)_2][Cr\ en_2(C_2O_4)]$, a glistening, bright red crystalline body; and *trans*-dichloro-diethylenediamino-cobaltic salt, $[Cr\ en(C_2O_4)_2][Co\ en_2Cl_2]$, which crystallises in violet leaflets.

Ammino-compounds containing **divalent anion** are unknown, and the group is only represented by such compounds as aquo-pentabromo-chromium, $[CrH_2O.Br_5]M_2$.

Class II. (B).—Polynuclear Chromi-ammines.

The number of ammines of this type is not large when compared with the mononuclear chromi-ammines.

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[1] Werner, *Annalen*, 1914, 406, 261.

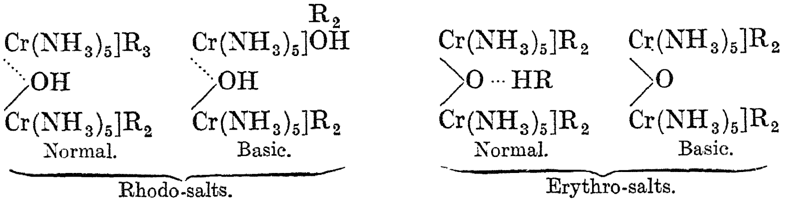
[2] Pfeiffer, *ibid.*, 1905, 342, 283.

Polynuclear metal-ammines contain several complexes in one molecule. The metallic atoms in these complexes may be linked together by a single atom, such as oxygen, or by groups, such as hydroxyl-, amino-, imino-, or nitro-groups. Such a compound is not easily broken at these linkings by ionisation or hydrolysis. These linking groups are usually referred to as "bridges," and the metallic atoms in the polynuclear compounds may be linked by one, two, three, or more such "bridges." On this account a very varied series of polynuclear metal-ammines is possible.

It is usual to divide the compounds into groups, depending on the number of bridges which are required to link together the metal atoms in the complex, thus :

1. *Polynuclear Compounds containing One Bridge.*

For example, *decammino-dichromic salts*, of formula $[(NH_3)_5Cr.OH.Cr(NH_3)_5]R_5$. The rhodo-chromic salts belong to this class of polynuclear compound. These pass by the action of ammonia into basic salts of formula $[(NH_3)_5Cr.OH.Cr(NH_3)_5]\underset{R_4}{OH}$, which latter, on loss of water, pass into another series of bridged compounds, the *decammino-oxo-dichromium salts*, of formula $[(NH_3)_5Cr.O.Cr(NH_3)_5]R_4$, the basic erythro-salts. The oxygen atom in these compounds is capable of uniting with acids, giving rise to the "normal erythro" salts or the *decammino-hydroxonium-dichromic salts*, of formula $[(NH_3)_5.Cr.\underset{\underset{R}{H}}{O}.Cr(NH_3)_5]R_4$, which are therefore isomeric with the normal rhodo-salts. Werner shows the relationship of the four types of compounds in the following manner :—



Rhodo-chromic Salts.—Jörgensen [1] in 1882 discovered this series of compounds and the isomeric erythro-chromic salts.

Rhodo-chromic Chloride, $[Cr_2(NH_3)_{10}(OH)]Cl_5.H_2O$, is prepared by mixing an air-free solution of chromous chloride with a strongly ammoniacal solution of ammonium chloride. The deep blue solution so obtained is oxidised by leading air or oxygen through it, when the colour changes to red, and red crystals of neutral rhodo-chromic chloride separate. The substance is purified by dissolving in water and precipitating the salt by the addition of hydrochloric acid. This salt forms the starting-point for the preparation of other salts of the series. It crystallises in deep red needles, which easily lose the one molecule of water of crystallisation and are soluble in water. By dissolving the substance in aqueous ammonia or sodium hydroxide the solution becomes

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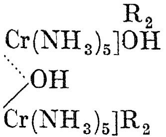
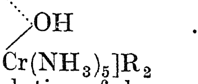
[1] Jörgensen, *J. prakt. Chem.*, 1882, 25, 321, 398.

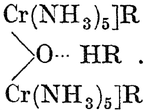
blue, and crystalline basic rhodo-chromic chloride separates on the addition of alcohol to the liquid. This reverts to the normal salt again on acidifying or on treating with ammonium chloride.

Normal rhodo-chromic salts are red crystalline bodies which are rather sparingly soluble in water, sensitive to light, and decompose on heating or on keeping.

The *bromide*, $[Cr_2(NH_3)_{10}(OH)]Br_5.H_2O$, may be obtained from the chloride by treating with hydrobromic acid or by heating erythro-chromic bromide to 100° C. The corresponding base of the series is formed in solution when the chloride is treated with moist silver oxide. A blue alkaline liquid is obtained, which soon becomes red and passes into the erythro-hydroxide.

Basic Rhodo-chromic Salts,  $\begin{array}{l} \quad\quad\quad\quad R_2 \\ Cr(NH_3)_5]OH \\ \rangle OH \\ Cr(NH_3)_5]R_2 \end{array}$.—These are blue crystalline substances which decompose on keeping and more quickly on heating to 100° C. Acid converts them into the normal salts, and the solution, which is alkaline in reaction, quickly changes colour, being transformed into the erythro-salt.

The *bromide*,  $\begin{array}{l} Cr(NH_3)_5]R_2OH \\ \rangle OH \\ Cr(NH_3)_5]R_2 \end{array}$ $.H_2O$, is prepared directly by oxidation with air of a solution of chromous bromide in ammoniacal ammonium chloride. It crystallises in dark blue octahedra, and loses one molecule of water over sulphuric acid.

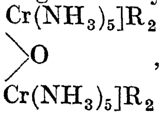
Normal Erythro-chromic Salts,  $\begin{array}{l} Cr(NH_3)_5]R \\ \rangle O \cdots HR \\ Cr(NH_3)_5]R \end{array}$.—These compounds are obtained from the rhodo-salts by dissolving them in water, adding ammonia, and allowing the solution to stand for some time, when a deep carmine solution containing basic erythro-salt is produced. From this by precipitation with nitric acid or hydrobromic acid the neutral salt is obtained.

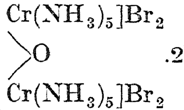
The *bromide*, $[Cr_2(NH_3)_{10}OH]Br_5.H_2O$, crystallises in carmine-red, easily soluble needles.

The *sulphate*, $[Cr_2(NH_3)_{10}OH]_2(SO_4)_5$, is almost insoluble in water, and may be prepared from the bromide by treating it with sulphuric acid and precipitating the solid with alcohol.

The salts are generally more soluble in water than the rhodo-salts, and are therefore less easily precipitated. They are carmine red in colour, and decompose on keeping or on heating to 100° C.

The aqueous solutions are acid in reaction, and yield with dilute or concentrated halogen acids the same products as the rhodo-salts. On treatment with sodium-hydroxide solution they dissolve, giving a beautiful red liquid containing basic erythro-salt.

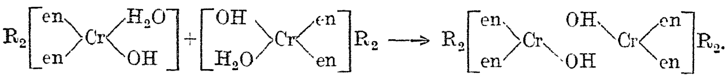
Basic Erythro-salts,  $\begin{array}{l} Cr(NH_3)_5]R_2 \\ \rangle O \\ Cr(NH_3)_5]R_2 \end{array}$, are the intermediate products in the preparation of the normal salts. They are red crystalline substances, soluble in water with neutral reaction.



The *bromide*, $\begin{matrix} Cr(NH_3)_5]Br_2 \\ \diagdown \\ >O \\ \diagup \\ Cr(NH_3)_5]Br_2 \end{matrix}$ $.2H_2O$, crystallises in violet-red crystalline leaflets which lose water over sulphuric acid and decompose at 100° C. The salts when they crystallise with water of crystallisation are isomeric with the rhodo-salts, and the oxygen atom being capable of uniting with acids gives rise to the normal erythro-salts, which thus resemble oxonium salts.

2. *Polynuclear Compounds containing Two Bridges.*

Tetraethylenediamino-diol-dichromic Salts, $[Cr_2en_4(OH)_2]R_4$.—When *cis*-hydroxo-aquo-diethylenediamino-chromic salts or the hydroxo-bisaquo-salts are heated they lose water, and form diol-chromium salts according to the equation



The acidic radicles are easily exchangeable and are ionised in solution, whilst the hydroxyl-groups are apparently within the co-ordination complex and linked to two chromium atoms. They are violet in colour, and yield reddish-violet neutral solutions. They are formed only from the *cis*-salts, hence giving a method for the determination of the configuration of this class of salts. The preparation of the diol salts may be carried out, using pyridine for the dehydration,[1] or acetic anhydride may be used, as it gives a somewhat better yield.[2]

The *bromide*, $[Cr_2\,en_4(OH)_2]Cl_4.2H_2O$, is stated by Dubsky to contain 2 molecules of water in the molecule, and by Pfeiffer 2·5 molecules. This salt is prepared by treating a dilute aqueous solution of *cis*-dibisaquo-diethylenediamino-chromic bromide with pyridine.[3] It separates in lustrous bluish-violet crystals, which are soluble in water with neutral reaction. Halogen acids transform it into the *cis*-diacido-salt; for example, with hydrochloric acid it forms dichloro-diethylenediamino-chromic chloride, $[Cr\,en_2Cl_2]Cl.H_2O$. Other salts of the series may be obtained from the bromide.

The *dithionate*, $[Cr_2en_4(OH)_2](S_2O_6)_2$, is produced by heating *cis*-hydroxo-aquo-diethylenediamino-chromic dithionate with excess of acetic anhydride for two hours.[2] From the product other salts may be prepared, such as the chloride, $[Cr_2en_4(OH)_2]Cl_4.2H_2O$, which separates in dark bluish-violet microcrystalline aggregates on treatment of the dithionate with ammonium chloride.

Octammino-diol-dichromic Salts, $[Cr_2(NH_3)_8(OH)_2]R_4$.—These salts correspond to the ethylenediamine derivatives described above, and are prepared in the same manner. Dubsky, in an attempt to ascertain the constitution of the diol salts, prepared a number of salts belonging to the series. Octammino-diol-dichromic sulphate is formed when hydroxo-aquo-tetrammino-chromic sulphate is heated with excess

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[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 278.

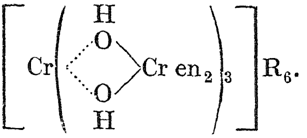
[2] Dubsky, *J. prakt. Chem.*, 1914, 90, 61.

[3] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 272.

of acetic anhydride, and from this the dithionate, $[Cr_2(NH_3)_8(OH)_2](S_2O_6)_2.4H_2O$, and the bromide are obtained in the usual way.

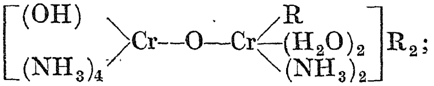
3. *Polynuclear Compounds containing Six Bridges.*

These compounds are represented by salts containing four chromium atoms in the molecule; for instance, the compound produced by replacing ethylenediamine in triethylenediamino-chromic salts by three molecules of dihydroxo-diethylenediamino-chromic salt, giving rise to the *hexaethylenediamino-hexol-tetrachromic salts*, of formula

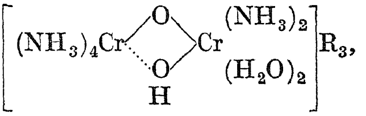


Polynuclear compounds containing other bridging groups are described under the cobalt-ammines.

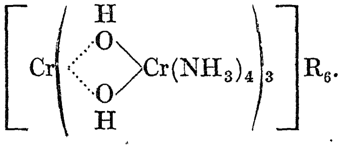
In 1892 Jörgensen[1] discovered a series of polynuclear chromic ammines which he obtained as by-products in the preparation of luteochromic salts. These he called **Rhodoso-chromic salts.** Later, in 1901, Pfeiffer[2] prepared by the same method rhodoso-chromic salts containing ethylenediamine in place of ammonia. The constitution of the rhodoso-salts is, however, still somewhat doubtful. Jörgensen gave to the compounds the constitutional formula



but this did not represent the complete properties of the salts, for all the acidic radicles appear to be ionised. Pfeiffer therefore modified the formula to



thus placing the acidic radicles outside the metallic complex. Later,[3] he modified the formula still further, and suggested that they are hexol-compounds, and should therefore be represented as



The salts are carmine-red, crystalline substances, and the aqueous solutions decompose on heating or on standing.

Rhodoso-chromic Chloride, $[Cr_2(O_4H_5)(NH_3)_6]Cl_3.H_2O$,[4] is formed

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[1] Jörgensen, *J. prakt. Chem.*, 1892, 45, 260, 274.
[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1901, 29, 107.
[3] Pfeiffer, *ibid.*, 1908, 58, 272.
[4] Using Jörgensen's formula.

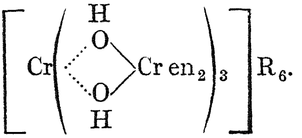
when a solution of chromous chloride, dissolved in ammoniacal ammonium chloride, is oxidised and allowed to stand for a long time until the hexammino-chromic salt is decomposed. The impure product containing ammonium chloride is decanted and washed with successive small quantities of water acidified with hydrochloric acid until free from ammonium chloride. It crystallises from water in carmine-red prisms, which lose water on standing over sulphuric acid and decompose on heating.

The *bromide*, $[Cr_2(O_4H_5)(NH_3)_6]Br_3.H_2O$,[1] is prepared from the chloride by treating with ammonium bromide.

The *sulphate*, $[Cr_2(O_4H_5)(NH_3)_6]_2(SO_4)_3.3H_2O$,[1] crystallises in short four- or six-sided prisms and is sparingly soluble in water.

The *nitrate*, $[Cr_2(O_4H_5)(NH_3)_6](NO_3)_3$,[1] crystallises in red needles and is soluble in water.

Ethylenediamino-rhodoso-chromic Salts or **Hexaethylenediamino-hexol-tetrachromic Salts,** $[Cr_4(OH)_6en_6]R_6$.—The series have properties very similar to the ammino-rhodoso-salts, and when dried at 100° C. they have the empirical formula $Cr_2O_3H_3en_3R_3$, whereas Jörgensen's compounds have the empirical formula $Cr_2O_4H_5(NH_3)_6R_3$, the difference being, therefore, one molecule of water. The formula suggested for the series by Pfeiffer shows the substances as compounds with six-bridge linkings, thus :



$$\left[\mathrm{Cr}\left(\begin{array}{c}\mathrm{H}\\ \mathrm{O}\\ \\ \mathrm{O}\\ \mathrm{H}\end{array}\mathrm{Cr\,en_2}\right)_3\right]\mathrm{R_6}.$$

They yield *cis*-dichloro-chromic chloride, $[Cr\,en_2Cl_2]Cl$, on treatment with concentrated hydrochloride, a fact which supports the suggested formula,[2] and are slightly alkaline in reaction.

Hexaethylenediamino-hexol-tetrachromic Sulphate, $[Cr_4(OH)_6en_6](SO_4)_3.10H_2O$, is prepared from partially dehydrated chromic alum. The bluish-grey powder obtained is heated with ethylenediamine monohydrate on a water-bath till a red-coloured mass is produced, which consists of a mixture of potassium sulphate, luteo-chromic sulphate, and the sulphate of the hexol compound, and from the mixture the latter compound is obtained by dissolving out the more soluble salts with water. The crude, difficultly soluble sulphate is purified by dissolving in dilute sulphuric acid and reprecipitating with excess of ammonia. It crystallises in small needles which are almost insoluble in water and soluble in dilute acids.

The *chloride*, $[Cr_4(OH)_6en_6]Cl_6.6H_2O$, is obtained from the crude sulphate by suspending it in a little water and adding drop by drop concentrated hydrochloric acid. The sulphate goes into solution, and on further addition of acid and on rubbing, the chloride is precipitated as a crystalline meal. A large excess of acid must be avoided, as the chloride is considerably soluble. The salt may be purified by dissolving in water and reprecipitating with hydrochloric acid or ammonium chloride, when it crystallises in small red needles which are soluble in water, giving a red solution. From the chloride by double decomposition the corre-

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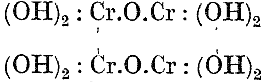
[1] Using Jörgensen's formula.

[2] Pfeiffer, *Zeitsch. anorg. Chem.*, 1908, 58, 272.

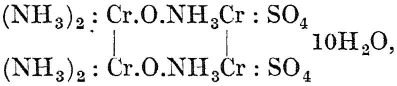
sponding *bromide*, $[Cr_4(OH)_6en_6]Br_6.4H_2O$; *iodide*, $[Cr_4(OH)_6en_6]I_6.4H_2O$; *dithionate*, $[Cr_4(OH)_6en_6](S_2O_6)_3.7H_2O$; *nitrate*, $[Cr_4(OH)_6en_6](NO_3)_6.6H_2O$, may be obtained.[1]

Among the few chromi-ammines described of unknown constitution may be mentioned the compounds prepared by Jovitschitsch [2] by dissolving chromic hydroxide in ammonia. The solution of chromic hydroxide is effected by treating the substance with just sufficient mineral acid, diluting with water, and adding an equal volume of ammonia. From the solution, substances containing hydroxyl groups, ammonia, and acidic radicles are obtained. These bodies appear to be of a complex type, and are considered to be derivatives of a hypothetical oxyhydroxide,[3]



$$\begin{array}{l}(OH)_2 : Cr.O.Cr : (OH)_2 \\ \qquad\quad | \qquad\qquad | \\ (OH)_2 : Cr.O.Cr : (OH)_2\end{array}$$

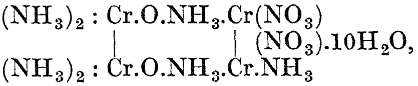
Tetrachromium Oxide-hexammino-disulphate,



$$\begin{array}{l}(NH_3)_2 : Cr.O.NH_3Cr : SO_4 \\ \qquad\qquad | \qquad\qquad | \qquad\quad 10H_2O, \\ (NH_3)_2 : Cr.O.NH_3Cr : SO_4\end{array}$$

is obtained by treating chromic hydroxide with sufficient dilute sulphuric acid to dissolve it, diluting the liquid with water and adding an equal volume of aqueous ammonia On addition of alcohol a red oil separates, which appears to be a mixture of the ammino-disulphate and ammonium sulphate. The disulphate is separated from the mixture by dissolving it in a little water and precipitating the compound by means of alcohol, when it separates as a red solid which is insoluble in water. The substance is stable in absolute alcohol, absorbs carbon dioxide from the air, and hydrolyses if left to stand with water, the acidic radicles being replaced by hydroxyl groups.

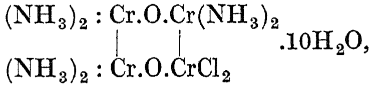
Tetrachromium Oxide-heptammino-trinitrate,



$$\begin{array}{l}(NH_3)_2 : Cr.O.NH_3.Cr(NO_3) \\ \qquad\qquad | \qquad\qquad\quad | \ (NO_3).10H_2O, \\ (NH_3)_2 : Cr.O.NH_3.Cr.NH_3\end{array}$$

is produced in the same manner as the sulphate, using nitric acid in place of sulphuric acid. It separates as a scarlet velvety powder which is soluble in water, stable in absolute alcohol, but gradually hydrolysed by water or dilute alcohol. Like the disulphate, it absorbs carbon dioxide from the air.

Tetrachromium Oxide-hexammino-dichloride,



$$\begin{array}{l}(NH_3)_2 : Cr.O.Cr(NH_3)_2 \\ \qquad\qquad | \quad\ \ | \qquad\qquad .10H_2O, \\ (NH_3)_2 : Cr.O.CrCl_2\end{array}$$

is difficult to isolate in the pure state. The method of preparation is similar to that for the above compounds, and the substance is precipitated on the addition of alcohol as a violet-red powder which is soluble in water and does not give an immediate precipitate with silver nitrate.

All three compounds yield red solutions in aqueous ammonia, and

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[1] Pfeiffer, *loc. cit.*

[2] Jovitschitsch, *Monatsh.*, 1913, 34, 225.

[3] Colson, *Ann. Chim. Phys.*, 1907, 12, 433.

on standing a violet-blue precipitate forms of diammino-chromium hydroxide, $Cr_4(OH)_6(NH_3)_2.10H_2O$.

A few chromi-ammines are described in the literature the constitution of which is not clearly understood, but the number of such compounds is small.

AMMINO-DERIVATIVES OF MOLYBDENUM SALTS.

Molybdenum forms many complex substances, but few ammino-compounds are described in the literature, and most of those described appear to be molybdates of other metal-ammines, the ammonia not being directly united with molybdenum. To this class of substancee belong the complex bodies described by Briggs[1] as ammoniacal doubls molybdates; for example, diammino-diammonium-cupric molybdate, $(NH_4)_2Cu(MoO_4)_2.2NH_3$ or $[Cu(NH_3)_2]MoO_4.(NH_4)_2MoO_4$, which is produced when aqueous ammonium molybdate is added to aqueous cupric sulphate containing concentrated ammonia. After leaving the solution in an open dish for some time bright blue crystals separate. The substance is decomposed by water and dissolves in dilute aqueous ammonia. If the liquid contains too small an amount of ammonia or is too dilute for formation of the double salt, diammino-cupric molybdate, $[Cu(NH_3)_2MoO_4.H_2O$, crystallises in deep blue prisms resembling in appearance tetrammino-cupric sulphate. This salt loses ammonia at ordinary temperature, and is soluble in dilute ammonia from which it may be crystallised.

The corresponding cadmium salt, $[Cd(NH_3)_2]MoO_4.(NH_4)_2MoO_4$, the nickel salt, $[Ni(NH_3)_2]MoO_4.(NH_4)_2MoO_4$, and the cobaltous salt, $[Co(NH_3)_2]MoO_4.(NH_4)_2MoO_4$, are formed in a similar manner.

The cadmium salt separates in colourless crystals, the nickel salt in green crystals, and the cobaltous salt in small violet crystals.

Two compounds of molybdenum chloride and ammonia are described.

Monammino-ammonium Molybdenum Dichloride, $NH_4Cl.3MoCl_2.NH_3$, is obtained by decomposing a concentrated solution of molybdenum dichloride in hydrochloric acid with ammonia, keeping the solution acid. On allowing the liquid to stand and removing ammonium chloride, the monammine crystallises in yellow needles.[2]

Decammino-dimolybdenum Triamine Trichloride, $Mo_2(NH_2)_3Cl_3.10NH_3$, is produced by keeping insoluble molybdenum trichloride in contact with liquid ammonia for some days, when the ammine forms as a brown powder which rapidly evolves ammonia on exposure to air, leaving a residue of the triamine, $Mo_2(NH_2)_3Cl_3$.[3]

AMMINO-DERIVATIVES OF TUNGSTEN SALTS.

One compound is recorded in the literature, namely, **semi-ammino-tungsten oxytetrafluoride,** $WOF_4.\frac{1}{2}(NH_3)$. The substance is orange-yellow, and is produced by passing ammonia gas over dry tungsten oxytetrafluoride in a tube until the weight of the product is constant. It is unstable, and becomes coated immediately with a white film on

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[1] Briggs, *Trans. Chem. Soc.*, 1904, 85, 675.

[2] Rosenheim and Kohn, *Zeitsch. anorg. Chem.*, 1910, 66, 5.

[3] Rosenheim and Braun, *ibid.*, 1905, 46, 311.

contact with air. It melts with formation of ammonium fluoride and hydrogen fluoride, leaving a residue of blue tungsten oxide, and on heating in ammonia explodes. It is insoluble in liquid ammonia, and dissolves in water with rise in temperature and development of a blue colour. The aqueous solution becomes cloudy on standing in the air, and yellow tungsten trioxyhydrate is gradually deposited.[1]

AMMINO-DERIVATIVES OF URANIUM SALTS.

Most of the ammines known are derivatives of uranyl salts. These substances are capable of uniting, in the dry state, with ammonia gas, yielding amorphous powders of yellow or orange colour having composition $[UO_2(NH_3)_2]R_2$, $[UO_2(NH_3)_3]R$, $[UO_2(NH_3)_4]R_2$. The tetrammino-compounds lose ammonia at ordinary temperature, passing into the triammino-compounds, which in turn lose ammonia on slight warming, forming the more stable diammines, and these on further warming decompose, yielding uranium dioxide and ammonium salt. In cold water the diammines are decomposed with precipitation of the yellow hydroxide, and on boiling the filtrate an almost colourless liquid is obtained containing a small quantity of uranium. The reaction may be represented thus :

$$[UO_2(NH_3)_2]R_2+2H_2O \longrightarrow UO_2(OH)_2+2NH_4R\,;$$
$$3[UO_2(NH_3)_2]R_2+3H_2O \longrightarrow (NH_4)_2U_2O_7+UO_2R_2+4NH_4R.$$

Liquid ammonia transforms the di- or tri-ammines into the tetrammines, the latter being capable of existence only below 5° C. Acids decompose the substances, with formation of uranyl and ammonium salts.

Diammino-uranyl Nitrate, $[UO_2(NH_3)_2](NO_3)_2$, is formed when dry gaseous ammonia is passed into a boiling solution of dry uranyl nitrate in amyl alcohol until the liquid is decolorised. A voluminous yellow precipitate is formed, which is collected and dried *in vacuo* over sulphuric acid. The product is only freed from amyl alcohol by repeated evacuation over fresh quantities of sulphuric acid. It is a yellow amorphous powder, which is insoluble in ether and amyl alcohol. If the diammine is prepared in ether the same reaction takes place, and, after evacuation over sulphuric acid, a bright yellow powder is obtained of composition $[UO_2(NH_3)_2](NO_3)_2.C_2H_{10}O$; this, on keeping *in vacuo*, gradually loses ether, yielding the diammino-nitrate.

Triammino-uranyl Nitrate, $[UO_2(NH_3)_3](NO_3)_2$, is produced from the diammino-derivative by keeping it in a closed flask with ammonia gas till the weight becomes constant, and thereafter removing the excess of ammonia *in vacuo*. It is a comparatively stable orange-yellow powder, and may be kept unaltered in a closed vessel for some time.

Tetrammino-uranyl Nitrate, $[UO_2(NH_3)_4](NO_3)_2.x(C_2H_{10}O)$, may be obtained from the diammino-uranyl ether compound by the action of liquid ammonia. It is a deep orange-red amorphous powder, which is stable below 5° C., but decomposes rapidly at ordinary temperature, yielding the triammino-derivative.[2]

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[1] Ruff, Eisner, and Heller, *Zeitsch. anorg. Chem.*, 1907, 52, 266.

[2] Gmelin and Kraut, *Handbuch der anorg. Chemie*, Band iii., SS. 1546, 1561 (Heidelberg, 1912).

Uranyl nitrate also unites with pyridine, yielding the compound $[UO_2(C_5H_5N)_3]NO_3.HNO_3$. It crystallises in bright yellow needles and is stable in air.[1]

Diammino-uranyl Chloride, $[UO_2(NH_3)_2]Cl_2$. is prepared by passing dry gaseous ammonia through an ethereal solution of uranyl chloride. A voluminous yellow precipitate separates, which on drying over sulphuric acid is obtained as a yellow powder of composition $[UO_2(NH_3)_2]Cl_2.C_2H_{10}O$. By leaving for a long time *in vacuo* the ether is removed and diammino-uranyl chloride is left. By exposing dry uranyl chloride, or the diammino-derivative, to gaseous ammonia, **triammino-uranyl chloride,** $[UO_2(NH_3)_3]Cl_2$, is produced. It is an orange-yellow amorphous powder, and is not decomposed on exposure to air, but loses ammonia on gentle heating.[2]

Tetrammino-uranyl Chloride, $[UO_2(NH_3)_4]Cl_2.C_2H_{10}O$, is obtained as a deep orange-red powder on treating the diammino-ether compound with liquid ammonia. It decomposes above 10° C. with loss of ammonia. Uranium tetrachloride in the dry state absorbs ammonia gas at ordinary temperature; rise in temperature occurs, and a compound of composition $[3U(NH_3)_4]Cl$ is produced.[3]

Diammino-uranyl Bromide, $[UO_2(NH_3)_2]Br_2$, is prepared by passing ammonia gas through a solution of uranyl bromide in amyl alcohol till the solution is decolorised and a flocculent yellow precipitate is produced; on drying *in vacuo* the substance is obtained as a yellow amorphous powder. In properties it resembles the chloride. An ether derivative, of composition $[UO_2(NH_3)_2]Cl_2.C_2H_{10}O$, is formed if ammonia is passed into an ethereal solution of uranyl bromide. **Triammino-uranyl bromide,** $[UO_2(NH_3)_3]Br_2$, and **tetrammino-uranyl bromide,** $[UO_2(NH_3)_4]Br_2$, are prepared by an analogous method to that for the preparation of the corresponding chlorides, and the properties are similar.

The iodides are also obtained by similar means. Three derivatives are known which correspond in appearance and properties to the chlorides.

The ammino-uranyl salts unite readily with ether, and many of the compounds described have not been obtained entirely free from ether, which appears to be united with the compounds in much the same manner as water of hydration in salts.[4]

Several additive compounds are known containing bases such as pyridine and quinoline; these resemble the ammino-derivatives in appearance, but are generally more stable.[5]

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[1] Pincussohn, *Beiträge zur Kenntniss der Pyridin Verh. Dissert.*, Berlin, 1897, 27; Leeds, *J. Amer. Chem. Soc.*, 1882, 3, 145, 148.

[2] Regelsberger, *Annalen*, 1885, 227, 119.

[3] Rammelsberg, *Pogg. Annalen*, 1842, 55, 77.

[4] Gmeln and Kraut, *Handbuch der anorg. Chemie*, Band iii., S. 1561 (Heidelberg, 1912).

[5] Renz, *Zeitsch. anorg. Chem.*, 1903, 36, 110.

CHAPTER X.

METAL-AMMINES OF THE ELEMENTS OF GROUP VII.

THE even series of Group VII. contains one element, manganese, the only metallic element of the group. It resembles chromium in some respects, and also iron, although the manganous salts are stable and the manganic salts unstable.

The salts of manganese unite with ammonia, forming some rather unstable ammines.

Ammino-manganous Fluoride.—Manganous fluoride is sparingly soluble in liquid ammonia, a crystalline powder being formed which is probably the sesquiammine, $[Mn_3(NH_3)_2]F_6$. It slowly evolves ammonia, and when heated to a temperature of 1200° C. in an atmosphere of ammonia the fluoride is partially reduced.[1]

Ammino-manganous Chlorides.—The anhydrous chloride absorbs ammonia gas rapidly at low temperature with formation of hexammino-manganous chloride, $[Mn(NH_3)_6]Cl_2$, a pure white body which, on thermal decomposition, loses ammonia and is converted into the diammine, $[Mn(NH_3)_2]Cl_2$. There is also evidence of the existence of a monammine.[2] All three substances are unstable and decompose on contact with water.[3]

Ammino-manganous Bromides.—Anhydrous manganous bromide absorbs ammonia gas readily with rise in temperature and increase in bulk, giving hexammino-manganous bromide, $[Mn(NH_3)_6]Br_2$, a white solid. The diammine, $[Mn(NH_3)_2]Br_2$, is produced on leaving the hexammine *in vacuo*.[4]

Ammino-manganous Iodides.—Hexammino-manganous iodide, $[Mn(NH_3)_6]I_2$, is formed when the anhydrous iodide is exposed to ammonia gas for some time, or by the action of ammonia on the iodide at low temperature. The compound loses one molecule of ammonia *in vacuo*, being converted into the pentammine, $[Mn(NH_3)_5]I_2$, and addition of ammonia to the pentammine does not take place.[5] By thermal decomposition of the hexammine, Biltz finds the only other ammine which exists is the diammine, $[Mn(NH_3)_2]I_2$.[6]

Ammino-manganous Nitrate.—One derivative is recorded having the composition $[Mn(NH_3)_9](NO_3)_2$, which is produced by treating the

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[1] Moissan and Venturi, *Compt. rend.*, 1900, 130, 1158.

[2] Rose, *Pogg. Annalen*, 1830, 20, 148.

[3] Peters, *Ber.*, 1909, 42, 4826; *Zeitsch. anorg. Chem.*, 1912, 77, 137; Biltz and Hüttig, *ibid.*, 1919, 109, 89.

[4] Ephraim, *Ber.*, 1912, 45, 1322.

[5] Peters, *ibid.*, 1909, 42, 4826; *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[6] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1919, 109, 89.

anhydrous nitrate with liquid ammonia. Colourless crystals are formed which rapidly become brown on exposure to air or light.[1]

Ammino-manganous Sulphates.—Anhydrous manganous sulphate slowly absorbs ammonia gas, increasing in volume with formation of *hexammino-manganous sulphate*, $[Mn(NH_3)_6]SO_4$. *In vacuo* it loses four molecules of ammonia and is transformed into the diammine, $[Mn(NH_3)_2]SO_4$. The latter, however, seems incapable of reabsorbing ammonia to form the hexammine.[2]

Tetrammino-manganous Sulphate, $[Mn(NH_3)_4]SO_4$, is described by Rose [3] as the compound which is formed by allowing anhydrous sulphate to absorb ammonia. The salt falls to a white powder, and if kept for some time in a closed tube it turns brownish white, and in air loses ammonia. Solution in water causes the precipitation of manganous hydroxide.

Pentammino-manganous Sulphate Monohydrate, $[Mn(NH_3)_5]SO_4.H_2O$, is produced by drying the hydrated salt at 160° C., when it slowly absorbs ammonia, increasing in volume and forming the pentammine.

Monammino-manganous Oxalate, $[Mn(NH_3)]C_2O_4.3H_2O$.—If a boiling solution of ammonium oxalate be treated with manganous oxalate till saturated and ammonia added, a white crystalline solid separates. It crystallises in microscopic quadratic prisms, loses water at 100° C., and is quickly decomposed by water.[4]

Manganous salts form addition compounds with bases such as pyridine, quinoline, hydroxylamine. These are generally more stable than the true ammines.

Dihydroxylamino-manganous Chloride, $[Mn(NH_2OH)_2]Cl_2$, may be formed by treating a hot aqueous solution of manganous chloride with hydroxylamine hydrochloride and adding a further quantity of the base in alcohol. On cooling the liquid crystals separate. The substance is white and very stable, only beginning to decompose at 150° C.[5]

Dipyridino-manganese Tetrachloride, $[Mn(C_5H_5N)_2]Cl_4$, is produced when freshly precipitated manganese dioxide is warmed with a solution of pyridine in hydrochloric acid. On filtering a dark green liquid is obtained, from which, on concentration, large light green crystals separate. The substance gives a colourless solution in water, and in air loses chlorine, and is transformed into dipyridino-manganous chloride.[6]

Dipyridino-manganous Chloride, $[Mn(C_5H_5N)_2]Cl_2$, appears to exist in two forms, one rose-coloured, the other brown. The rose-coloured variety is obtained from the manganic derivative described above by pressing it between filter-paper for several days, or it may be precipitated from a solution of manganous chloride in absolute alcohol by excess of pyridine. It may also be produced by recrystallising the brown compound from absoluet alcohol. The conductivity is the same for both forms. The brown modification is prepared from a concentrated solution of the chloride mixed with excess of pyridine. The solution turns brown and a solid is precipitated. In the dry state

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[1] Guntz and Martin, *Bull. Soc. chim.*, 1910, 7, 313.
[2] Peters, *Ber.*, 1909, 42, 4826; *Zeitsch. anorg. Chem.*, 1912, 77, 137.
[3] Rose, *Pogg. Annalen*, 1830, 20, 148.
[4] Souchay and Lenssen, *Annalen*, 1857, 102, 52.
[5] Feldt, *Ber.*, 1894, 27, 405.
[6] Reitzenstein, *Zeitsch. anorg. Chem.*, 1898, 18, 290.

the substance smells of pyridine, and loses on heating at 160° to 165° C. half a molecule of pyridine, becoming pink in colour.[1]

The corresponding *diquinolino-chloride*, $[Mn(C_9H_7N)_2]Cl_2$, is also known, as also *dianilino-manganous chloride*, $[Mn(C_6H_5NH_2)_2]Cl_2$.[2]

Manganous bromide unites with pyridine, forming the *dipyridino-derivative*, $[Mn(C_5H_5N)_2]Br_2$. It crystallises in white needles on the addition of the base to an aqueous solution of manganous bromide.[3] By precipitation from an alcoholic solution of the bromide with pyridine it crystallises in rose-coloured, short prismatic needles.[4] The compound loses pyridine on warming with water.

Hexapyridino-manganous Bromide, $[Mn(C_5H_5N)_6]Br_2$, is produced by dissolving anhydrous manganous bromide in excess of pyridine. It crystallises in glistening rhombic plates of a slightly green colour, and very easily loses pyridine.[4]

Hydroxylamino-manganous Sulphate, $[Mn(NH_2OH)]SO_4.2H_2O$, is a white powder insoluble in water.[5]

Dihydrazino-manganous Sulphate, $[Mn(N_2H_4)_2]SO_4$, is a white crystalline unstable powder.[6]

Dipyridino-manganous Nitrate, $[Mn(C_5H_5N)_2](NO_3)_2.2H_2O$, is obtained by adding pyridine to an aqueous solution of manganous nitrate and concentrating the liquid over sulphuric acid.[7]

Manganous thiocyanate forms two compounds with pyridine, **dipyridino-manganous thiocyanate**, $[Mn(C_5H_5N)_2](SCN)_2$, which is yellow, and **tetrapyridino-manganous thiocyanate**, $[Mn(C_5H_5N)_4](SCN)_2$, a colourless substance crystallising in monoclinic prisms. The tetra-derivative is unstable in air.[8]

Trihydroxylamino-manganous Carbonate, $[Mn(NH_2OH)_3]CO_3.2H_2O$, is produced as a white or grey powder when a solution of sodium carbonate and hydroxylamine hydrochloride is added to an aqueous solution of manganous chloride.[9]

Manganous salts unite with organic bases, generally with formation of di-derivatives.

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[1] Reitzenstein, *Zeitsch. anorg. Chem.*, 1898, 18, 292.

[2] Leeds, *J. Amer. Chem. Soc.*, 1888, 3, 112.

[3] Meyer and Best, *Zeitsch. anorg. Chem.*, 1899, 22, 169.

[4] Grossmann, *Ber.*, 1904, 37, 564.

[5] Feldt, *loc. cit.*

[6] Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1909, 60, 247.

[7] Grossmann, *Ber.*, 1904, 37, 1253.

[8] Grossmann, *ibid.*, 1904, 37, 559.

[9] Goldschmidt and Syngros, *Zeitsch. anorg. Chem.*, 1894, 5, 138.

CHAPTER XI.

METAL-AMMINES OF IRON, COBALT, AND NICKEL.

In Group VIII. of the periodic classification occur the triad of elements, iron, cobalt, and nickel. These elements, which resemble one another in general characteristics, form compounds containing divalent or trivalent metal, but whereas, in the simple salts, ferrous salts are relatively unstable and ferric salts stable, nickelous and cobaltous salts are much more stable than nickelic and cobaltic salts. All three elements form complex salts where the metal is united with ammonia, cyanogen, pyridine, or other groups forming a complex anion or cation. Cobalt, however, has a greater tendency to complex-ion formation with ammonia than either of the other two elements, and the number of such derivatives is very great.

AMMINO-DERIVATIVES OF IRON SALTS.

Although iron, cobalt, and nickel occur in the same triad in Group VIII., the three elements differ considerably in their ability to form addition compounds with ammonia. Iron forms few ammino-salts, most of which are unstable, and its tendency to complex-salt formation of the ammine type appears in the complex cyanides and not in the ammines themselves.

Ammino-ferrous Salts.

Hexammino-ferrous Chloride, $[Fe(NH_3)_6]Cl_2$.—Ferrous chloride absorbs six molecules of ammonia at ordinary temperature with production of a white powder, the hexammine. It readily oxidises in air, and if heated to 100° C. in an atmosphere of hydrogen loses ammonia, and is transformed into **diammino-ferrous chloride,** $[Fe(NH_3)_2]Cl_2$.[1] It is probable that the monammine, $[Fe(NH_3)]Cl_2$, also exists.[2] From a study of the tension of dissociation, the reaction of ammonia with ferrous chloride appears to be reversible between the temperatures of $-18°$ and 350° C., hexammino-ferrous chloride being stable only at low temperature.[3]

Ammino-ferrous Bromides.—Ferrous bromide readily absorbs ammonia at low temperatures with formation of *hexammino-ferrous bromide,* $[Fe(NH_3)_6]Br_2$. The substance is a white powder which, on rise of temperature, dissociates, giving the *diammine,* $[Fe(NH_3)_2]Br_2$, at

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[1] Miller, *Amer. Chem. J.*, 1895, 17, 570 ; Fowler, *Chem. News*, 1900, 82, 245.

[2] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1919, 109, 89.

[3] Girardet, *Bull. Soc. chim.*, 1910, [4], 7, 1028.

the same time darkening in colour. Finally, at more elevated temperature the *monammine*, $[Fe(NH_3)]Br_2$, is produced.[1]

Ammino-ferrous Iodides.—Only the hexammine and the diammine appear to exist. *Hexammino-ferrous iodide*, $[Fe(NH_3)_6]I_2$, is a white amorphous powder which is rapidly decomposed by water and by bromine vapour.

Ammino-ferrous Sulphate.—When hydrated ferrous sulphate is heated to 115° C. it loses six molecules of water, leaving a pale yellow substance, the monohydrate, $FeSO_4.H_2O$. This salt readily absorbs ammonia gas, becoming reddish brown in colour with formation of *pentammino-ferrous sulphate*, $[Fe(NH_3)_5]SO_4.H_2O$. *In vacuo* the pentammine loses two molecules of ammonia and is converted into the diammine, $[Fe(NH_3)_2]SO_4.H_2O$. The diammine, on exposure to more ammonia, gives a triammino-derivative, $[Fe(NH_3)_3]SO_4.H_2O$, but no further absorption of ammonia takes place.[2]

Iron salts also form addition compounds with bases such as pyridine, quinoline, and hydrazine.

Tripyridino-ferrous Chloride, $[Fe(C_5H_5N)_3]Cl_2.2H_2O$, is produced when solid ferrous chloride is mixed with pyridine. It is a yellow crystalline powder, has a strong odour of pyridine, and is easily decomposed by water, in which it is slightly soluble.[3]

It is probable that the compound described is not the tri-derivative but impure tetrapyridino-ferrous chloride, for Costăchescu and Spacu [4] claim to have isolated, in a pure state, a yellow crystalline body of composition $[Fe(C_5H_5N)_4]Cl_2$ by the interaction of ferrous chloride and excess of pyridine in an atmosphere of carbon dioxide at −15° C. The substance changes quickly on exposure to air and is decomposed by water.

Tetrapyridino-ferrous Thiocyanate, $[Fe(C_5H_5N)_4](SCN)_2$, is produced when a concentrated solution of ammonium thiocyanate is mixed with the chloride described above. It separates as a yellow powder.

Tripyridino-ferrous Sulphate, $[Fe(C_5H_5N)_3]SO_4.2H_2O$, is formed when pyridine is added to an aqueous solution of ferrous sulphate. The brownish-yellow crystals precipitated have a strong odour of pyridine and decompose easily with formation of basic salts.[3]

Dihydrazino-ferrous Chloride, $[Fe(N_2H_4)_2]Cl_2$, and **dihydrazino-ferrous oxalate,** $[Fe(N_2H_4)]C_2O_4$, have also been prepared. They are pale yellow solids.[5]

Ferric Salts.

Ammino-ferric Chloride.—Anhydrous ferric chloride forms *hexammino-ferric chloride*, $[Fe(NH_3)_6]Cl_3$, on exposure to ammonia gas. The compound loses one molecule of ammonia on keeping in a dry atmosphere at ordinary temperature, giving the pentammine, $[Fe(NH_3)_5]Cl_3$, and on heating to 100° C. the tetrammino-derivative, $[Fe(NH_3)_4]Cl_3$, is formed. Further heating causes complete dissociation with formation of ammonium chloride. The addition compounds are not deliquescent and are insoluble in water, but lose ammonia and chlorine when repeatedly washed with water.[6]

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[1] Biltz and Hüttig, *loc. cit.*

[2] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 161.

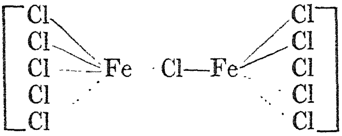
[3] Reitzenstein, *ibid.*, 1898, 18, 253.

[4] Costăchescu and Spacu, *Ann. Sci. Univ. Jassy*, 1912, 7, 132.

[5] Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1909, 60, 247.

[6] Christensen, *ibid.*, 1893, 4, 227 ; Miller, *Amer. Chem. J.*, 1895, 17, 570.

Pyridino- and Quinolino-ferric Chlorides.—A number of complex substances containing ferric chloride and the bases pyridine and quinoline have been prepared, such as pyridino-tetrachloro-ferrate, $[FeCl_4]H.C_5H_5N$; tripyridino-trichloro-hexachloro-diferrate, $[2FeCl_3].3HCl.3C_5H_5N$; tetraquinolino-μ-dichloro-octachloro-diferrate, $[Fe_2Cl_{10}]H_4(C_9H_7N)_4$. It is difficult to decide the constitution of these substances, and it is assumed that each molecule contains a complex anion containing two atoms of metal each having co-ordination number six, with one, two, or three chlorine atoms acting as bridges. Thus:



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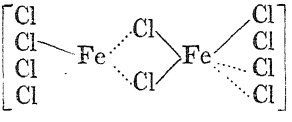

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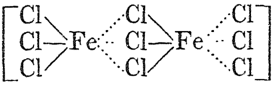

.[1]

AMMINO-DERIVATIVES OF COBALT SALTS.

As far back as 1799 Tassaert observed that an ammoniacal solution of a cobaltous salt became brown if left exposed to air, and if the solution were boiled it turned red. Thénard, in 1802, stated that this change was due to absorption of oxygen; and Proust confirmed this, as he found, on evaporation of the liquid, cobaltic oxide was left as a residue. These early observations mark the commencement of research on the action of ammonia on metallic salts. Research on the action of ammonia and air on cobaltous salts naturally led to much speculation on the structure of the compounds formed, an account of which early work and the theories put forward is given very completely by Rose.[2] An historical account of the later work on these derivatives has been given by Werner.[3] Both cobaltous salts and cobaltic salts unite with ammonia, forming addition compounds, but the cobaltous derivatives are unstable, whilst the cobaltic derivatives are mostly rather stable, bodies. The number of ammino-cobalt salts is exceedingly large; they are therefore divided into groups according to the following scheme:—

CLASS I. COBALTOUS SALT AMMINES.

These form a comparatively small and unimportant class. They are all unstable, easily lose ammonia, and in general chemical behaviour resemble the ammino-cupric salts.

CLASS II. COBALTIC SALT AMMINES. THE COBALT-AMMINES.

This class comprises a very large number of compounds and is subdivided into three groups.

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[1] Weinland and Kissling, *Zeitsch. anorg. Chem.*, 1921, 120, 209.
[2] Rose, *Untersuchungen über ammoniakalische Kobalt-Verbindungen.*
[3] Werner, *Ber.*, 1907, 40, 15.

A. Mononuclear Cobalt-ammines containing One Atom of Cobalt in the Molecule.

This group is by far the largest and contains most of the well-known cobalt-ammines. Originally the ammines were distinguished by their colour, or by the name of the investigator who first prepared them. Now they are conveniently classified in the following manner :—

1. *Cobaltic Salts with Trivalent Cation,* $[CoA_6]R_3$

(where A represents ammonia or substituted ammonia and R a monovalent acidic radicle).

(*a*) Hexammino-cobaltic salts, luteo salts, $[Co(NH_3)_6]R_3$.
(*b*) Hexahydroxylamino-cobaltic salts, $[Co(NH_2OH)_6]R_3$.
(*c*) Triethylenediamino-cobaltic salts, $[Co\ en_3]R_3$.
(*d*) Diethylenediamino-diammino-cobaltic salts, $[Co\ en_2(NH_3)_2]R_3$.
(*e*) Aquo-pentammino-cobaltic salts, $[Co(NH_3)_5H_2O]R_3$.
(*f*) Diaquo-tetrammino-cobaltic salts, $[Co(NH_3)_4(H_2O)_2]R_3$.
(*g*) Triaquo-triammino-cobaltic salts, $[Co(NH_3)_3(H_2O)_3]R_3$.

2. *Cobalt-ammines containing Divalent Cation,* $[CoA_5R]R_2$.

(*a*) Hydroxo-pentammino-cobaltic salts, $[Co(NH_3)_5OH]R_2$.
(*b*) Hydroxo - aquo - tetrammino - cobaltic salts, $[Co(NH_3)_4H_2O(OH)]R_2$.
(*c*) Acido-pentammino-cobaltic salts, $[Co(NH_3)_5R]R_2$.
(*d*) Acido-aquo-tetrammino-cobaltic salts, $[Co(NH_3)_4H_2O.R]R_2$.
(*e*) Acido-diaquo-triammino-cobaltic salts, $[Co(NH_3)_3(H_2O)_2R]R_2$.
(*f*) Acido-triaquo-diammino-cobaltic salts, $[Co(NH_3)_2(H_2O)_3R]R_2$.

3. *Cobalt-ammines containing Monovalent Cation,* $[CoA_4R_2]R$.

(*a*) Hydroxo-acido-tetrammino-cobaltic salts, $[Co(NH_3)_4R(OH)]R$.
(*b*) Diacido-tetrammino-cobaltic salts, $[Co(NH_3)_4R_2]R$.
(*c*) Diacido-diethylenediamino-cobaltic salts, $[Co\ en_2R_2]R$.
(*d*) Diacido-aquo-triammino-cobaltic salts, $[Co(NH_3)_3H_2O.R_2]R$.
(*e*) Diacido-diaquo-diammino-cobaltic salts, $[Co(NH_3)_2(H_2O)_2R_2]R$.

4. *Cobalt-ammines consisting of a Non-dissociable Complex,* $[CoA_3R_3]$.
Triacido-triammino-cobalt, $[Co(NH_3)_3R_3]$.

5. *Cobalt-ammines containing Monovalent Anion,* $[CoA_2R_4]M$.

6. *Cobalt Salts containing Trivalent Anion,* $[CoR_6]M_3$.

These are comparable with the ammines, and are mentioned here merely to illustrate the completion of the series.

B. Polynuclear Cobalt-ammines containing Two or more Cobalt Atoms in the Molecule.

1. Dicobalt-ammines.
2. Tricobalt-ammines.
3. Tetracobalt-ammines.

C. Cobalt-ammines of Unknown Constitution.

The types of compounds in the foregoing table are derivatives of simple cobaltic salts. The complex radicle inside the square bracket consists of one cobalt atom united with six monovalent groups or atoms or their equivalent, and ammonia in the complex is readily replaced by other atoms or groups. Thus, if ammonia be replaced by water, aquo-salts are formed, but it is to be noted that the exchange of ammonia for water does not change the valency of the complex as a whole. For instance, the complex, $[Co(NH_3)_6]^{\cdots}$, is trivalent, as is also the complex, $[Co(NH_3)_5(H_2O)]^{\cdots}$ or $[Co(NH_3)_4(H_2O)_2]^{\cdots}$. On the other hand, if ammonia be replaced by an acidic group or atom, the valency of the complex is diminished to the extent of the valency of the entering group or atom. Thus, $[Co(NH_3)_6]^{\cdots}$ is trivalent, $[Co(NH_3)_5Cl]^{\cdot\cdot}$ is divalent, and $[Co(NH_3)_4Cl_2]^{\cdot}$ or $[Co(NH_3)_4(NO_2)_2]^{\cdot}$ is monovalent.

As an example of this, consider the three compounds obtained from hexammino-cobaltic chloride by replacing ammonia by nitrito-groups. The same total number of acidic radicles is retained in the molecule, but the derivatives differ in electrical conductivity in equivalent solutions. The molecular conductivity of hexammino-cobaltic chloride at 25° C. and 1000 litres dilution is 431·6; of the mononitrito-derivative, $[Co(NH_3)_5(NO_2)]Cl_2$, is 246·4; of the di-derivative, $[Co(NH_3)_4(NO_2)_2]Cl$, is 98·83; and of the trinitrito-derivative, $[Co(NH_3)_3(NO_2)_3]$, is zero, this being a non-electrolyte. Further substitution transforms the complex from cation to anion thus: $[Co(NH_3)_2(NO_2)_4]K$.

As in the case of the chromi-ammines (see p. 79), isomerism arises in the cobalt-ammines through different causes.

Ionisation Metamerism.—Numerous examples of this type of isomerism occur in the cobalt-ammine series, such as the two metameric substances, chloro-nitrito-tetrammino-cobaltic chloride, $[Co(NH_3)_4Cl.NO_2]Cl$, and dichloro-tetrammino-cobaltic nitrite, $[Co(NH_3)_4Cl_2]NO_2$.[1]

Also two salts are known of molecular formula $Co(NH_3)_5Br(SO_4)$; one is reddish violet in colour, and a freshly prepared aqueous solution contains sulphate ions; the other is red in colour, and a freshly prepared aqueous solution contains bromine ions but no sulphate ions. The former substance is bromo-pentammino-cobaltic sulphate, $[Co(NH_3)_5Br]SO_4$; the latter is sulphato-pentammino-cobaltic bromide, $[Co(NH_3)_5SO_4]Br$.[2] It is interesting to note that in the second compound the sulphate radicle occupies one co-ordinate position, but it also requires two principal valencies, and thus the complex ion is monovalent.

Polymerisation Isomerism.—Many cases of this form of isomerism occur in the cobalt-ammines.

For example, dodeca-ammino-hexol-tetracobaltic salts are polymers of hexammino-triol-dicobaltic salts. The former have molecular formula $Co_4(NH_3)_{12}(OH)_6R_6$, and the latter, $Co_2(NH)_6(OH)_3R_3$. Represented by constitutional formulæ the two substances are:

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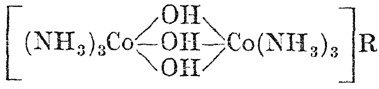
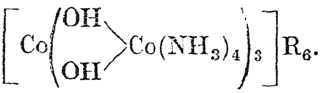
[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 7, 290; Werner and Klien, *ibid.*, 1897, 14, 35.

[2] Jörgensen, *J. prakt. Chem.*, 1885, 31, 270; 1879, 19, 63.



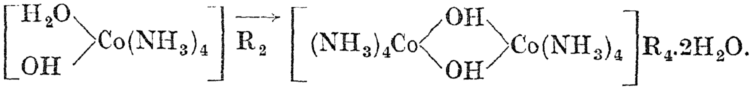
$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]R_3$$

and



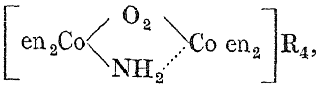
$$\left[Co\left(\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right)_3\right]R_6.$$

Also the hydroxo-aquo-tetrammino-cobaltic salts polymerise to the octammino-diol-dicobaltic salts thus :



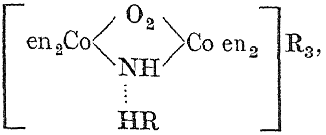
$$\left[\begin{matrix}H_2O\\OH\end{matrix}Co(NH_3)_4\right]R_2 \longrightarrow \left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]R_4.2H_2O.$$

Valency Isomerism.—This type of isomerism is possible in the dicobalt-ammines, depending on the position of the subsidiary valence ; that is, whether a bridging group is linked to both cobalt atoms by principal valencies or by one principal and one subsidiary valence. Tetraethylenediamino-μ-amino-peroxo-dicobaltic salts,



$$\left[en_2Co\begin{matrix}O_2\\NH_2\end{matrix}Co\ en_2\right]R_4,$$

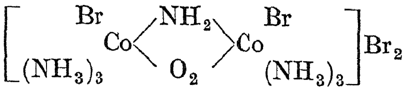
and tetraethylenediamino-μ-ammonium-peroxo-dicobaltic salts,



$$\left[en_2Co\begin{matrix}O_2\\NH\\\vdots\\HR\end{matrix}Co\ en_2\right]R_3,$$

are examples of valency isomerism. The two isomeric series of salts differ in colour, the former being green and the latter red. Also, the first class of compounds are neutral in reaction whilst the second are acidic.[1]

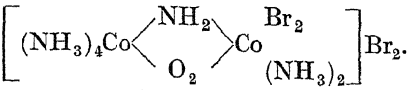
Co-ordination Position Isomerism.—Here the isomerism occurs through the arrangement of the groups around each cobalt atom with respect to the bridged linkage. For example, there are two dibromo-hexammino-amino-peroxo-dicobaltic bromides which are represented thus :



$$\left[\begin{matrix}Br\\(NH_3)_3\end{matrix}Co\begin{matrix}NH_2\\O_2\end{matrix}Co\begin{matrix}Br\\(NH_3)_3\end{matrix}\right]Br_2$$

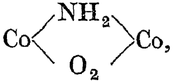
Symmetrical.

and



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\O_2\end{matrix}Co\begin{matrix}Br_2\\(NH_3)_2\end{matrix}\right]Br_2.$$

Asymmetrical.

The corresponding chlorides may be obtained in symmetrical and asymmetrical forms also. These isomers have the same nucleus,  $Co\begin{matrix}NH_2\\O_2\end{matrix}Co$, and the difference lies in the disposition of the ammonia molecules and the acidic radicles in the complex. Both the symmetrical and the asymmetrical salts are intensely green in colour, but they differ in chemical reactions.[1]

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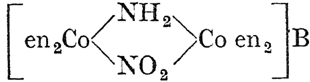
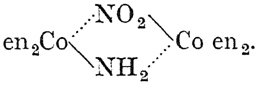
[1] Werner, *Annalen*, 1910, 375, 1.

Isomerism due to Asymmetric Cobalt Atoms.—As has been mentioned already, Werner further established his formulæ for the cobalt-ammines by proving the fact suggested by the theory that certain of the cobalt atoms were centres of asymmetry and therefore should be capable of existing in different optically active forms. He established this for some of the simple cobalt-ammines, and further showed that in many of the polynuclear compounds optical activity exists. For instance, tetraethylenediamino-μ-amino-nitro-dicobaltic bromide,  $\left[en_2Co \begin{matrix} NH_2 \\ NO_2 \end{matrix} Co\ en_2 \right] Br_4$, may be obtained in four isomeric forms, namely, the *dextro-rotatory* and the *lævo-rotatory* forms, with equal and opposite rotation of $\alpha \pm 164$; the *racemic* form, made up of equal quantities of *d*- and *l*-forms; and a modification which could not be resolved by any means, namely, the *meso*-form, which is inactive by internal compensation. These isomers may be regarded as the cobalt analogues of the isomeric tartaric acids.[1]

Prior to this resolution, Werner indicated that the compound mentioned, and similar compounds with two cobalt atoms joined by bridged linkages, contained two different kinds of valency bonds thus:



$$en_2Co \begin{matrix} NO_2 \\ NH_2 \end{matrix} Co\ en_2.$$

The optical investigation described does not indicate any such difference, and by this and other observations it seems likely that there is no essential difference between principal and auxiliary valency.

CLASS I.—COBALTOUS SALT AMMINES.

The ammonia addition compounds of cobaltous salts are unstable, and on that account there is no long series of these salts as in the case of the ammino-cobaltic salts, where ammonia groups may be partially replaced by acidic groups, water, and other molecules, and where the complex is sufficiently stable to allow of different salts being prepared by double decomposition.

These cobaltous addition compounds, therefore, resemble the preceding group of additive substances rather than the cobaltic salts, and the series illustrate the statement previously made that the most highly saturated compounds of an element have greater capacity for the formation of complex addition compounds. In this connection, for example, one might compare the relative instability of hexammino-cobaltous chloride, $[Co(NH_3)_6]Cl_2$, with the high stability of the ammine of the more saturated cobaltic chloride, hexammino-cobaltic chloride, $[Co(NH_3)_6]Cl_3$.[2]

Hexammino-cobaltous Nitrate, $[Co(NH_3)_6](NO_3)_2.2H_2O$, is formed by passing ammonia gas into an aqueous solution of cobaltous nitrate in absence of air. The precipitate of basic nitrate first formed dissolves in excess of ammonia, and a red solution is obtained from which are precipitated bright red crystals of the hexammine. These

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[1] Werner, *Ber.*, 1913, 46, 3674.

[2] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137; Briggs, *Trans. Chem. Soc.*, 1917, 113, 253.

are collected on a filter, washed quickly with water containing ammonia, pressed between filter-paper and dried *in vacuo*.

The salt is stable in dry air, crystallises in rose-red cubes, and is decomposed on treatment with water yielding ammonia and basic salt.

Hexammino-cobaltous Sulphate, $[Co(NH_3)_6]SO_4$.—Anhydrous cobaltous sulphate rapidly absorbs dry ammonia gas, heat is developed, increase in volume takes place, and the salt becomes pale red in colour with formation of the hexammine, which is soluble in water with decomposition. On heating, the compound melts easily, and becomes blue in colour with elimination of ammonia. The same substance is formed if ammonia gas is passed into a concentrated aqueous solution of cobaltous sulphate in absence of air. The compound, being soluble in excess of ammonia, is precipitated from solution by the addition of alcohol. The corresponding hydrazine compound, **trihydrazino-cobaltous sulphate,** $[Co(N_2H_4)_3]SO_4.H_2O$, is prepared from aquo-pentammino-cobaltic sulphate, $[Co(NH_3)_5H_2O]_2(SO_4)_3$, by dissolving it in water and treating the cold solution with 50 per cent. hydrazine hydrate. A precipitate of the hydrazino-cobaltous salt is formed, and this is filtered, washed with water, alcohol, and ether, and dried *in vacuo* over sulphuric acid. The compound is a brownish-yellow powder which is insoluble in water but decomposed by boiling water. It is also soluble in dilute sulphuric acid and in dilute aqueous ammonia.[1]

Hydroxylamino-cobaltous Sulphate, $[Co(NH_2OH)]SO_4.2H_2O$, is also known, and is obtained by mixing an aqueous solution of cobaltous sulphate with hydroxylamine in absence of air. It is insoluble in cold water, dissolves in hot water, but readily decomposes, due to oxidation.

Cobaltous chloride unites with ammonia, forming three ammino-derivatives, viz.:

Diammino-cobaltous Chloride, $[Co(NH_3)_2]Cl_2$, is formed when ammonia gas is led slowly into a cold solution of cobaltous chloride in acetone,[2] or from hexammino-derivative by heating it to 120° C.

It is a light blue powder, which becomes red on exposure to moist air or on solution in water.

Tetrammino-cobaltous Chloride, $[Co(NH_3)_4]Cl_2$, is produced if ammonia gas is passed over anhydrous cobaltous chloride. Ammonia is rapidly absorbed, increase in volume takes place, and a reddish-white powder is formed. This decomposes on heating with evolution of ammonia, leaving a residue of cobalt oxide.

Hexammino-cobaltous Chloride, $[Co(NH_3)_6]Cl_2$, is the most stable of the three ammines of cobaltous chloride and may be prepared in aqueous solution. If ammonia gas be passed into a concentrated aqueous solution of cobaltous chloride the greenish precipitate at first formed dissolves in excess of ammonia in absence of air, giving a red solution. From the liquid, on standing, pale red octahedral crystals of pentammino-cobaltous chloride separate. The crystals are stable in absence of air but lose ammonia if kept over sulphuric acid. On heating to 120° C. the substance loses four molecules of ammonia and is transformed into diammino-cobaltous chloride. It is soluble in aqueous ammonia without decomposition and insoluble in alcohol. With platinous chloride it forms a double salt, $[Co(NH_3)_6]PtCl_4$.[3] Cobaltous

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[1] Franzen and Mayer, *Ber.*, 1906, 39, 3379.

[2] Naumann, *ibid.*, 1904, 37, 4334.

[3] Kournakoff, *Zeitsch. anorg. Chem.*, 1898, 17, 210.

chloride also forms addition compounds with hydroxylamine, such as dihydroxylamino-cobaltous chloride, $[Co(NH_2OH)_2]Cl_2$. This derivative is produced when cobaltous chloride is mixed with alcohol in an atmosphere of hydrogen and an excess of hydroxylamine hydrochloride in alcohol is added; on warming, rose-red crystalline needles separate. The compound may be kept out of contact with air, but on exposure to the atmosphere it decomposes with evolution of nitrous acid, and on heating it decomposes with loss of ammonia and formation of ammonium chloride.[1]

Cobaltous bromide and cobaltous iodide in the solid state absorb ammonia with formation of **hexammino-cobaltous bromide,** $[Co(NH_3)_6]Br_2$, and **hexammino-cobaltous iodide,** $[Co(NH_3)_6]I_2$, respectively. The compounds are unstable, and rapidly lose ammonia on heating and decompose on solution in water. **Tetrammino-cobaltous iodide,** $[Co(NH_3)_4]I_2$, is also known. It may be prepared by treating a concentrated solution of cobaltous iodide with ammonia; a pale red precipitate is formed, which gradually dissolves on warming, giving a violet-coloured liquid from which small rose-red crystals of the tetrammine separate. It also is unstable, and decomposes on heating or on standing in air with loss of ammonia and formation of cobalt oxide. In aqueous solution it turns brown, ammonia is evolved, and a precipitate of cobaltous oxyiodide separates.

CLASS II.—COBALTIC SALT AMMINES. THE COBALT-AMMINES.

A. Mononuclear Cobalt-ammines containing One Atom of Cobalt in the Molecule.

1. COBALTIC SALTS WITH TRIVALENT CATION, $[CoA_6]^{\cdots}$.

(a) *Hexammino-cobaltic Salts, Luteo-cobaltic Salts,* $[Co(NH_3)_6]R_3$.

These salts are formed from dilute ammoniacal solutions of cobaltous salts in air, or by heating aquo-pentammino-salts with ammonia. Frequently they are obtained as decomposition products of acidopentammino-salts. They may be obtained directly from the corresponding cobaltous salt by heating with excess of ammonia and ammonium chloride,[2] or from the corresponding ammonium salt by addition of lead peroxide to the aqueous solution.

The hexammino-salts are yellow or brownish compounds, easily crystallised and fairly stable. They withstand the action of boiling water for some time, and can therefore be crystallised from aqueous solution if crystallisation be carried out quickly. Acid solutions of the salts are very stable, but alkaline and neutral solutions are decomposed on heating. The salts are more soluble than the corresponding aquo-pentammino-salts, and their solutions are brownish yellow in colour. The hydrated salts effloresce in air and become opaque and reddish brown in colour. On heating they lose ammonia, leaving cobaltic oxide and a cobaltous salt. In cold solution they give no precipitate with sodium hydroxide, ammonium hydroxide, or alkali

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[1] Feldt, *Ber.*, 1894, 27, 401.

[2] Klobb, *Bull. Soc. chim.*, 1901, [3], 25, 1022.

phosphate or carbonate. Ammonium sulphide, however, precipitates cobalt sulphide, and chloroplatinic acid gives a yellow crystalline precipitate.

Hexammino-cobaltic Hydroxide, or Luteo-cobaltic Hydroxide, $[Co(NH_3)_6](OH)_3$, the parent substance from which the hexammino-salts are derived, is obtained in aqueous solution by treating the corresponding sulphate, $[Co(NH_3)_6]_2(SO_4)_3.5H_2O$, with baryta water,

$$[Co(NH_3)_6]_2(SO_4)_3+3Ba(OH)_2 \longrightarrow 2[Co(NH_3)_6](OH)_3+3BaSO_4.$$

The solution obtained, after removal of insoluble barium sulphate, is yellow, strongly alkaline, and decomposes on heating with loss of ammonia. It readily absorbs carbon dioxide, forming a soluble carbonate.

Hexammino - cobaltic Chloride, or Luteo-cobaltic Chloride, $[Co(NH_3)_6]Cl_3$.—Several methods of preparation have been described. The best method is that of Jörgensen,[1] whereby the salt is prepared by warming chloro-pentammino-cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, in a pressure flask with 20 per cent. aqueous ammonia and ammonium chloride for several hours with constant shaking. After cooling, the mixture is removed from the flask and ammonia allowed to evaporate. The liquid is then diluted, hydrochloric acid added, and the whole heated on the water-bath, thus changing any aquo-pentammino-chloride into chloro-pentammino-chloride. More concentrated hydrochloric acid is added and the mixture cooled and filtered. The residue on the filter consists of ammonium chloride, chloro-pentammino-chloride, and hexammino-cobaltic chloride. Ammonium chloride is removed by treating with a 20 per cent. solution of hydrochloric acid, and the residue is then treated on a filter with cold water in which chloro-pentammino-cobaltic chloride is insoluble and hexammino-cobaltic chloride soluble. The salt is precipitated from its warm solution by the addition of half its volume of concentrated hydrochloric acid.

The salt forms brownish-orange to red crystals belonging to the monoclinic system. It is very stable towards hydrochloric acid and towards heat, and may be heated to 100° C. and even higher without decomposition. On prolonged heating with water it loses ammonia, and leaves a residue of cobaltous hydroxide. It readily forms double salts, such as the mercuric-chloride double salt, $[Co(NH_3)_6]Cl_3.HgCl_2$, an orange-coloured compound, and it reacts with chloroplatinic acid, yielding a yellow-brown crystalline body, $[Co(NH_3)_6]_2(PtCl_6)_3.6H_2O$. This salt crystallises in short, six-sided prisms.

Hexammino-cobaltic Bromide, $[Co(NH_3)_6]Br_3$, is obtained from the chloride by precipitating the solution with aqueous potassium bromide, or better, by saturating a solution of hexammino-cobaltic hydroxide with hydrogen bromide. The precipitate formed is recrystallised from water and obtained in glistening rhombic plates.

Hexammino-cobaltic Iodide, $[Co(NH_3)_6]I_3$, is produced by the method described above, using hydrogen iodide. It is a dark orange-coloured body, less soluble in water than the bromide, being almost insoluble in cold water and only sparingly soluble in hot.

Hexammino-cobaltic Fluoride, $[Co(NH_3)_6]F_3$, is also known. It forms yellow prismatic crystals.

Hexammino-cobaltic Nitrate, $[Co(NH_3)_6](NO_3)_3$.—The salt is formed by air oxidation of an ammoniacal solution of cobaltous nitrate,

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1898, 17, 455.

or from the corresponding sulphate by treating an aqueous solution with barium nitrate, or by treating a solution of hexammino-cobaltic chloride with dilute nitric acid. The nitrate is precipitated, filtered, and washed first with dilute nitric acid and then with 90 per cent. alcohol. It crystallises in mosaic gold plates or orange-yellow needles, is soluble in water, one part dissolving in sixty parts of water at ordinary temperature, and is almost insoluble in acids. It readily forms an acid nitrate, $[Co(NH_3)_6](NO_3)_3.HNO_3$, and if a 1 per cent. solution of the normal salt is treated with excess of concentrated nitric acid and allowed to stand for some time, fine orange-yellow needles of the acid salt are precipitated.

Hexammino-cobaltic Sulphate, $[Co(NH_3)_6]_2(SO_4)_3.5H_2O$.—This is best prepared from hexammino-cobaltic chloride. A solution of the chloride in hot water is mixed with dilute sulphuric acid and heated to 60° C., alcohol is then added, the mixture kept heated for a short time and allowed to cool slowly. After standing for a day the precipitate formed is filtered, washed with 75 per cent. alcohol, dissolved in warm dilute sulphuric acid, and on cooling, the pure acid sulphate, $[Co(NH_3)_6](SO_4)_2H$, is deposited and converted into the normal salt by dissolving in water and precipitating with alcohol. The salt crystallises in monoclinic prisms which are somewhat sparingly soluble in cold but readily soluble in hot water. Sulphuric acid does not precipitate the salt from solution, and hydrochloric and nitric acids precipitate mixtures of the sulphate with the chloride or the nitrate. The salt loses four molecules of water at 100° C., and further heating decomposes it with formation of an unstable sulphato-sulphate, ammonium sulphate, cobaltous sulphate, and some unchanged salt.

Hexammino-cobaltic Carbonate, $[Co(NH_3)_6]_2(CO_3)_3.7H_2O$, is likewise prepared from the chloride by treating an aqueous solution with silver carbonate. It crystallises from hot water in yellowish-brown rhombic crystals containing seven molecules of water. The water of hydration is lost on exposure to dry air and the compound becomes opaque and powdery.

(b) *Hexahydroxylamino-cobaltic Salts,* $[Co(NH_2OH)_6]R_3$.

Several salts are known belonging to the hexammino-series, where hydroxylamine takes the place of ammonia. Feldt [1] prepared the first compound of the series, and the exact constitution of the series was worked out by Werner and Berl.[2]

Hexahydroxylamino-cobaltic Chloride, $[Co(NH_2OH)_6]Cl_3$, is produced when an alcoholic solution of cobaltous chloride is mixed with hydroxylamine and saturated with oxygen in a closed flask until there is no further change in colour. An unstable precipitate of composition $CoOCl.2NH_2OH$, is formed, and is suspended in alcohol and cooled in a freezing mixture. Alcohol, saturated with hydrogen chloride, is then added until the solid dissolves, the solution allowed to stand several hours, and the precipitated hexahydroxylamino-cobaltic chloride collected, washed with alcohol, and recrystallised from dilute hydrochloric acid. It crystallises in golden-yellow leaflets which are stable towards hydrochloric acid, darken on exposure to light, and decompose on boiling with acetic anhydride, giving cobaltous chloride.

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[1] Feldt, *Ber.*, 1894, 27, 404.

[2] Werner and Berl, *ibid.*, 1905, 38, 895.

Hexahydroxylamino-cobaltic Nitrate, $[Co(NH_2OH)_6](NO_3)_3$, is prepared from the chloride by treating a concentrated solution with nitric acid, free from nitric oxide, at a low temperature. The solid which separates is drained on a filter, washed with acid, and reprecipitated three times. It crystallises in long needle-shaped crystals of a golden-yellow colour. As it may decompose explosively into cobaltous salt, it should be handled carefully and must not be washed with alcohol.

The corresponding **sulphate,** $[Co(NH_2OH)_6]_2(SO_4)_3.2H_2O$, is also known.

(c) *Triethylenediamino-cobaltic Salts,* $[Co\ en_3]R_3$.

Ethylenediamine may replace all or part of the ammonia in the hexammino-salts, giving rise to the triethylenediamino-cobaltic salts or the diethylenediamino-diammino-cobaltic salts. The first of this series was described by Jörgensen in 1889, and later Werner, Grossmann, Pfeiffer, and others prepared a complete series of these salts.

Triethylenediamino-cobaltic Hydroxide, $[Co\ en_3](OH)_3$, is the parent base of the series, and is prepared from the chloride, $[Co\ en_3]Cl_3$, by shaking it with freshly precipitated silver oxide. An orange-coloured solution is thus obtained which has a strongly alkaline reaction, and is capable of removing ammonia from ammonium salts and absorbing carbon dioxide from the air. On concentrating the liquid over sulphuric acid a dark yellow crystalline mass is obtained, which deliquesces in air and always contains carbonate. It gives, however, the corresponding salts on neutralising with acids, and is therefore the impure hydroxide.[1]

Triethylenediamino - cobaltic Chloride, $[Co\ en_3]Cl_3.3H_2O$, is formed from chloro-pentammino-cobaltic chloride by mixing it with water, adding ethylenediamine, and heating the mixture until the liquid has acquired a deep orange colour and a drop gives on the addition of alcohol a yellow precipitate. It crystallises in glistening yellow-brown prisms which are easily soluble in water. It is not readily decomposed, and may be heated with 6 per cent. sodium-hydroxide solution without decomposition. Nitrous acid does not act upon it,[2] and ammonium sulphide gives no immediate precipitate. The behaviour of the ethylenediamino-series of salts resembles that of the hexammino-salts, and compounds exist where both ammonia and ethylenediamine are present in the complex.

(d) *Diethylenediamino-diammino-cobaltic Salts,* $[Co\ en_2(NH_3)_2]R_3$.

This series of salts exists in two isomeric forms, namely, *cis*-salts and *trans*-salts.

Cis-salts.

The members of the *cis*-series are characterised by the sparing solubility of the salts in water. They are formed by the interaction of di-iso-thiocyanato-diethylenediamino-cobaltic salts with chlorine. The configuration of the series is derived from their relationship, through the di-iso-thiocyanato-diethylenediamino-salts, with the 1, 2-dichloro-diethylenediamino-cobaltic salts, the violeo-salts.

Cis-diethylenediamino-diammino-cobaltic Chloride, $[Co\ en_2(NH_3)_2]Cl_3.H_2O$, is prepared by the action of chlorine on di-iso-thio-

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[1] Jörgensen, *J. prakt. Chem.*, 1889, 39, 8.

[2] Grossmann and Shück, *Ber.*, 1906, 39, 1899.

cyanato-diethylenediamino-cobaltic chloride in cold aqueous solution. It crystallises in long yellow asymmetric prisms or in thin needles. From the aqueous solution other salts may be produced by the addition of acids.

The **bromide,** $[Co\ en_2(NH_3)_2]Br_3$, crystallises in long flat prisms, the **iodide** as an amorphous, brownish-yellow powder, and the **thiocyanate** in orange-coloured crystals.

Trans-salts.

The *trans*-salts are readily soluble in water, and are prepared by the action of concentrated aqueous ammonia or liquid ammonia on dinitrato-diethylenediamino-cobaltic salts.

Trans-diethylenediamino-diammino-cobaltic Nitrate, $[Co\ en_2(NH_3)_2](NO_3)_3$, is formed when 1-, 2-dinitrito-diethylenediamino-cobaltic nitrate, $[Co\ en_2(NO_2)_2]NO_3$, is heated with nitric acid. It is first converted into the dinitrato-salt, which separates in dark red triclinic crystals. This then reacts with liquid ammonia, forming diethylenediamino-diammino-cobaltic nitrate together with a small quantity of the *cis*-salt. The nitrate forms a red viscid syrup which is soluble in water and on the addition of potassium iodide yields the **iodide,** which separates from hot water in small orange-yellow crystals or refractive rhombic plates.

The **bromide,** $[Co\ en_2(NH_3)_2]Br_3$, is prepared from the iodide by the action of silver nitrate and hydrobromic acid.[1]

(e) *Aquo-pentammino-cobaltic Salts, Roseo-cobaltic Salts,* $[Co(NH_3)_5.H_2O]R_3$.

The salts of this series are formed by replacing one molecule of ammonia in the complex by one molecule of water.

The name *roseo*-cobaltic salts was given to the series by Frémy, but it is due to the research of later investigators, notably Jörgensen, that the roseo-salts were shown to be derived from the hexammino-compounds by replacement of ammonia by water. The salts are clearly marked off from those of the acido-pentammino-series, the purpureo-salts, where acid radicle replaces ammonia in the complex ion. The valency of the complex in the aquo-pentammino-salts is not changed by the entrance of water in place of ammonia.

Aquo-pentammino-cobaltic Hydroxide.—A hydroxide, possibly of formula $[Co(NH_3)_5H_2O](OH)_3$, has been formed in solution either by the decomposition of the chloride, $[Co(NH_3)_5H_2O]Cl_3$, of the series with moist silver oxide, or by the decomposition of a cold aqueous solution of the sulphate with barium hydroxide thus :

$$[Co(NH_3)_5H_2O]_2(SO_4)_3+3Ba(OH)_2 \rightarrow [Co(NH_3)_5H_2O](OH)_3+3BaSO_4.$$

The solution is red in colour, alkaline in reaction, and very easily decomposed. It absorbs carbon dioxide readily from the air, forming a carbonate, and if neutralised with acids it yields the corresponding aquo-pentammino-salts.[2]

Aquo-pentammino-cobaltic Nitrate, $[Co(NH_3)_5H_2O](NO_3)_3$, is obtained when nitrato-pentammino-cobaltic nitrate, $[Co(NH_3)_5NO_3]$

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[1] Werner, *Annalen,* 1907, 351, 65.

[2] Jörgensen, *J. prakt. Chem.,* 1878, 18, 220.

$(NO_3)_2$, is dissolved in water, mixed with dilute aqueous ammonia and heated on a water-bath. On adding a large excess of concentrated nitric acid the aquo-pentammino-salt is precipitated. It is collected, washed with concentrated nitric acid at 0° C., then with dilute acid, and finally with alcohol. The substance is a red crystalline powder, and may be crystallised from concentrated aqueous solution by precipitation with nitric acid, when it is obtained in large glistening quadratic plates mixed with prisms. On heating it decomposes at 100° C., with loss of water and the entrance of a nitrate radicle into the complex thus :

$$[Co(NH_3)_5H_2O](NO_3)_3 \longrightarrow [Co(NH_3)_5(NO_3)](NO_3)_2 + H_2O.$$

Aquo-pentammino-cobaltic Sulphate, $[Co(NH_3)_5H_2O]_2(SO_4)_3 . 3H_2O$.—This salt is prepared by neutralising the corresponding carbonate, $[Co(NH_3)_5H_2O]_2(CO_3)_3$, with dilute sulphuric acid and evaporating the liquid over sulphuric acid. It may also be obtained by decomposition of the corresponding oxalate. The salt crystallises in red plates which are soluble in water. If heated to 98° C. it loses three molecules of water and retains the character of the aquo-salt, but if heated in a stream of air four molecules of water are lost and it passes gradually into the acido-compound, sulphato-pentammino-cobaltic sulphate, $[Co(NH_3)_5SO_4]_2SO_4$.[1]

Aquo-pentammino-cobaltic Chloride, $[Co(NH_3)_5.H_2O]Cl_3$, is also best prepared from the oxalate. The oxalate is moistened with water and brought into solution by the addition of normal hydrochloric acid. On the addition of concentrated acid the chloride is precipitated as an indistinctly crystalline brick-red powder. The salt is soluble in cold water, and is readily transformed into the acido-salt on heating to 100° C. It also passes into the acido-salt on heating in hydrochloric acid solution thus :

$$[Co(NH_3)_5.H_2O]Cl_3 \longrightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O.$$

If heated in neutral solution it is completely decomposed. Aquo-pentammino-cobaltic bromide, $[Co(NH_3)_5H_2O]Br_3$, and aquo-pentammino-cobaltic iodide, $[Co(NH_3)_5H_2O]I_3$, are prepared by similar means.

Aquo-pentammino-cobaltic Oxalate, $[Co(NH_3)_5H_2O]_2(C_2O_4)_3 . 4H_2O$, is prepared from chloro-pentammino-cobaltic chloride. The finely powdered chloride is heated with water and dilute aqueous ammonia, the deep red liquid is filtered, and the filtrate cooled and saturated with oxalic acid. Ammonium oxalate in aqueous solution is then added to complete the precipitation of the salt, and the residue is collected on a filter, washed free from the chloride with water and finally with alcohol.[2] The substance does not lose water if kept over concentrated sulphuric acid, but if heated to 100° C. it decomposes.

(f) *Diaquo-tetrammino-salts*, $[Co(NH_3)_4.(H_2O)_2]R_3$.

The series was first remarked upon by Vortmann in 1877.[3] He prepared and described the chloride and the sulphate of the series; but

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[1] Jörgensen, *J. prakt. Chem.*, 1885, 31, 72 ; *Zeitsch. anorg. Chem.*, 1898, 17, 462.

[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1898, 17, 461.

[3] Vortmann, *Ber.*, 1877, 10, 1454 ; 1882, 15, 1891.

was unable to determine their constitution. The salts were shown later to be derivatives of the hexammino-cobaltic salts by replacement of ammonia by two molecules of water thus :

$$[Co(NH_3)_6]R_3+2H_2O \longrightarrow [Co(NH_3)_4.(H_2O)_2]R_3+2NH_3.$$

Diaquo-tetrammino-cobaltic Sulphate, $[Co(NH_3)_4.(H_2O)_2]_2(SO_4)_3.3H_2O$, crystallises in bright red prisms which are soluble in water, giving a violet solution. It is more easily soluble in water containing sulphuric acid, and loses water if kept over concentrated sulphuric acid, yielding the anhydrous salt, $[Co(NH_3)_4.(H_2O)_2]_2(SO_4)_3$. It is prepared by heating the corresponding carbonato-salt with sulphuric acid and precipitating the sulphate with alcohol.

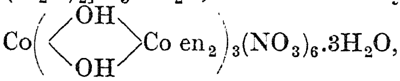
Diaquo-tetrammino-cobaltic Chloride, $[Co(NH_3)_4.(H_2O)_2]Cl_3$.—The salt has been obtained water free as above or containing one molecule of water, $[Co(NH_3)_4.(H_2O)_2]Cl_3.H_2O$. This salt is also prepared from the carbonato-salt by dissolving it in water containing a little hydrochloric acid. The liquid is then cooled in ice and the diaquo-tetrammino-cobaltic chloride precipitated by the addition of concentrated hydrochloric acid. It is filtered off, washed with acid, then with 95 per cent. alcohol, and dried in air.

It forms dark red octahedral crystals which are soluble in water, and if heated to 100° C. it loses one molecule of water and passes over into chloro-aquo-tetrammino-cobaltic chloride, $[Co(NH_3)_4.H_2O.Cl]Cl_2$.[1]

Other salts of the series are known. They have the same general characteristics of those described, and the methods used for their preparation are similar to those mentioned above.

A series of compounds is known belonging to the diaquo-series, where ethylenediamine replaces ammonia, the **diaquo-diethylenediamino-cobaltic salts,** $[Co\,en_2(H_2O)_2]R_3$. These exist in isomeric forms, intensely red *cis*-diaquo-salts and brownish-red *trans*-diaquo-salts. The *trans*-series may be produced from the *cis*-series by treating it with some potassium hydroxide and rubbing the *trans*-hydroxo-aquo-salt, $[Co\,en_2H_2O(OH)]R_2$, produced with concentrated mineral acid.

Cis-series.

Diaquo-diethylenediamino-cobaltic Chloride, $[Co\,en_2(H_2O)_2]Cl_3.2H_2O$, is obtained by treating hexol-tetracobalti-nitrate,  $Co\left(\left<\begin{matrix}OH\\OH\end{matrix}\right>Co\,en_2\right)_3(NO_3)_6.3H_2O$, with concentrated hydrochloric acid. It forms red crystals which are easily soluble in water, and on heating with a solution of hydrochloric acid pass into the *trans*-modification.

The **bromide,** $[Co\,en_2(H_2O)_2]Br_3.2H_2O$, is formed in the same manner by the action of concentrated hydrobromic acid. It crystallises in shining red plates which dissolve in water, giving an intensely red solution which is acid in reaction.[2]

Trans-series.

The **chloride,** $[Co\,en_2(H_2O)_2]Cl_3$ or $[Co\,en_2(H_2O)_2]Cl_3.2H_2O$, is prepared from *trans*-hydroxo-aquo-cobaltic bromide, $[Co\,en_2(H_2O)$

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1892, 2, 294.

[2] Werner, *Ber.*, 1907, 40, 265.

$(OH)]Br_2$, by treating it with concentrated hydrochloric acid. It crystallises in glistening reddish-brown needles and is soluble in water.[1]

Diaquo-dipyridino-diammino-cobaltic chloride, $[Co\,py_2(NH_3)_2(H_2O)_2]Cl_3$, is one of the most stable of the aquo-salts, and requires to be heated for a considerable time before it passes into dichloro-dipyridino-diammino-cobaltic chloride, $[Co\,py_2(NH_3)_2Cl_2]Cl$. The aquo-pentammino-cobaltic salts, on treatment with ammonia, may be changed into hydroxo-pentammino-cobaltic salts thus :

$$[Co(NH_3)_5H_2O]Cl_3+NH_3\longrightarrow[Co(NH_3)_5(OH)]Cl_2+NH_4Cl.$$

(g) *Triaquo-triammino-cobaltic Salts*, $[Co(NH_3)_3(H_2O)_3]R_3$.

The ammonia content of the complex may be still further reduced, giving rise to the *triaquo-triammino-derivatives*.

Triaquo-triammino-cobaltic Nitrate, $[Co(NH_3)_3(H_2O)_3](NO_3)_3$.—This substance is formed from the corresponding triacido-cobalt, $[Co(NH_3)_3(NO_3)_3]$. If the salt is allowed to stand for some time with water it goes into solution, and on evaporation deliquescent carmine-red crystals of the triaquo-triammino-nitrate separate out.

Triaquo-triammino-cobaltic Chloride, $[Co(NH_3)_3(H_2O)_3]Cl_3$, is produced by dissolving trinitrato-triammine cobalt in water with the addition of a little acetic acid and allowing the liquid to stand for twenty hours. It is then cooled and treated with hydrochloric acid at 0° C., when a yellowish-red crystalline powder is precipitated. This is quickly separated from the mother-liquor and dried on a porous plate.[2] Other triaquo-triammino-salts have been prepared.

The aquo-salts generally readily pass into the acido-ammino salts; for example, aquo-pentammino-cobaltic chloride and diaquo-tetrammino-cobaltic chloride are transformed into chloro-pentammino-cobaltic chloride and dichloro-tetrammino-cobaltic chloride respectively on leaving concentrated aqueous solutions to stand for some time.

2. COBALT-AMMINES CONTAINING DIVALENT CATION, $[CoA_5R]^{\cdot\cdot}$.

(a) *Hydroxo-pentammino-cobaltic Salts*, $[Co(NH_3)_5.OH]R_2$.

The first member of this series to be prepared was the dithionate, but the constitution was not then understood, and it was described as a basic dithionate belonging to the aquo-pentammino-series.[3]

The hydroxo-pentammino-salts are obtained from the aquo-pentammino-salts, $[Co(NH_3)_5H_2O]R_2$, on treatment with aqueous ammonia, and they pass quickly into the aquo-salts again on treating with acid thus :

$$[Co(NH_3)_5H_2O]R_3+NH_3\longrightarrow[Co(NH_3)_5OH]R_2+NH_4R;$$
$$[Co(NH_3)_5OH]R_2+HR\longrightarrow[Co(NH_3)_5H_2O]R_3.$$

This series of salts contains a hydroxyl group in the nucleus, and shows a distinctly alkaline reaction in aqueous solution, although they do not precipitate silver oxide from silver nitrate. With concentrated solutions of ammonium salts ammonia is evolved and the corresponding aquo-pentammino-salt is formed.[4]

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[1] Werner, *Ber.*, 1907, 40, 269.
[2] Werner, *ibid.*, 1906, 39, 2678.
[3] Jörgensen, *J. prakt. Chem.*, 1882, 25, 418.
[4] Werner, *Ber.*, 1907, 40, 4098.

Hydroxo-pentammino-cobaltic Nitrate, $[Co(NH_3)_5OH](NO_3)_2.H_2O$, is prepared by dissolving aquo-pentammino-cobaltic nitrate in concentrated aqueous ammonia. The dark carmine-coloured liquid is filtered, warmed gently, and treated with boiling alcohol, and, on cooling and standing for some time, large carmine-red needle-shaped crystals separate. The crude product is purified by dissolving in ammonia solution and treating with alcohol and ether, when the salt crystallises in violet-red scales.

It is fairly soluble in water, giving a bluish-red alkaline liquid, which gives no precipitate with silver nitrate. When added to ammonium salts, ammonia is liberated and the aquo-salt formed thus:

$$[Co(NH_3)_5OH](NO_3)_2+NH_4NO_3 \longrightarrow [Co(NH_3)_5H_2O](NO_3)_3+NH_3.$$

Carbon dioxide reacts with an aqueous solution of the salt, yielding the **bicarbonato-salt** thus:

$$[Co(NH_3)_5OH](NO_3)_2+CO_2 \longrightarrow [Co(NH_3)_5HCO_3](NO_3)_2;$$

and acetic anhydride transforms it into the **acetato-derivative**,

$$[Co(NH_3)_5(OCOCH_3)](NO_3)_2.$$

The **chloride**, $[Co(NH_3)_5OH]Cl_2.H_2O$, is formed from aquo-pentammino-cobaltic chloride by dissolving it in aqueous ammonia, warming the solution and mixing it with alcohol. It separates as a crystalline meal, and is purified by redissolving it in ammoniacal solution and adding alcohol. It crystallises in glistening scales and has similar properties to the nitrate.

The **bromide**, $[Co(NH_3)_5OH]Br_2.H_2O$, is prepared from the corresponding aquo-salt in the same manner as the chloride, and separates from alcohol and water as a violet powder. The **iodide**, $[Co(NH_3)_5OH]I_2$, is obtained from the chloride by dissolving it in aqueous ammonia and adding solid potassium iodide. The **dithionate**, $[Co(NH_3)_5OH]S_2O_6.H_2O$, obtained from the chloride by treating it with ammonia and sodium dithionate, crystallises in short red prisms or leaflets.

(b) *Hydroxo-aquo-tetrammino-cobaltic Salts*, $[Co(NH_3)_4H_2O.OH]R_2$.

The series is obtained by the removal of a molecule of acid from the diaquo-salts by the action of ammonia. They are also alkaline in reaction when dissolved in water, and behave towards silver nitrate and ammonium salts like the hydroxo-pentammino-salts.

Hydroxo-aquo-tetrammino-cobaltic Chloride, $[Co(NH_3)_4H_2O.OH]Cl_2$, is prepared by mixing diaquo-tetrammino-cobaltic chloride with concentrated aqueous ammonia and adding alcohol to the solution till precipitation is complete. It is a violet-red crystalline powder and is soluble in water. On leading carbon dioxide into a saturated aqueous solution of the salt a precipitate of chloro-aquo-tetrammino-cobaltic chloride is formed, whilst carbonato-tetrammino-chloride goes into solution. Other salts of the series are obtained from the chloride by treating the aqueous solution with the corresponding alkali salt. They are violet or red in colour, and pass readily into the diaquo-salts on treatment with acid.[1]

A series of *hydroxo-aquo-diethylenediamino-cobaltic salts* is known.

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[1] Werner, *Ber.*, 1907, 40, 4113, 4104.

These exist in two isomeric forms: *cis*-salts which are violet-red in colour, and *trans*-salts which are light violet-red in colour.

Cis-series.

These are prepared by the addition of pyridine to an aqueous solution of *cis*-diaquo-diethylenediamino-cobaltic salts.

Hydroxo-aquo-diethylenediamino-cobaltic Chloride, $[Co\,en_2\,H_2O.OH]Cl_2.H_2O$, is a brownish-red crystalline powder which is easily converted into the diaquo-salt on treatment with concentrated hydrochloric acid.

The **bromide,** $[Co\,en_2H_2O.OH]Br_2.H_2O$, is obtained from the chloride or from *trans*-dichloro-diethylenediamino-cobaltic chloride by treating it with concentrated aqueous potassium hydroxide and, after cooling to 0° C., neutralising the solution obtained with concentrated hydrobromic acid. It is a red crystalline powder, and resembles the chloride in properties.

The **iodide,** $[Co\,enH_2O.OH]I_2.H_2O$, is prepared from *cis*-diaquo-diethylenediamino-cobaltic bromide by acting upon it with pyridine and powdered potassium iodide.

The **dithionate,** $[Co\,en_2H_2O.OH]S_2O_6$, separates in slender violet-red needles.

Trans-series.

Trans-hydroxo-aquo-diethylenediamino-cobaltic Chloride, $[Co\,en_2H_2O.OH]Cl_2$, is prepared from aqueous *trans*-diaquo-diethylenediamino-cobaltic chloride by the addition of potassium hydroxide or pyridine. It crystallises in pearly bluish-red leaflets.

The **bromide,** $[Co\,en_2H_2O.OH]Br_2$, is obtained in a similar manner, or from the *cis*-salt by boiling the aqueous solution with potassium hydroxide for a short time and neutralising the solution with well-cooled hydrobromic acid. It is a light red powder, and is less soluble in water than the chloride.

The **iodide** crystallises in reddish-brown leaflets and the dithionate in glistening red needles.

The salts of both series are rather sparingly soluble in water, have a faintly alkaline reaction, and dissolve readily in water containing acetic acid. Mineral acids convert them into diaquo-salts. The formation of the compounds by the action of pyridine on the diaquo-salts may be represented generally thus:[1]

$$[Co\,en_2(H_2O)_2]R_3+C_5H_5N \longrightarrow [Co\,en_2H_2O.OH]R_2+C_5H_5N.HR.$$

(c) *Acido-pentammino-cobaltic Salts,* $[Co(NH_3)_5R]R_2$.

Nitro-pentammino-cobaltic Salts, Xantho-cobaltic Salts, $[Co(NH_3)_5(NO_2)]R_2$.—The series was first described by Gibbs in 1852, and later, in conjunction with Genth, it was further examined and the constitution investigated. The series is given the name xantho-salts on account of their golden-yellow colour.

Nitro-pentammino-cobaltic Nitrite, $[Co(NH_3)_5(NO_2)](NO_2)_2.2H_2O$, is prepared by heating aquo-pentammino-cobaltic sulphate with barium nitrite, or by treating a solution of chloro-pentammino-cobaltic

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[1] Werner, *Ber.*, 1907, 40, 284.

chloride with silver nitrite, a double nitrite, $[Co(NH_3)_5NO_2](NO_2)_2.AgNO_2$, being formed at the same time.[1] The salt crystallises in dark wine-coloured crystals.

Nitro-pentammino-cobaltic Nitrate, $[Co(NH_3)_5NO_2](NO_3)_2$.—This salt is obtained by leading nitrous fumes into a neutral or acid solution of aquo-pentammino-cobaltic nitrate or acido-pentammino-cobaltic nitrate until the colour changes to saffron yellow, and then precipitating the substance by means of dilute nitric acid.[2] It crystallises in small, glistening, brownish-yellow crystals of tetragonal shape, is slightly soluble in cold water and easily soluble in hot water. On heating to 100° C. it decomposes, and if boiled with nitric acid it is transformed into aquo-pentammino-cobaltic nitrate, $[Co(NH_3)_5.H_2O](NO_3)_3$. Treatment with other acids yields the corresponding acido-salt.

The **sulphate,** $[Co(NH_3)_5NO_2]SO_4$, crystallises in brownish-yellow leaflets or prisms, is soluble in hot water and slightly soluble in cold water. In neutral solution it decomposes, and prolonged heating with hydrochloric acid transforms it into chloro-pentammino-cobaltic chloride.

Nitro-pentammino-cobaltic Chloride, $[Co(NH_3)_5NO_2]Cl_2$, may be obtained from the corresponding sulphate by decomposing a solution with barium chloride, or from chloro-pentammino-cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, by dissolving it in water containing ammonia, acidifying the liquid, after filtration with hydrochloric acid, and heating with sodium nitrite until the precipitate first formed completely dissolves. On cooling the brownish solution the xantho-salt is precipitated by the addition of concentrated hydrochloric acid. The substance is collected on a filter and washed first with acid and then with alcohol.

The salt crystallises in large brownish-yellow monoclinic crystals, which are very sparingly soluble in cold water. If the neutral aqueous solution is heated it decomposes, as does the slightly acid solution. Excess of hydrochloric acid transforms it into chloro-pentammino-cobaltic chloride.

Isomeric with the nitro-pentammino-salts are the **isoxantho-salts** or **nitrito-pentammino-cobaltic salts;** for example, $[Co(NH_3)_5(ONO)]Cl_2$. These differ in colour from the nitro-salts and are labile isomers. Most members of this series are completely transformed into the stable nitro-salts on keeping, or more quickly on heating. Jörgensen[3] was the first to investigate the isomerism in the xantho-salts, for he noticed that when nitro-pentammino-cobaltic salts are prepared from aquo-pentammino-cobaltic salts, intermediate bodies are produced which have a lighter colour than the final product. These he concluded are unstable salts containing the (ONO) group, which pass into the stable substances containing the (NO_2) group. On account of the instability of the compounds they could not be thoroughly examined. Werner,[4] however, succeeded in preparing a more stable series of compounds corresponding to Jörgensen's xantho- and isoxantho-salts. He prepared two isomeric xantho-dipyridino-diammino-cobaltic salts, namely, **dinitrito-dipyridino-diammino-cobaltic salts,** $[Co(NH_3)_2py_2(ONO)_2]R$, and **dinitro-dipyridino-diammino-cobaltic salts,**

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[1] Gibbs, *Proc. Amer. Acad.*, 1875, 10, 29.
[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 5, 170.
[3] Jörgensen, *ibid.*, 1893, 5, 168; 1899, 19, 149.
[4] Werner, *Ber.*, 1907, 40, 768; 1903, 35, 27.

$[\mathrm{Co(NH_3)_2py_2(NO_2)_2}]\mathrm{R}$. Also, he showed that there are four isomeric salts of molecular formula $[\mathrm{Co(en)_2(NO_2)_2}]\mathrm{R}$. In this series position isomerism, as well as isomerism of the nitro-group, play a part.

There are two dinitro-diethylenediamino-cobaltic salts, namely,

$$\left[\begin{array}{ll}\mathrm{1\text{-}NO_2} & \\ & \mathrm{Co\ en_2} \\ \mathrm{2\text{-}NO_2} & \end{array}\right]\mathrm{R} \quad \text{and} \quad \left[\begin{array}{ll}\mathrm{1\text{-}NO_2} & \\ & \mathrm{Co\ en_2} \\ \mathrm{6\text{-}NO_2} & \end{array}\right]\mathrm{R};$$

1-, 2-dinitro-diethylenediamino-cobaltic salt. 1-, 6-dinitro-diethylenediamino-cobaltic salt.

and isomeric with these two there are two dinitrito-salts, namely,

$$\left[\begin{array}{ll}\mathrm{1\text{-}(ONO)} & \\ & \mathrm{Co\ en_2} \\ \mathrm{2\text{-}(ONO)} & \end{array}\right]\mathrm{R} \quad \text{and} \quad \left[\begin{array}{ll}\mathrm{1\text{-}(ONO)} & \\ & \mathrm{Co\ en_2} \\ \mathrm{6\text{-}(ONO)} & \end{array}\right]\mathrm{R}.$$

1-, 2-dinitrito-diethylenediamino-cobaltic salt. 1-, 6-dinitrito-diethylenediamino-cobaltic salt.

The isomers differ in colour; the nitro-series are yellow or yellowish brown, whilst the nitrito-series are brick-red in colour. The stability of the two series is also different, for the nitro-salts are quite stable towards acids, whilst the nitrito-salts are decomposed by acids with liberation of nitrous acids. The nitrito-salts readily pass into the more stable isomers if kept, transformation taking about forty-eight hours at ordinary temperature, and at 60° C. being immediate.

More complex salts are also known belonging to the series. For instance, if a solution of nitro-pentammino-cobaltic chloride be treated with an aqueous solution of sodium cobaltic nitrite, $\mathrm{Na_3Co(NO_2)_6}$, a yellowish-brown crystalline precipitate of nitro-pentammino-cobaltic cobalti-nitrite, $[\mathrm{Co(NH_3)_5(NO_2)}]_3[\mathrm{Co(NO_2)_6}]_2$, is formed. Also the corresponding ferrocyanide may be prepared by treating nitro-pentammino-salts with potassium ferrocyanide. The compound obtained is a reddish-yellow substance of composition $[\mathrm{Co(NH_3)_5(NO_2)}]_2[\mathrm{Fe(CN)_6}].6\mathrm{H_2O}$.

Nitrato-pentammino-cobaltic Salts or Nitrato-purpureo-cobaltic Salts.—The first salt of this series, the nitrate, was described by Frémy in 1852. In 1856 Gibbs and Genth described it as water-free *roseo-cobaltic nitrate*; but later, in 1876, Gibbs recognised the compound as an acido-pentammino-salt. Jörgensen,[1] in 1881, succeeded in distinguishing the nitrate from aquo-pentammino-nitrate by examining its reactions.

Nitrato-pentammino-cobaltic Nitrate, $[\mathrm{Co(NH_3)_5NO_3}](\mathrm{NO_3})_2$.—If an aqueous ammoniacal solution of cobaltous nitrate be oxidised by means of air and then heated with excess of ammonium nitrate, the nitrato-salt is formed. It is more easily prepared by dissolving cobaltous carbonate in warm dilute nitric acid and then warming the mixture with concentrated aqueous ammonia. Iodine is thereafter added, one atom for every atom of cobalt in solution, and the whole warmed until the iodine dissolves and a precipitate of hexammino-cobaltic iodido-nitrate is formed. It is filtered and the residue washed with dilute aqueous ammonia. The filtrate is treated with nitric acid, and the precipitate of aquo-pentammino-nitrate is converted into the nitrato-salt by heating with more nitric acid. The change from aquo-

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[1] Jörgensen, *J. prakt. Chem.*, 1881, **23**, 227.

to nitrato-salt may be brought about by heating to 100° C. for several hours thus :

$$[Co(NH_3)_5H_2O](NO_3)_3 \rightarrow [Co(NH_3)_5NO_3](NO_3)_2+H_2O.$$

The salt is a reddish-violet crystalline substance which is slightly soluble in cold water, but easily soluble in hot water containing nitric acid, forming the aquo-salt.

Nitrato-pentammino-cobaltic Chloride, $[Co(NH_3)_5NO_3]Cl_2$, is formed by mixing finely powdered nitrato-pentammino-nitrate with water containing a small quantity of dilute sulphuric acid and allowing the solution to run slowly into excess of well-cooled hydrochloric acid. The precipitate formed is collected and washed with acid and then with alcohol. It crystallises in reddish-violet octahedra which are slightly soluble in cold water, and if crystallised from water containing hydrochloric acid it is transformed into chloro-pentammino-cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$.[1]

Aquo-derivatives of nitrato-pentammino-salts are known. For example, **nitrato-aquo-tetrammino-cobaltic nitrate,** $[Co(NH_3)_4(H_2O)(NO_3)](NO_3)_2$, is prepared from carbonato-tetrammino-cobaltic nitrate, $[Co(NH_3)_4(CO_3)]NO_3$,[2] by treating it in aqueous solution with concentrated nitric acid, when the aquo-salt is precipitated.

Chloro-pentammino-cobaltic Chloride, Purpureo-cobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$, was first described by Claudet and Genth.[3] Gibbs and Genth[4] gave to the compound and the corresponding chloro-pentammino-salts the name **purpureo-salts,** and distinguished them from the aquo-salts, roseo-cobaltic salts. Later, Jörgensen[5] examined the series and proved them to be acido-salts, containing chlorine in the complex cation.

Chloro-pentammino-cobaltic chloride was first prepared by the oxidation of an ammoniacal solution of cobaltous chloride containing ammonium chloride and the subsequent precipitation of the oxidation product with hydrochloric acid. It is the best known and the longest known of the cobalt-ammines.

The substance is best prepared by dissolving cobaltous carbonate in the smallest possible quantity of hydrochloric acid, treating the cold solution with a mixture of concentrated aqueous ammonia and ammonium carbonate, and oxidising by means of a stream of air drawn through the liquid. When oxidation is complete ammonium chloride is added and the whole evaporated to a syrup; dilute hydrochloric acid is added to remove carbon dioxide, and the liquid is saturated with ammonia gas to decompose any tetrammino-salt formed. On the addition of concentrated hydrochloric acid the salt crystallises out on cooling.[6]

Chloro-pentammino-cobaltic chloride forms carmine-red rhombic crystals which are slightly soluble in water, insoluble in water containing hydrochloric acid or ammonium chloride, and insoluble in alcohol. The aqueous solution is decomposed on warming, and the compound,

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[1] Jörgensen, *J. prakt. Chem.*, 1881, 23, 237.
[2] Vortmann and Blasberg, *Ber.*, 1889, 22, 2652.
[3] Claudet and Genth, *Phil. Mag.*, 1851, 2, 253.
[4] Gibbs and Genth, *J. prakt. Chem.*, 1857, 72, 156.
[5] Jörgensen, *ibid.*, 1878, 18, 216.
[6] Sörensen, *Zeitsch. anorg. Chem.*, 1894, 5, 369.

if heated alone, decomposes, leaving a residue of cobaltous chloride. One atom of chlorine in the molecule is not precipitated on treating the salt with silver-nitrate solution at ordinary temperature, but on warming precipitation takes place. Sulphuric acid transforms it into the corresponding acid sulphate, $[Co(NH_3)_5Cl]SO_4.(H_2SO_4)_2$. It forms double salts with many metallic salts, and both potassium ferrocyanide and potassium ferricyanide yield sparingly soluble coloured compounds thus :

$$2[Co(NH_3)_5Cl]Cl_2+K_4[Fe(CN)_6]\longrightarrow\underset{\text{Chocolate-brown.}}{[Co(NH_3)_5Cl]_2[Fe(CN)_6]}+4KCl$$

and

$$3[Co(NH_3)_5Cl]Cl_2+2K_3[Fe(CN)_6]\longrightarrow\underset{\text{Orange-red.}}{[Co(NH_3)_5Cl]_3[Fe(CN)_6]_2}+6KCl.$$

Chloro-pentammino-cobaltic Chloroplatinate, $[Co(NH_3)_5Cl][PtCl_6]$, is formed on adding chloroplatinic acid to a chloro-pentammino-salt. It forms a crystalline powder of brownish-red colour which is almost insoluble in cold and only slightly soluble in hot water.

The corresponding chloro-pentammino-nickel salt is not prepared by the above method, and the formation of chloro-pentammino-cobaltic chloride has been used as a means of purifying cobalt salts from nickel.[1]

Chloro-pentammino-cobaltic Bromide, $[Co(NH_3)_5Cl]Br_2$, may be prepared from the chloride by treating a solution, which has been made slightly acid with dilute sulphuric acid, with well-cooled hydrobromic acid. The precipitate formed is washed with dilute aqueous hydrogen bromide and then with alcohol. It may be formed also from the corresponding chloro-carbonate by precipitating from solution with concentrated hydrobromic acid. It crystallises in red octahedra, and is more easily soluble than the chloride.

The **iodide,** $[Co(NH_3)_5Cl]I_2$, is prepared in the same manner as the bromide from the chloride and hydriodic acid. It is much more soluble than the chloride or the bromide, and may be crystallised in brownish-violet octahedra from a solution of hydriodic acid.

Chloro-pentammino-cobaltic Nitrate, $[Co(NH_3)_5Cl](NO_3)_2$, is obtained from the chloride by mixing it with water and a little dilute sulphuric acid, washing the mixture on to a filter with water at 50° C., and running the solution obtained into excess of nitric acid at 0° C. The precipitate formed is collected, washed with water containing nitric acid and then with hot alcohol. It crystallises in small red octahedra which are insoluble in cold water and somewhat soluble in hot water.

Chloro-pentammino-cobaltic Sulphate.—By treating the chloride with sulphuric acid three sulphates have been obtained: (1) *the anhydrous salt,* $[Co(NH_3)_5Cl]SO_4$, which crystallises in purple octahedra which are soluble in hot water; (2) *the hydrated salt,* $[Co(NH_3)_5Cl]SO_4.3H_2O$, which crystallises in deep purple crystals; (3) *the acid sulphate,* $[Co(NH_3)_5Cl]SO_4.(H_2SO_4)_2$, which crystallises in dark violet-red prisms or needles more easily soluble than the normal salt. If the sulphate is heated with water alone it decomposes with formation of cobaltic hydroxide, but decomposition does not take place in presence of sulphuric acid.

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[1] Biltz, *Laboratory Methods of Inorganic Chemistry,* translated by Hall and Blanchard (Chapman & Hall, 1909), p. 173.

If treated with barium hydroxide in aqueous solution a liquid is produced which contains aquo-pentammino-cobaltic chloride, $[Co(NH_3)_5H_2O]Cl_3$, and aquo-pentammino-cobaltic hydroxide, $[Co(NH_3)_5H_2O](OH)_3$.

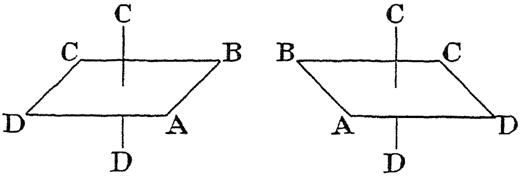
The base of the series, namely, $[Co(NH_3)_5Cl](OH)_2$, which might be expected on decomposing the sulphate with the calculated quantity of barium hydroxide, apparently does not exist.[1]

Ethylenediamino-derivatives of the series are known; for example, **chloro-ammino-diethylenediamino-cobaltic nitrate,** $[Co(NH_3)(en)_2Cl](NO_3)_2$; **chloro-ammino-diethylenediamino-cobaltic chloride,** $[Co(NH_3)(en)_2Cl]Cl_2$; and **bromo-ammino-diethylenediamino-cobaltic bromide,** $[Co(NH_3)(en)_2Br]Br_2$.

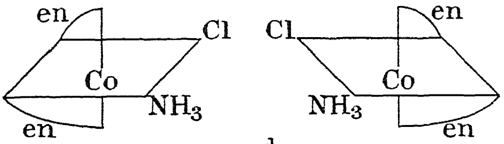
These show the general chemical reactions of the series.

The compounds are of interest, as they may be resolved into optically active isomerides.

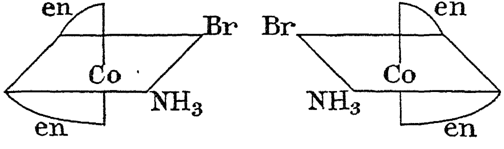
According to Werner's co-ordination theory, compounds containing the radicles A, B, C, D, united with metal atom, should give optical isomers, the groups combined with metal taking up the positions,



Werner[2] has shown that C and D need not be different by preparing the optical isomerides of chloro-ammino-diethylenediamino-cobaltic salts and of bromo-ammino-diethylenediamino-cobaltic salts. The salts may be represented by the space formulæ



and



The resolution was carried out by means of d-bromo-camphor-sulphonic acid. The salts of the bromo-series are more easily resolved on account of the great difference between the isomeric d-bromo-camphor sulphonates. In both series the d-bromo-camphor sulphonate of the d-isomer is more sparingly soluble. These active compounds are very stable, and aqueous solutions of the bromides of the bromo-ammine series may be kept for a considerable time at ordinary temperatures, and even on heating to boiling racemisation does not occur. If the bromine in the complex be removed by means of silver nitrate activity

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[1] Jörgensen, *J. prakt. Chem.*, 1878, 18, 212.
[2] Werner, *Ber.*, 1911, 44, 1887.

still remains, as the aquo-salt formed also gives optical isomerides. The reaction may be represented thus :

$$[Co(NH_3)(en)_2Br]Br_2+3AgNO_3+H_2O \longrightarrow [Co(NH_3)(en)_2H_2O](NO_3)_3+3AgBr.$$

No racemisation takes place on formation of various salts of the two series.

(d) *Acido-aquo-tetrammino-cobaltic Salts*, $[Co(NH_3)_4H_2O.R]R_2$.

Nitro-aquo-tetrammino-cobaltic Salts, Aquo-xantho-cobaltic Salts, $[Co(NH_3)_4H_2O(NO_2)]R_2$.—These salts were first prepared by Jörgensen in 1894, and were further examined by Werner and Klien in 1900.[1]

Nitro-aquo-tetrammino-cobaltic Nitrate, $[Co(NH_3)_4H_2O(NO_2)](NO_3)_2$, crystallises in brownish-yellow octahedra which are soluble in cold water. It is prepared from the chloride of the series or from dinitro-tetrammino-cobaltic sulphate.[2]

Nitro-aquo-tetrammino-cobaltic Chloride, $[Co(NH_3)_4H_2O(NO_2)]Cl_2$, and the **bromide,** $[Co(NH_3)_4H_2O(NO_2)]Br_2$, are yellow crystalline substances which are prepared from hydroxo-nitro-cobaltic salts by the action of hydrochloric or hydrobromic acids respectively.

They are isomeric with chloro-nitro-tetrammino-cobaltic chloride, $[Co(NH_3)_4(NO_2)Cl]Cl.H_2O$, and bromo-nitro-tetrammino-cobaltic bromide, $[Co(NH_3)_4(NO_2)Br]Br.H_2O$, the substances originally described by Jörgensen as aquo-salts. These salts are red, whereas all the aquo-nitro-salts are yellow in colour. Both salts are easily transformed into the isomeric nitro-halogeno-compounds on treatment with water.[3]

Chloro-aquo-tetrammino-cobaltic Salts, $[Co(NH_3)_4H_2O.Cl]R_2$.—The first member of the series described is the chloride, prepared by Vortmann in 1877.[4] Later, Jörgensen showed that these salts must be regarded as derivatives of the chloro-pentammino-cobaltic salts where ammonia has been replaced by water.

Chloro-aquo-tetrammino-cobaltic Chloride, $[Co(NH_3)_4H_2O.Cl]Cl_2$, is prepared by dissolving cobaltous carbonate in the calculated quantity of dilute hydrochloric acid, cooling the liquid obtained, and treating it with concentrated aqueous ammonia and ammonium carbonate. The deep blue solution formed is then oxidised, by passing air through it for several hours, and evaporated on a water-bath, ammonium carbonate being added from time to time. After cooling, the solution is acidified with hydrochloric acid and the mixture allowed to crystallise. The solid formed is filtered off, washed with dilute acid to remove ammonium chloride and with alcohol to remove acid. The compound may be mixed with chloro-pentammino-chloride and dichloro-tetrammino-chloride, and should therefore be further purified by collecting it on a filter and treating with water made slightly acid with sulphuric acid. The impurities remain on the filter, and the filtrate is allowed to stand with addition of some ammonium sulphate, when

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 7, 297; Werner and Klien, *ibid.*, 1900, 22, 122.

[2] Jörgensen, *loc. cit.*; 1898, 17, 467.

[3] Werner, *Ber.*, 1907, 40, 4126.

[4] Vortmann, *ibid.*, 1877, 10, 1451.

chloro-aquo-tetrammino-cobaltic sulphate separates and is transformed into the chloride by stirring with cold hydrochloric acid.[1]

It separates in small violet rhombic crystals which resemble chloro-pentammino-cobaltic chloride in appearance. It is soluble in cold water to a certain extent, and only two-thirds of the chlorine is precipitated from solution by silver nitrate at ordinary temperature. In aqueous solution the salt is gradually transformed into the diaquo-salt, $[Co(NH_3)_4(H_2O)_2]Cl_3$; dilute nitric acid, if rubbed with the substance, gives reddish-violet crystals of the *nitrate*, $[Co(NH_3)_4(H_2O)Cl](NO_3)_2$; and a cold concentrated solution of ammonium sulphate yields the *sulphate*, $[Co(NH_3)_4(H_2O)Cl]SO_4$. The corresponding *bromide*, $[Co(NH_3)_4(H_2O)Cl]Br_2$, is obtained by filtering a cold saturated solution of the chloride into concentrated hydrobromic acid at 0° C. The precipitate formed is washed with hydrobromic acid and then with alcohol. The bromide is almost insoluble in hydrobromic acid, but more easily soluble in water than the chloride.[2]

Bromo-aquo-tetrammino-cobaltic Bromide, $[Co(NH_3)_4H_2O.Br]Br_2$, may be prepared by warming dibromo-tetrammino-cobaltic bromide, $[Co(NH_3)_4Br_2]Br$, with water and a little hydrobromic acid. It crystallises in brownish-violet prisms.[3]

(e) *Acido-diaquo-triammino-cobaltic Salts*, $[Co(NH_3)_3(H_2O)_2R]R_2$.

Chloro-diaquo-triammino-cobaltic Salts.—The sulphate of the series was the first member prepared.[4]

Chloro-diaquo-triammino-cobaltic Sulphate, $[Co(NH_3)_3(H_2O)_2Cl]SO_4$, exists in two modifications, a blue-green modification and a violet form. It is prepared from acid dichloro-aquo-triammino-cobaltic sulphate, $[Co(NH_3)_3(H_2O)Cl_2]SO_4H$, by treating a saturated aqueous solution with an equal volume of alcohol. The precipitate of green-coloured salt is collected and dried over sulphuric acid. It separates as a fine crystalline powder, and if crystallised from an aqueous solution is gradually transformed into the isomeric violet salt. Concentrated hydrochloric acid precipitates from the aqueous solution dichloro-aquo-tetrammino-cobaltic chloride.

Chloro-diaquo-triammino-cobaltic Chloride, $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, is produced from the above salt by rubbing it with concentrated hydrochloric acid. It is a dark violet crystalline substance which is soluble in water, giving a violet solution.

Chloro-diaquo-triammino-cobaltic Bromide, $[Co(NH_3)_3(H_2O)_2Cl]Br_2$, is prepared by the addition of the chloride to hydrobromic acid. It crystallises in dark blue needles and is unstable in moist air, forming chloro-bromo-aquo-triammino-cobaltic bromide, $[Co(NH_3)_3(H_2O)ClBr]Br$, a green salt, from which the original bromide may be regenerated in small quantity by suspending it in alcohol and gradually adding water.

A solution of chloro-diaquo-triammino-cobaltic bromide is blue in colour, and on the addition of hydrobromic acid the isomeric chloro-bromo-aquo-triammino-cobaltic bromide monohydrate, $[Co(NH_3)_3(H_2O)ClBr]Br.H_2O$, separates in brown needles even at temperatures below

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[1] Jörgensen, *J. prakt. Chem.*, 1890, 42, 211; *Zeitsch. anorg. Chem.*, 1898, 17, 465.

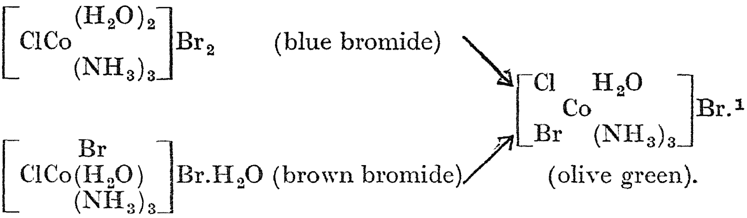
[2] Jörgensen, *J. prakt. Chem.*, 1890, 42, 215.

[3] Werner and Wolberg, *Ber.*, 1905, 38, 2009.

[4] Werner and Grün, *ibid.*, 1904, 37, 4700.

0° C. It is more stable than the blue diaquo-compound. Below 0° C. it forms a green solution in water, at ordinary temperatures a bluish-violet solution, and at higher temperatures a red solution. When chloro-diaquo-triammino-cobaltic sulphate is triturated with fuming hydrobromic acid, anhydrous chloro-bromo-aquo-cobaltic bromide is formed in olive-green crystals.

The relationship of the three compounds is expressed by Werner and Grün thus :



$$\begin{tikzcd}[column sep=small]
\left[\mathrm{ClCo}\begin{matrix}(\mathrm{H_2O})_2\\(\mathrm{NH_3})_3\end{matrix}\right]\mathrm{Br_2}\ \text{(blue bromide)} \arrow[dr] & \\
& \left[\begin{matrix}\mathrm{Cl} & & \mathrm{H_2O}\\ & \mathrm{Co} & \\ \mathrm{Br} & & (\mathrm{NH_3})_3\end{matrix}\right]\text{Br.[1]}\ \text{(olive green).} \\
\left[\begin{matrix}\mathrm{Br}\\ \mathrm{ClCo(H_2O)}\\ (\mathrm{NH_3})_3\end{matrix}\right]\mathrm{Br.H_2O}\ \text{(brown bromide)} \arrow[ur] &
\end{tikzcd}$$

(f) *Acido-triaquo-diammino-cobaltic Salts.*

Chloro-triaquo-diammino-cobaltic Sulphate, $[Co(NH_3)_2(H_2O)_3Cl]SO_4.H_2O$, is obtained by decomposing an aqueous solution of acid dichloro-diaquo-diammino-cobaltic sulphate, $[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H$, with a small quantity of sulphuric acid and evaporating the solution *in vacuo*. It separates in indigo-coloured crystals and is soluble in water, giving a blue solution.

A series of cobalt-ammines has been described which may be classed with this series although their cation is monovalent. These are compounds of the type $[Co(NH_3)_5Y]R$, where Y represents a divalent radicle such as $(SO_4)''$, $(SO_3)''$, or $(CO_3)''$.

It has been shown that a divalent acidic radicle may occupy one or two co-ordinate positions. In this case, therefore, the divalent radicle occupies only one co-ordinate position, but as a divalent radicle it satisfies two principal valencies of the cobalt atom, and hence the complex cation is monovalent.

The Sulphato-pentammino-cobaltic Salts, $[Co(NH_3)_5(SO_4)]R$, are isomeric with the acido-pentammino-sulphate series ; thus, sulphato-pentammino-cobaltic bromide, $[Co(NH_3)_5(SO_4)]Br$, and bromo-pentammino-cobaltic sulphate, $[Co(NH_3)_5Br]SO_4$, are isomeric, as also are $[Co(NH_3)_5(SO_4)]Cl$ and $[Co(NH_3)_5Cl]SO_4$ (see p. 130).

The sulphato-salts are unstable, and readily change in aqueous solution into aquo-pentammino-salts.

Sulphato-pentammino-cobaltic Bromide, $[Co(NH_3)_5SO_4]Br$, is prepared from chloro-pentammino-chloride by transforming it by means of concentrated sulphuric acid. The following reaction takes place :—

$$[Co(NH_3)_5Cl]Cl_2+2H_2SO_4 \longrightarrow [Co(NH_3)_5SO_4]SO_4H+3HCl.$$

The sulphate is then dissolved in cold water and the calculated quantity of dilute hydrobromic acid added. The bromide so formed is precipitated from solution with alcohol as a violet-red powder. It may be recrystallised from a dilute solution of hydrobromic acid and alcohol, when it is obtained in rectangular plates.

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[1] Werner and Grün, *Ber.*, 1904, 37, 4700.

Carbonato-pentammino-cobaltic Nitrate, $[Co(NH_3)_5(CO_3)]NO_3.H_2O$.—Salts of this series were described by Vortmann and Blasberg.[1] They regarded the nitrate, however, as nitrato-pentammino-cobaltic carbonate. Later, Werner and Goslings[2] found that it did not give the reactions of a carbonate, and concluded that the carbonate radicle must be within the complex cation.

It may be prepared by mixing a solution of cobaltous nitrate with a mixture of ammonium carbonate and ammonia solution and allowing the liquid to stand for some time. Dark red crystals separate and are collected and recrystallised from hot water. In order to obtain the salt in a pure state it is transformed into the iodide by treating with hydriodic acid, the iodide precipitated from solution with alcohol, crystallised from water, and transformed into the nitrate by the addition of a concentrated solution of silver nitrate to an aqueous solution. The silver iodide is filtered off and the nitrate separated from the filtrate by the addition of alcohol. The salt does not give the normal reactions for a carbonate and is unstable towards acids.[2]

A more convenient method of preparation is described by Briggs, according to which the cobaltous carbonate is dissolved in the smallest possible quantity of nitric acid, the solution poured into aqueous ammonia containing ammonium carbonate, and air drawn through the liquid for some time. It is then heated on a water-bath with frequent additions of ammonium carbonate, when the colour of the liquid changes to deep red, and allowed to stand till crystallisation is complete. The water of hydration is not removed on heating to 100° C., nor *in vacuo* over sulphuric acid at ordinary temperature.[3]

3. COBALT-AMMINES CONTAINING MONOVALENT CATION, $[CoA_4R_2]^{\cdot}$.

(a) *Hydroxo-acido-tetrammino-cobaltic Salts,* $[Co(NH_3)_4R_2(OH)]R$.

This series is represented by the nitro-salts, $[Co(NH_3)_4(NO_2)(OH)]R$, which are formed by the action of ammonia on aqueous solutions of aquo-nitro-tetrammino-cobaltic salts thus :

$$[Co(NH_3)_4NO_2.H_2O]R_2+NH_3 \longrightarrow [Co(NH_3)_4(NO_2)(OH)]R+NH_4R.$$

In aqueous solution the salts are strongly alkaline, and precipitate silver oxide immediately from silver-nitrate solution. In the moist state they readily combine with carbon dioxide, with formation of a bicarbonate thus :

$$[Co(NH_3)_4NO_2(OH)]R+CO_2 \longrightarrow [Co(NH_3)_4NO_2.HCO_3]R.$$

The salts were at first described by Jörgensen as aquo-salts, as they are formed from acido-nitro-salts by the action of dilute aqueous ammonia ; but this was contradicted by Werner, who showed that they contain a hydroxo-group in the nucleus.[4]

The **chloride,** $[Co(NH_3)_4(NO_2)(OH)]Cl.H_2O$, crystallises in glistening red needles.

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[1] Vortmann and Blasberg, *Ber.*, 1889, 22, 2652.

[2] Werner and Goslings, *ibid.*, 1903, 36, 2378.

[3] Briggs, *Trans. Chem. Soc.*, 1919, 115, 75.

[4] Werner, *Ber.*, 1907, 40, 4133.

The **bromide,** $[Co(NH_3)_4NO_2(OH)]Br.H_2O$, is a dark red crystalline powder, and the **nitrate,** $[Co(NH_3)_4(NO_2)(OH)]NO_3$, crystallises in dark red needles.[1]

(b) *Diacido-tetrammino-cobaltic Salts,* $[Co(NH_3)_4R_2]R$.

In 1856 Gibbs and Genth obtained a green substance by the decomposition of aquo-pentammino-cobaltic sulphate, to which they gave the name *praseo-salt.* In 1871 Rose described a green salt, which he isolated from the oxidation products of an ammoniacal solution of cobaltous chloride. He identified the compound with that obtained by Gibbs and Genth, and showed it to have the composition $Co(NH_3)_4Cl_3.H_2O$. Some time later green salts were prepared by Vortmann[2] from acido-aquo-tetrammino-salts, and in 1897 Werner and Jörgensen[3] carried out researches on these praseo-salts and definitely characterised the compounds as diacido-tetrammino-cobaltic salts. These salts are easily transformed into aquo-salts in aqueous solution.

1-, 6-Dichloro-tetrammino-cobaltic Chloride, Dichloro-praseo-cobaltic Chloride, $[Co(NH_3)_4Cl_2]Cl$.—The compound may be obtained by decomposing a solution of chloro-aquo-tetrammino-cobaltic chloride or the carbonato-tetrammino-salt in concentrated sulphuric acid by the cautious addition of hydrochloric acid, or by precipitation from the acid sulphate of the series, $[Co(NH_3)_4Cl_2]SO_4H$, with concentrated hydrochloric acid. It forms glistening needle-shaped crystals of a green colour which are soluble in water. The aqueous solution is green, but gradually turns violet and then red, due to the formation of chloro-aquo- and diaquo-tetrammino-salts. On heating, the aqueous solution decomposes, and if the salt be dissolved in aqueous ammonia and the liquid treated with hydrochloric acid, chloro-pentammino-cobaltic chloride is formed.

Dichloro-tetrammino-cobaltic chloride forms several crystalline double salts. Thus, with mercuric chloride it gives a pale green crystalline substance of composition $2[Co(NH_3)_4Cl_2]Cl.HgCl_2$, which is only slightly soluble in cold water, and a chloroplatinate, $[Co(NH_3)_4Cl_2]_2PtCl_6$, which is dark green in colour and very stable.

The *bromide,* $[Co(NH_3)_4Cl_2]Br$, and the *iodide,* $[Co(NH_3)_4Cl_2]I$, of the series are also green bodies, and are formed by the addition of hydrobromic and hydriodic acids respectively to the acid sulphate.

The *normal sulphate,* $[Co(NH_3)_4Cl_2]_2SO_4$, has not been isolated, but the acid sulphate has been prepared.

The *acid sulphate,* $[Co(NH_3)_4Cl_2]SO_4H$, is prepared from carbonato-tetrammino-cobaltic chloride by treating it first with hydrochloric acid to remove carbon dioxide and then allowing the reaction mixture to dissolve in concentrated sulphuric acid. The acid salt formed is precipitated with hydrochloric acid.[4] The crude product is dissolved in water and reprecipitated with sulphuric acid. It crystallises in dark green needles and is very soluble in water, giving an acid liquid which is stable.

Isomeric with the praseo-salts just described, Werner[5] prepared a

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[1] Werner, *Ber.*, 1907, 40, 4117; Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 7, 295.

[2] Vortmann, *Ber.*, 1877, 10, 1454.

[3] Werner, *Zeitsch. anorg. Chem.*, 1897, 14, 33; Jörgensen, *ibid.*, 1897, 14, 415.

[4] Werner and Klien, *Zeitsch. anorg. Chem.*, 1897, 14, 28; Werner and Wolberg, *Ber.*, 1905, 38, 992.

[5] Werner, *Ber.*, 1908, 40, 4817.

series of violet-coloured salts, which he named the *violeo-series*, or 1-, 2-*series*.

1-, 2-Dichloro-tetrammino-cobaltic Chloride, Dichloro-violeo-cobaltic Chloride, $[Co(NH_3)_4Cl_2]Cl$, is prepared by the action of hydrochloric acid on octammino-diol-dicobaltic chloride at low temperature. The reaction proceeds thus:

$$[(NH_3)_4Co(OH)_2.Co(NH_3)_4]Cl_4+2HCl \longrightarrow [(NH_3)_4Co(H_2O)_2]Cl_3 + [Co(NH_3)_4Cl_2]Cl.$$

That is, a mixture of 1-, 2-diaquo-tetrammino-cobaltic chloride and 1-, 2-dichloro-tetrammino-cobaltic chloride is formed. The aquo-salt is readily soluble in water but the dichloro-salt sparingly so. The last named forms intense blue crystals which are contaminated with small quantities of the praseo-salt, from which it may be freed by transforming it into the dithionate. The dithionate is practically insoluble, but the chloride may be regenerated from it by rubbing it with ammonium chloride. The *bromide*, the *iodide*, and the *nitrate* have all been prepared.

The chloride crystallises with $\frac{1}{2}H_2O$, which may be removed on heating the salt to 60° C. The other salts are anhydrous. All are intensely blue in colour, and their solutions in water are less stable than the praseo-salts. Even at 0° C. the solutions rapidly change to reddish violet, due to formation of chloro-aquo-salts. If suspended in concentrated hydrochloric acid the chloride is converted into the praseo-salt.

Dibromo-tetrammino-cobaltic Salts, $[Co(NH_3)_4Br_2]R$.—Again there are two series of salts, *praseo-salts* and *violeo-salts*, or the 1-, 6-series and the 1-, 2-series.

1-, 6-Dibromo-tetrammino-cobaltic Bromide, $[Co(NH_3)_4Br_2]Br$, is prepared from carbonato-tetrammino-cobaltic bromide by acting upon it with fuming hydrobromic acid, when the following reaction takes place:—

$$[Co(NH_3)_4CO_3]Br+2HBr \longrightarrow [Co(NH_3)_4Br_2]Br+CO_2+H_2O.$$

The substance is a green amorphous solid.

The corresponding **chloride**, $[Co(NH_3)_4Br_2]Cl.H_2O$, is produced by treating the bromide with concentrated hydrochloric acid. It crystallises in green prismatic needles which are soluble in water and quickly hydrolyse in solution at ordinary temperature, with formation of the aquo-salt.

The **iodide**, $[Co(NH_3)_4Br_2]I$, may be prepared from the chloride by treating it with potassium iodide. It crystallises in greenish-brown needles.

Dibromo-tetrammino-cobaltic Sulphate, $[Co(NH_3)_4Br_2]_2SO_4$, may be obtained, as well as the acid sulphate.[1] All the salts and their derivatives are green in colour, and all decompose in solution with formation of aquo- and diaquo-salts.

The violeo- or 1-, 2-dibromo-tetrammino-cobaltic salts may be prepared by methods similar to those used for the corresponding 1-, 2-dichloro-salts.

1-, 2-Dibromo-tetrammino-cobaltic Nitrate, $[Co(NH_3)_4Br_2]NO_3$, **1-, 2-dibromo-tetrammino-cobaltic sulphate**, $[Co(NH_3)_4Br_2]_2SO_4$, and **1-, 2-dibromo-tetrammino-cobaltic dithionate**,

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[1] Werner and Wolberg, *Ber.*, 1905, 38, 992.

$[Co(NH_3)_4Br_2]_2S_2O_6$, have been prepared. All possess an intense violet-blue colour.

Dinitro-tetrammino-cobaltic Salts, $[Co(NH_3)_4(NO_2)_2]R$.—Two series of salts of this composition are known, the **croceo-salts** and the **flavo-salts**. The two are isomeric, and differ in colour and in method of preparation. They correspond to the isomeric series already described, the croceo-salts being the 1-, 6-, or *trans*-series, and the flavo-salts the 1-, 2-, or *cis*-series.

1-, 6-Dinitro-tetrammino-cobaltic Salts, Croceo-cobaltic Salts.

Trans-series.

1-, 6-Dinitro-tetrammino-cobaltic Nitrate, Croceo-cobaltic Nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3$, is formed when an aqueous solution of 1-, 6-dinitro-tetrammino-cobaltic sulphate is decomposed by the calculated quantity of barium nitrate.[1] It crystallises in orange-yellow needles or prisms, is slightly soluble in cold, and soluble in hot, water.

1-, 6-Dinitro-tetrammino-cobaltic Sulphate, $[Co(NH_3)_4(NO_2)_2]_2SO_4$, is prepared by the action of ammonia and potassium nitrite on an aqueous solution of cobaltous sulphate, or from nitro-pentammino-cobaltic chloride by mixing it with water and sodium nitrite and decomposing the mixture by the gradual addition of 30 per cent. acetic acid. The precipitated *trans*-dinitro-tetrammino-cobaltic nitrite is dissolved in hot water and treated with ammonium-sulphate solution; after standing, a crystalline body separates which is filtered off and washed with water and finally with alcohol. The salt crystallises from water containing a little sulphuric acid in glistening reddish-yellow scales. It is less soluble than the nitrate, and on heating with hydrochloric acid is transformed into chloro-pentammino-cobaltic chloride.[2]

1-, 6-Dinitro-tetrammino-cobaltic Chloride, $[Co(NH_3)_4(NO_2)_2]Cl$, is obtained from the sulphate by treating it with barium chloride, or by heating a solution of dichloro-tetrammino-cobaltic chloride in dilute acetic acid with sodium nitrite.[3] It is soluble in water, and separates from solution in reddish-yellow rhombic crystals. The aqueous solution, however, decomposes on standing. If a cold aqueous solution be treated with dilute nitric acid the nitrate separates; concentrated hydrochloric acid decomposes the salt with formation of the chloro-nitro-chloride, $[Co(NH_3)_4(NO_2)Cl]Cl$.[3]

The *chloroplatinate*, $[Co(NH_3)_4(NO_2)_2]_2PtCl_6$, is obtained by the addition of sodium chloroplatinate to an aqueous solution of the nitrate of the series. It separates in orange-brown prismatic crystals which are readily decomposed and therefore not easily crystallised without decomposition.

1-, 2-Dinitro-tetrammino-cobaltic Salts, Flavo-cobaltic Salts.

Cis-series.

1-, 2-Dinitro-tetrammino-cobaltic Nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3$, is prepared from carbonato-tetrammino-cobaltic nitrate by dis-

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 5, 161.

[2] Jörgensen, *ibid.*, 1898, 17, 472.

[3] Werner, *ibid.*, 1895, 8, 182; Jörgensen, *ibid.*, 1896, 11, 430.

solving it in water and nitric acid, adding sodium nitrite, and warming the mixture until it becomes deep brown in colour. It is then cooled, nitric acid added, and allowed to stand for several hours, when a precipitate of acid and neutral dinitro-tetrammino-cobaltic nitrate is formed. This is collected and washed with dilute nitric acid and then with 95 per cent. alcohol, when the acid salt passes into the neutral salt. The crude product is recrystallised from hot water containing a little acetic acid. It crystallises in yellowish-brown thick prisms, which are more soluble in water than the *trans*-salt, into which it may be converted through the nitro-pentammino-salt.[1]

Acid dinitro-tetrammino-cobaltic Nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3.HNO_3$.—This compound is the first-formed product in the above reaction. It may be obtained by treating the normal nitrate with water and nitric acid. It forms glistening yellow-brown microscopic plates, and is decomposed by alcohol with formation of the normal nitrate.

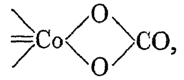
1-,2-Dinitro-tetrammino-cobaltic Sulphate, $[Co(NH_3)_4(NO_2)_2]_2SO_4$, is formed from the nitrate by treating it with water and a solution of ammonium sulphate. The sulphate is precipitated, washed with water, and recrystallised from hot water containing acetic acid.

The *chloride*, $[Co(NH_3)_4(NO_2)_2]Cl$, is formed in the same way by the addition of ammonium chloride. It crystallises in dull yellow rectangular plates or in needles which are very soluble in water. It may also be prepared from chloro-aquo-tetrammino-cobaltic chloride by treating it with sodium nitrite and acetic acid.

Tetrammino-salts containing One Acidic Group in the Complex.

Tetrammino-salts are also known in which a divalent acidic radicle takes the place of two monovalent acidic radicles in the diacido-tetrammino-series, giving rise to *cis*-compounds such as the carbonato-tetrammino- and the oxalato-tetrammino-cobaltic salts.

Carbonato-tetrammino-cobaltic Salts, $[Co(NH_3)_4CO_3]R$.—The examination of this series has been valuable in the investigation of stereo-isomerism in the cobalt-ammines. It is well known that one of the methods by which the configuration of organic isomers is determined depends on the property of the *cis*-forms to yield ring compounds or to be derived by the breaking down of ring compounds. Among inorganic isomers, therefore, similar differences were suggested by Werner. It has been proved that the formation of a ring in inorganic complexes obeys the same laws that apparently control their formation in carbon and nitrogen organic compounds. Hence it is supposed that in the carbonato-complexes, where the carbonato-group occupies two coordinate positions in the octahedron, there must be ring formation giving a complex of the type



where the oxygen atoms directly linked to the metal are in the *cis*-position rather than in the *trans*-position, as such linking seems unlikely between two spatially separated positions thus :

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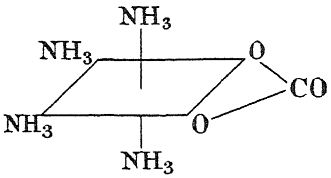
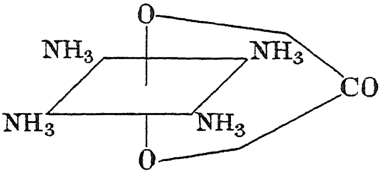
[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 5, 162 ; 1898, 17, 473.

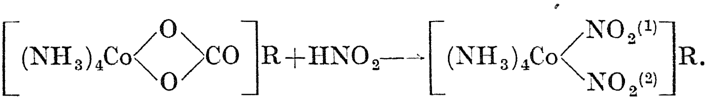


I.
Cis.



II.
Trans.

The *cis*-position is assigned to the carbonato-series, and this seems to be supported by the experimental evidence. Only one series of salts has been prepared, and these salts have been used in the determination of the configuration of the diacido-tetrammino-cobaltic salts. Thus, carbonato-tetrammino-cobaltic salts when treated with acid and sodium nitrite yield *cis*-dinitro-tetrammino-salts. The reaction may be formulated:



$$\left[(NH_3)_4Co\left\langle\begin{matrix}O\\ \\ O\end{matrix}\right\rangle CO\right]R+HNO_2\longrightarrow\left[(NH_3)_4Co\left\langle\begin{matrix}NO_2{}^{(1)}\\ \\ NO_2{}^{(2)}\end{matrix}\right.\right]R.$$

From these salts and from other series of salts where ring formation takes place, such as the oxalato-salts and the diol-dicobaltic salts, the configuration of the *cis*-salts has been deduced.

Carbonato-tetrammino-cobaltic Sulphate, $[Co(NH_3)_4CO_3]_2SO_4.3H_2O$.—The compound was first prepared by Vortmann in 1877, and later examined by him.[1] It is prepared by dissolving cobaltous carbonate in the calculated quantity of warm dilute sulphuric acid and pouring the liquid into concentrated aqueous ammonia and ammonium-carbonate solution. It is then oxidised by leading air through it for two to three hours and the solution concentrated on a water-bath with frequent additions of ammonium carbonate. The cobaltic oxide formed is removed from the solution and the filtrate still further concentrated. On cooling, crystals of the sulphate separate. The salt crystallises in beautiful brownish-red quadratic prisms. It is soluble in dilute sulphuric acid, with evolution of carbon dioxide and formation of diaquo-tetrammino-cobaltic sulphate, $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$. It is sparingly soluble in cold water, and on standing over sulphuric acid the crystals lose water.[2]

Carbonato-tetrammino-cobaltic Nitrate, $[Co(NH_3)_4CO_3]NO_3.\frac{1}{2}H_2O$, is prepared in the same way as the sulphate by the action of nitric acid on cobaltous carbonate. It crystallises in glistening carmine-red rhombic plates and dissolves in water, giving a deep red solution. The crystals lose water at 100° C., but take up water again on standing in air.

The **chloride,** $[Co(NH_3)_4CO_3]Cl$, crystallises in rhombic plates which resemble the nitrate. The *iodide*, $[Co(NH_3)_4CO_3]I$, is prepared in similar manner, using hydriodic acid to decompose the cobaltous carbonate. It forms brownish-violet needles which are sparingly soluble in water.

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[1] Vortmann, *Ber.*, 1877, 10, 1457; 1889, 22, 2650.

[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1892, 2, 281.

The **carbonate,** $[Co(NH_3)_4CO_3]_2CO_3.3H_2O$, is obtained from the iodide by rubbing it with freshly precipitated silver carbonate and a little water. The filtrate, after removal of silver iodide, is gradually treated with three volumes of alcohol, and the precipitate formed is washed with alcohol. It crystallises in red microscopic leaflets belonging to the rhombic system. The substance is soluble in water, the solution obtained being alkaline in reaction. It loses water over sulphuric acid but regains it on standing in air. If heated to 100° C. it decomposes, and only one-third of the carbon dioxide is precipitated by cold aqueous calcium chloride.

Oxalato-tetrammino-cobaltic Salts, $[Co(NH_3)_4(C_2O_4)]R$.—These salts are analogous to the carbonato-salts, and were first described by Jörgensen in 1894.

Oxalato-tetrammino-cobaltic Chloride, $[Co(NH_3)_4(C_2O_4)]Cl$, is prepared by dissolving chloro-aquo-tetrammino-cobaltic chloride in an aqueous solution of oxalic acid and heating the mixture for some time. The oxalato-compound gradually crystallises from the warm solution, and the crystals are collected and washed on the filter with alcohol until the filtrate is free from chlorine and from oxalic acid. It crystallises in carmine-red six-sided plates; if dissolved in concentrated sulphuric acid and concentrated hydrochloric acid is added to the liquid, it is transformed into dichloro-tetrammino-cobaltic chloride. Sodium nitrite and acetic acid convert it into dinitro-tetrammino-cobaltic chloride.[1]

The *bromide*, $[Co(NH_3)_4(C_2O_4)]Br$, is obtained from the chloride by treating a saturated aqueous solution with excess of hydrobromic acid and precipitating the salt from solution with alcohol.

The *sulphate*, $[Co(NH_3)_4(C_2O_4)]_2SO_4.2H_2O$, is formed when an aqueous solution of the chloride is treated with dilute sulphuric acid. It may be precipitated from solution by means of alcohol, and separates in microscopic red plates which are sparingly soluble in water.

The *oxalate*, $[Co(NH_3)_4(C_2O_4)]_2(C_2O_4)$, is also prepared from the chloride by warming it with water and ammonia until it dissolves, and then adding oxalic acid. On cooling, the salt crystallises in glistening reddish-violet plates.

(c) *Diacido-diethylenediamino-cobaltic Salts,* $[Co\ en_2R_2]R$.

Dichloro-diethylenediamino-cobaltic Salts, $[Co\ en_2Cl_2]R$.—This series of salts exists in isomeric forms, the *cis*-series and the *trans*-series. Jörgensen, in 1889, prepared green salts of composition $[Co\ en_2Cl_2]R$,[2] and showed their analogy to the tetrammino-salts. In the following year he described a violet salt, and proved it to be isomeric with the green salts. Werner, in 1901,[3] showed that the salts were stereo-isomers, and that the green salts belonged to the *trans*- or 1-, 6-series, and the violet salts to the *cis*- or 1-, 2-series.

Cis- or 1-, 2-*Salts.*

1-, 2-Dichloro-diethylenediamino-cobaltic Chloride, $[Co\ en_2Cl_2]Cl$, is formed from the *trans*-salt by evaporating a solution of the salt at 100° C. till the weight is constant. The change is almost com-

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1896, 11, 429.

[2] Jörgensen, *J. prakt. Chem.*, 1889, 39, 16; 1890, 41, 448.

[3] Werner, *Ber.*, 1901, 34, 1705.

plete, but the salt is further purified by treating it with small quantities of cold water in which the *trans*-salt is more easily soluble than the *cis*-salt. The treatment is continued until the solution is violet in colour, and the residue is then washed with alcohol and dried in air. The compound is obtained as a dull violet-coloured powder containing one molecule of water, which is lost on heating to 100° C. and regained on exposure to moist air. It dissolves in water, forming a violet-coloured solution, and may be precipitated from aqueous solution with alcohol and ether in microscopic needles which contain no water and which, on exposure, absorb very little moisture. If a solution in dilute hydrochloric acid be evaporated the *trans*-salt is re-formed.

1-, 2-Dichloro-diethylenediamino-cobaltic Nitrate, $[\mathrm{Co\ en_2Cl_2}]\mathrm{NO_3}$, is prepared by treating a solution of the chloride with an equal volume of cold dilute nitric acid, the mixture being stirred constantly during the addition of the acid. The precipitate is collected and washed several times with nitric acid and finally with alcohol. The salt is obtained in small violet prisms which are sparingly soluble in water. If the cold solution in water is treated with chloroplatinic acid a precipitate of the *chloroplatinate*, $[\mathrm{Co\ en_2Cl_2}]_2\mathrm{PtCl_6}$, is produced. This compound is almost insoluble in water and insoluble in alcohol. It crystallises in violet, microscopic, star-like crystals.

Silver nitrate does not precipitate the chlorine in dichloro-diethylenediamino-cobaltic nitrate in cold aqueous solution, but on standing or on heating silver chloride is slowly formed.

Trans- or 1-, 6-*Salts.*

1-, 6-Dichloro-diethylenediamino-cobaltic Chloride, Praseo-salt, $[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$, is obtained from the acid chloride of the series, $[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl.HCl}$, by washing the acid salt with a mixture of alcohol and ether or by heating it to 100° C. It crystallises in dark green eight-sided prisms, is slightly soluble in water, and decomposes in solution on heating or long standing. Fairly strong hydrochloric acid transforms it again into the acid chloride. Sodium nitrite reacts with the salt, forming *cis*-chloro-nitro-salt.[1]

The *acid chloride*, $[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl.HCl.2H_2O}$, is formed by mixing a solution of cobaltous chloride with an aqueous solution of ethylenediamine monohydrate and oxidising the mixture with air. Concentrated hydrochloric acid is then added and the whole heated on a water-bath for one hour. The liquid is allowed to stand, when crystals separate, and are filtered and washed with concentrated hydrochloric acid.[2] The salt crystallises in dark green rhombic plates. It is soluble in water, though less soluble than the normal salt, and on heating to 100° C. is transformed into the normal salt.

1-, 6-Dichloro-diethylenediamino-cobaltic Nitrate, $[\mathrm{Co\ en_2Cl_2}]\mathrm{NO_3}$, is precipitated almost completely from a solution of the chloride by nitric acid. The precipitate is collected, washed with acid and then with alcohol. It is sparingly soluble in water, and if heated with water for some time gives a violet solution.

The corresponding dichloro-tetrapyridino-cobaltic salts, $[\mathrm{Co\ py_4Cl_2}]\mathrm{R}$, have also been prepared. These are analogous to the *trans*-tetrammino-series. All are green crystalline salts.[3]

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[1] Werner and Gerb, *Ber.*, 1901, 34, 1739.

[2] Werner, *ibid.*, 1901, 34, 1733.

[3] Werner and Fenstra, *ibid.*, 1906, 39, 1543.

(d) *Diacido-aquo-triammino-cobaltic Salts*, $[Co(NH_3)_3H_2O.R_2]R$.

Aquo-salts of the dichloro-series are known. These appear to exist in isomeric forms. The constitution of the salts was proved by Werner and Jörgensen.[1]

Dichloro - aquo - triammino - cobaltic Chloride (Dichro - chloride), $[Co(NH_3)_3H_2O.Cl_2]Cl$, may be prepared from trinitrato-triammine cobalt by treatment with concentrated sulphuric acid and subsequent treatment with concentrated hydrochloric acid, or from trinitro-triammino-cobalt on treatment with concentrated hydrochloric acid.[2]

It forms glistening crystals of deep green colour. Under the microscope they are dichroic, and appear to crystallise in pointed hexagonal prisms. The salt is soluble in water, yielding a green solution which changes later to violet. On warming with ammonia, aquo-pentammino-cobaltic chloride is produced.

A chloride of the same composition, but grey in colour, is produced from chloro-diaquo-triammino-cobaltic sulphate by rubbing it with concentrated hydrochloric acid. This salt is a grey powder which dissolves in water, giving a blue solution which quickly changes to violet. Nitric acid converts it into the nitrate, which is light green in colour, and with hydrochloric acid and sulphuric acid it yields the same derivatives as the green dichloride. It is not, however, identical with the green salt, and is probably a stereo-isomer.

The **nitrate**, $[Co(NH_3)_3H_2O.Cl_2]NO_3$, is a greyish-green crystalline powder showing again dichroic properties. It may be obtained in quadratic plates, and is soluble in water.

An **acid sulphate**, $[Co(NH_3)_3H_2O.Cl_2]SO_4H$, is also known. It is prepared from the chloride of the series. It crystallises in short prisms which are almost black in colour. It is easily soluble in water and the solution is acid in reaction.

(e) *Diacido-diaquo-diammino-cobaltic Salts*, $[Co(NH_3)_2(H_2O)_2R_2]R$.

These salts resemble closely the salts just described. The chloride of the series exists, like dichloro-aquo-triammino-cobaltic chloride, in two stereo-isomeric forms.

Dichloro - diaquo - diammino - cobaltic Chloride, $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$, is prepared from potassium tetranitro-diammine cobalt, $[Co(NH_3)_2(NO_2)_4]K$, by mixing it with concentrated sulphuric acid, cooling, and decomposing the sulphate with concentrated hydrochloric acid. It crystallises in light green dichroic needles.

A blue modification is obtained when chloro-triaquo-diammino-cobaltic sulphate, $[Co(NH_3)_2(H_2O)_3Cl]SO_4$, is rubbed with concentrated hydrochloric acid. The salt is green, but on solution in water yields a blue liquid, whilst the first chloride described gives a green liquid.[3]

4. COBALT-AMMINES CONSISTING OF A NON-DISSOCIABLE COMPLEX, $[Co(NH_3)_3R_3]$.

This group of compounds is characterised by the fact that it is not ionised in solution. In 1866 Erdmann[4] prepared a compound to which

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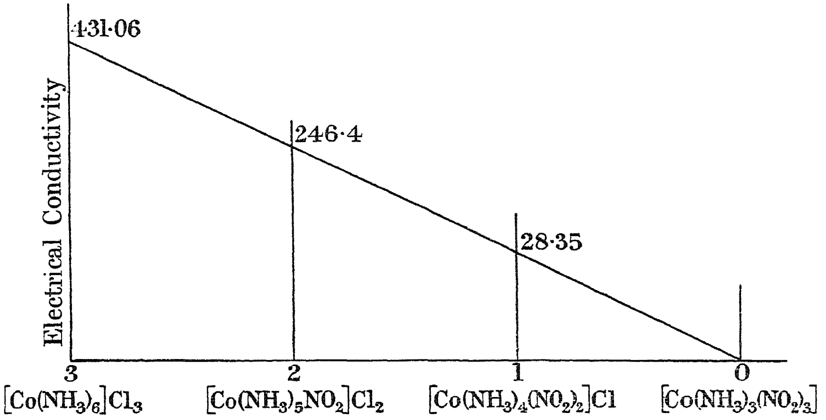
[1] Werner, *Zeitsch. anorg. Chem.*, 1895, 8, 161; Jörgensen, *ibid.*, 1897, 14, 418.

[2] Jörgensen, *ibid.*, 1898, 17, 475.

[3] Werner, *ibid.*, 1897, 15, 172.

[4] Erdmann, *J. prakt. Chem.*, 1866, 97, 412.

he gave the composition $Co_2(NH_3)_6(NO_2)_6$, and the name hexammino-cobalt nitrite. Gibbs, in 1875, showed that the compound did not give the reactions of the hexammino-, pentammino-, or even tetrammino-salts.[1] In 1894 Jörgensen[2] not only prepared the compound by other methods, but also several substances of the same type. Controversy arose regarding the constitution of these bodies, which lasted over some years, until Werner succeeded in proving that the compounds contain equal numbers of basic and acidic radicles symmetrically disposed around the central metallic atom. He assumed that the acidic and ammino-groups are directly linked to the central atom, and the observation is supported by the properties of the compounds. For example, trinitro-triammino-cobalt, $[Co(NH_3)_3(NO_2)_3]$, may be crystallised from hot water containing acetic acid without liberation of nitrous acid, nor is the substance attacked by cold dilute mineral acids. The argument is further supported by determination of the molecular conductivities of different cobalt-ammines. Thus, determining the conductivities of the hexammino-cobaltic chloride, pentammino-nitro-cobaltic chloride, dinitro-tetrammino-cobaltic chloride, and trinitro-triammino-cobalt, the results shown in the following scheme were obtained :—



At 1000 litres dilution at 25° C.

The trinitro-triammine cobalt has practically no conductivity.[3] Werner's theory is further supported by the fact that by the introduction of a fourth molecule of ammonia into the triacido-triammine compound the solution becomes once more conducting, as one (NO_2) group is displaced from the co-ordination complex. The cobalt-ammino-compounds, therefore, containing fewer than three ammino-radicles, contain non-ionisable acidic radicle, and those containing more than three contain ionisable acidic radicles. The generalisation made in connection with the triammino-compounds led, therefore, to the establishment of the constitution of other ammino-derivatives, and also to the constitution of some of the ammino-salts of divalent and tetravalent metals.

Many examples of the triacido-triammine cobalt series are known, and isomerism occurs in the group.

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[1] Gibbs, *Proc. Amer. Acad.*, 1875, 10, 14.

[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1894, 5, 192 ; 1894, 7, 302.

[3] Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, 12, 48 ; 1896, 21, 227.

Trinitro-triammino-cobalt, $[Co(NH_3)_3(NO_2)_3]$, was the first member of the series prepared. It is best prepared by treating a solution of cobaltous chloride with an ammoniacal solution of sodium nitrite and oxidising the mixture by means of air. The liquid after oxidation is allowed to stand for some days, when crystals separate; these are filtered and washed with cold water to free them from chloride, and dissolved in hot water containing a little acetic acid. On cooling the acid liquid trinitro-triammine cobalt separates out, and later, from the same solution, the double salt, $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, separates.[1]

The crude substance is then recrystallised from water containing acetic acid. The compound was originally believed to exist in two isomeric forms, but Jörgensen found the crystalline form depends on the concentration of acetic acid used for crystallisation, inasmuch as rhombic leaflets separate from hot dilute acetic acid, and from hot concentrated acid the substance separates in yellow-brown needles. The complex is sparingly soluble in water, and gives no precipitate in aqueous solution with silver nitrate or potassium chromate. If treated with cold hydrochloric acid it is transformed into chloro-dinitro-triammino cobalt, $[Co(NH_3)_3(NO_2)_2Cl]$, and if warmed with concentrated hydrochloric acid gives dichloro-aquo-triammino-cobaltic chloride.

Trinitrato-triammino-cobalt, $[Co(NH_3)_3(NO_3)_3]$, is produced by passing air for thirty-six hours through an aqueous solution of cobaltous nitrate containing ammonia and ammonium nitrate. The liquid is then evaporated until there is no evolution of ammonia, nitric acid in the proportions of one volume of concentrated acid to two volumes of water is added, and the precipitate of anhydroxy-cobaltate nitrate, $[Co_2O_2(NH_3)_{10}(NO_3)_5]$, removed by filtration. The filtrate is again evaporated and any aquo-pentammino-cobaltic nitrate formed is thus transformed into nitrato-pentammino-cobaltic nitrate, which is precipitated on cooling the solution. The violet filtrate is thereafter evaporated almost to dryness, when trinitrato-triammino-cobalt separates as a violet powder. The substance crystallises in red-violet prisms which are insoluble in cold water. If the aqueous solution be left to stand for several hours, or if warmed, it is gradually transformed into a solution of triaquo-triammino-cobaltic nitrate, $[Co(NH_3)_3(H_2O)_3](NO_3)_3$.[2]

Oxalato-nitro-triammino-cobalt, $[Co(NH_3)_3(C_2O_4)(NO_2)]$, is prepared from oxalato-aquo-triammino-cobaltic nitrate, $[Co(NH_3)_3C_2O_4.H_2O]NO_3$, by treating the warm aqueous solution with acetic acid and sodium nitrite. The precipitate formed is filtered, washed, and finally rubbed with dilute sulphuric acid until no more nitrous acid is evolved. It is then collected and washed free from acid with water and alcohol. It crystallises in brick-red shining scales which are almost insoluble in water.[3]

Tschugaeff[4] prepared a dimethylglyoxime derivative of this series, chloro-ammino-dimethylglyoxime-cobalt, $[Co(NH_3)(D_2H_2)Cl]$ (where D_2H_2 represents two molecules of dimethylglyoxime), from chloro-pentammino-cobaltic chloride and dimethylglyoxime. It crystallises in dark-brown needles or prisms, is stable towards acids and alkali, and forms a non-conducting solution. The corresponding nitro-compound,

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1897, 13, 175; 1898, 17, 475.
[2] Jörgensen, *ibid.*, 1895, 5, 185.
[3] Werner, *ibid.*, 1897, 15, 164.
[4] Tschugaeff, *Ber.*, 1906, 39, 2694.

$[Co(NH_3)(D_2H_2)(NO_2)]$, has also been prepared. It separates from hot water in small yellow-brown prisms and the nitro-group is un-ionised.

5. COBALT-AMMINES CONTAINING MONOVALENT ANION, $[CoA_2R_4]'$.

Tetra-acido-diammino-series, $[Co(NH_3)_2R_4]M$.

Erdmann,[1] in 1866, prepared the first member of this series, namely, **ammonium tetranitrito-diammino-cobaltate,** $[Co(NH_3)_2(NO_2)_4]NH_4$. The salt is sometimes referred to as "Erdmann's salt" on that account. Later, Gibbs prepared other salts of the same type, and showed that in these salts the cobalt atom, united with ammonia and acidic radicles, forms a negative radicle.[2] Werner then showed that these salts form the connecting link between the neutral un-ionised complex triacido-triammino-cobalt compounds and the double salt, such as potassium cobalti-nitrite. Thus, by replacement of ammonia molecules by acid radicles a transition takes place from trinitrito-triammino-cobalt to potassium tetranitrito-diammino-cobaltate, $[Co(NH_3)_2(NO_2)_4]K$, then to potassium pentanitrito-ammino-cobaltate, $[Co(NH_3)(NO_2)_5]K$, and finally to hexanitrito-cobaltate, $[Co(NO_2)_6]K_3$. Tetra-acido-diammino-cobaltates are therefore the salts of the acid tetra-acido-diammino-cobaltic acid, $[Co(NH_3)_2R_4]H$.

Tetranitrito-diammino-salts, $[Co(NH_3)_2(NO_2)_4]M$.

Ammonium Tetranitrito-diammino-cobaltate, $[Co(NH_3)_2(NO_2)_4]NH_4$, is prepared from cobaltous chloride by mixing an aqueous solution of the salt with aqueous ammonium-chloride solution, sodium nitrite, and ammonia, and oxidising the mixture by passing air through it for several hours. The solution is allowed to stand in air for some days, when crystals gradually separate. These are collected, washed, and recrystallised from water.[3] The substance crystallises in brown rhombic prisms. It is decomposed on treatment with potassium hydroxide with evolution of ammonia, and a cold solution reacts with ammonia in presence of ammonium salts, with formation of flavo-dinitro double salts, of which $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$ is typical. Oxalic acid transforms it into the oxalato-dinitrito-diammino-salt, $[Co(NH_3)_2(NO_2)_2(C_2O_4)]NH_4$.

Potassium Tetranitrito-diammino-cobaltate, $[Co(NH_3)_2(NO_2)_4]K$.—The salt is produced by treating cobaltous chloride with excess of ammonium chloride and potassium nitrite, and warming the liquid to 50° C. It is then allowed to stand at low temperature for several hours, when crystals separate. They are dissolved in boiling water, filtered and cooled, when lustrous brown rhombic crystals separate. The salt may be obtained from the ammonium salt by treating a warm aqueous solution with potassium acetate.

The **dichloro-tetra-aquo-chromic salt,** $[Co(NH_3)_2(NO_2)_4][Cr(H_2O)_4Cl_2].2H_2O$, is formed when the ammonium salt is mixed with green chromic chloride in water, the reaction being represented thus:

$$[Co(NH_3)_2(NO_2)_4]NH_4 + CrCl_3.6H_2O \longrightarrow [Co(NH_3)_2(NO_2)_4][Cr(H_2O)_4Cl_2].2H_2O + NH_4Cl.$$

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[1] Erdmann, *J. prakt. Chem.*, 1866, 97, 410.

[2] Gibbs, *Proc. Amer. Acad.*, 1875, 10, 10.

[3] Jörgensen, *Zeitsch. anorg. Chem.*, 1898, 17, 477.

Chromic bromide reacts in the same way, yielding the dibromotetraquo-chromic salt, $[Co(NH_3)_2(NO_2)_4][Cr(H_2O)_4Br_2].2H_2O$, and hexammino-cobaltic chloride forms the double salt, $[Co(NH_3)_2(NO_2)_4]_3[Co(NH_3)_6]$.

A large number of double salts of this series are therefore possible, as also a number of salts where one or more nitrito-groups in the complex is replaced by other acidic radicles.

6. COBALT SALTS CONTAINING TRIVALENT ANION, $[CoR_6]'''$.

These are not, strictly speaking, members of the metal-ammines, inasmuch as all ammonia is replaced by acid groups, but they are the ultimate complex compounds arrived at in the systematic replacement of ammonia, and must therefore be briefly discussed at this stage.

The best known of these compounds is **potassium cobalti-nitrite,** $[Co(NO_2)_6]K_3$.[1] This salt was originally regarded as a double salt of cobaltic nitrite with potassium nitrite, and represented by the formula $Co(NO_2)_3.3KNO_2$. Such a formula, however, does not represent the reactions of the substance, as the nitrite radicle is held firmly, and nitrous acid is not liberated when the compound is treated with cold dilute acids, as it would be if it were a double salt as the formula indicates. Molecular conductivity measurements also indicate that it is a complex salt comparable with the metal-ammines. Many compounds of cobalt of this type are known. They may be regarded as the salts of the complex acid hexanitrito-cobaltic acid, $[Co(NO_2)_6]H_3$.

Other acid radicles may be united with cobalt in the complex; for instance, potassium cobalti-cyanide, $[Co(CN)_6]K_3$, and potassium cobalti-oxalate, $[Co(C_2O_4)_3]K_3$.[2]

B. Polynuclear Cobalt-ammines.

These compounds contain two or more cobalt atoms in the molecule linked together by oxygen, amino- or hydroxyl-groups, or by more than one of these groups.

Compounds belonging to this class of complex ammines have been known for a long time. The oxy-cobalt-ammino-salts, produced by the action of air on an ammonia solution of cobaltous salt, were produced about 1852; and later, Gibbs and Vortmann[3] examined these compounds, but did not succeed in explaining their constitution. In 1898 Werner and Mylius[4] examined the nitrate of the series and showed it to be an oxy-cobalt-ammine in which two molecules of pentammino-cobaltic salt are linked together by oxygen. Other members of the series were prepared later, and in 1910 Werner[5] published a summary of the investigations into the constitution of the polynuclear cobalt-ammines, and also described the preparation and properties of several compounds not before prepared.

It has been proved that in those compounds cobalt atoms are never linked directly to one another, but always through oxygen, amino-,

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[1] For further details of this salt see Vol. IX., Part I., of this series.

[2] *Ibid.*, pp. 60, 69.

[3] Gibbs, *Proc. Amer. Acad.*, 1876, 11, 38; Vortmann, *Monatsh.*, 1885, 6, 404.

[4] Werner and Mylius, *Zeitsch. anorg. Chem.*, 1898, 16, 245.

[5] Werner, *Annalen*, 1910, 375, 1.

imino-, or hydroxo-groups. The polynuclear cobalt-ammines are classified, first, by the number of cobalt atoms in the molecule, and, further, by the number of bridged linkages in the complex. It is found that oxygen of a hydroxyl group linked to cobalt is capable of uniting with another cobalt atom, giving rise to the linkage, $\mathrm{Co—\overset{H}{\dot{O}}\cdots Co}$. In the same way an amino-group linked to cobalt is able to attract to itself another cobalt atom giving rise to the linkage, $\mathrm{Co—\overset{H_2}{\dot{N}}\cdots Co}$. This type of linking seems to be very firm, and gives rise to the polynuclear compounds of cobalt. Further, an oxygen molecule may form the connecting link, in which case the peroxo-compounds are produced.

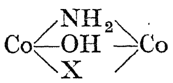
The substances are conveniently classified by the number of cobalt atoms in the molecule into (1) dicobalt-ammines, (2) tricobalt-ammines, (3) tetracobalt-ammines.

Class (1) is further subdivided into:

(*a*) Compounds with one bridged linkage, represented by the general formula Co—X—Co (where X represents (NH_2) or O_2).

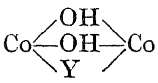
(*b*) Compounds with two bridged linkages, represented by the general formula $\mathrm{Co}\left\langle\begin{matrix}\mathrm{X}\\ \mathrm{Y}\end{matrix}\right\rangle\mathrm{Co}$, where X represents (OH) or NH_2, and Y, NH_2, (OH), O_2, NO_2; and by the formula $\mathrm{Co}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{Y}\end{matrix}\right\rangle\mathrm{Co}$, where Y represents (SO_4) or (C_2O_4).

(*c*) Compounds with three bridged linkages, represented by the general formula



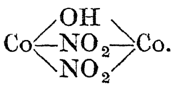
$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\\ \mathrm{X}\end{matrix}\right\rangle\mathrm{Co}$$

or



$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{Y}\end{matrix}\right\rangle\mathrm{Co}$$

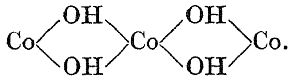
or



$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{NO_2}\\ \mathrm{NO_2}\end{matrix}\right\rangle\mathrm{Co}.$$

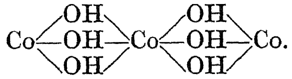
Class (2) is subdivided into:

(*a*) Compounds with four bridged linkages, represented by the general formula



$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right\rangle\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right\rangle\mathrm{Co}.$$

(*b*) Compounds with six bridges, represented by the formula



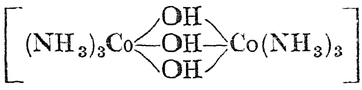
$$\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right\rangle\mathrm{Co}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right\rangle\mathrm{Co}.$$

At least twenty different cobalt nuclei have been found in these compounds, but in all of these the number of bridges never exceeds three between any two cobalt atoms.

In these compounds the maximum co-ordination, whether of trivalent or tetravalent cobalt, appears to be six, as in the case of the simpler cobalt-ammines.

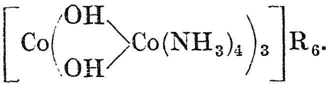
Isomerism in the Polynuclear Cobalt-ammines.—The isomerism in the series has been classified in the following way. Polymerisation isomerism, valency isomerism, co-ordination isomerism, and isomerism due to asymmetric cobalt complexes respectively.

1. *Polymerisation isomerism* may be compared with polymerisation in organic compounds, and just as benzene may be regarded as a polymer of acetylene, so in the polynuclear cobalt-ammines the same type of isomerism may occur. For example, dodecammino-hexol-tetracobaltic salts are polymers of hexammino-triol-dicobaltic salts thus :



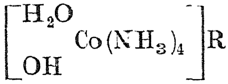
$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]R_3$$

and



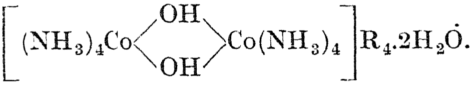
$$\left[Co\left(\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right)_3\right]R_6.$$

Also hydroxo-aquo-tetrammino-cobaltic salts polymerise to give octammino-diol-dicobaltic salts thus :



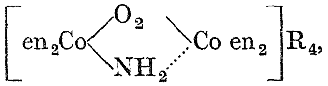
$$\left[\begin{matrix}H_2O\\ & Co(NH_3)_4\\OH\end{matrix}\right]R_2$$

and



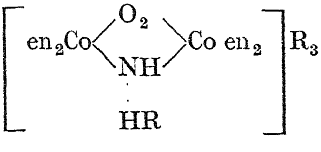
$$\left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]R_4.2H_2O.$$

2. *Valency isomerism* is possible, depending on whether the bridging nitrogen of an amino-group is linked to one cobalt atom through a principal valency bond, and to the other cobalt atom by a subsidiary valence, as in the formula



$$\left[en_2Co\begin{matrix}O_2\\NH_2\end{matrix}Co\ en_2\right]R_4,$$

which represents tetraethylenediamino-μ-amino-peroxo-dicobaltic [1] salts, or by the bridging atom of the amino-group being linked to both cobalt atoms by principal valency bonds, and one hydrogen atom being linked by principal, and the other by subsidiary, valence, as in the formula

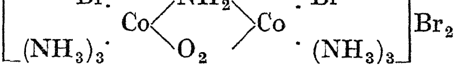


$$\left[\begin{matrix}en_2Co\begin{matrix}O_2\\NH\end{matrix}Co\ en_2\\ \cdot\\ HR\end{matrix}\right]R_3$$

tetraethylenediamino-μ-ammonium-peroxo-dicobaltic salts.

These two isomeric complex salts differ in colour, the former being green and the latter red. Also, the former are neutral in reaction, whilst the latter have an acid reaction in solution.[2]

3. *Co-ordination Position Isomerism.*—This type of isomerism occurs through the arrangement of the groups around each cobalt atom with respect to the bridged linkage. For example, there are two dibromo-hexammino-μ-amino-peroxo-dicobaltic bromides which are represented by the formulæ



$$\left[\begin{matrix}Br. & & & & .\ Br\\ & Co\begin{matrix}NH_2\\O_2\end{matrix}Co & & & \\(NH_3)_3\cdot & & & & \cdot\ (NH_3)_3\end{matrix}\right]Br_2$$

The symmetrical bromide.

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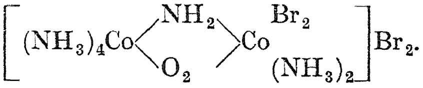
[1] The linking group common to two cobalt atoms is denoted by μ. For example, $\mu-NH_2$ in this series.

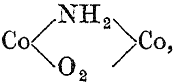
[2] Werner, *Annalen*, 1910, 375, 1.

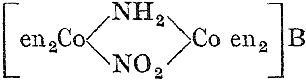
and



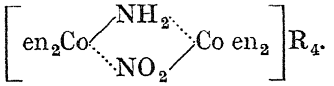
$$\left[(NH_3)_4Co\begin{matrix}\diagup NH_2\diagdown\\ \diagdown O_2\diagup\end{matrix}Co\begin{matrix}Br_2\\ (NH_3)_2\end{matrix}\right]Br_2.$$

Asymmetrical bromide.

The corresponding chlorides may be obtained in symmetrical and asymmetrical forms. These isomers have the same nucleus,  $Co\begin{matrix}\diagup NH_2\diagdown\\ \diagdown O_2\diagup\end{matrix}Co$, and the difference lies in the disposition of the ammonia molecules and the acidic radicles in the complex. Both the symmetrical and the asymmetrical salts are intensely green in colour, and resemble one another closely in appearance although differing in chemical reactions.

4. *Isomerism due to Asymmetric Cobalt Atoms.*—Werner established his formulæ for the cobalt-ammines by proving the fact suggested by his theory that certain of the cobalt atoms in the ammines were centres of asymmetry, and therefore optical activity should be possible. Having established this for some of the simple cobalt-ammines, he then showed that in many of the polynuclear compounds optical activity exists. Thus he prepared optically active isomers of tetraethylenediamino-μ-amino-nitro-dicobaltic bromide,  $\left[en_2Co\begin{matrix}\diagup NH_2\diagdown\\ \diagdown NO_2\diagup\end{matrix}Co\,en_2\right]Br_4$,[1] and proved it to exist in four isomeric forms, namely, lævo-rotatory and dextro-rotatory isomers, with equal and opposite rotation of $[\alpha]^{16}\pm 164°$; a racemic form made up of equal quantities of l- and d-forms ; and finally a form which could not be resolved by any means, the meso-isomer, which is inactive by reason of internal compensation. This substance may be regarded as the cobalt analogue of tartaric acid.

Previous to this resolution Werner had represented the compound and similar compounds with the two cobalt atoms linked slightly differently thus :



$$\left[en_2Co\begin{matrix}\diagup NH_2\cdot.\\ \cdot.NO_2\diagup\end{matrix}Co\,en_2\right]R_4.$$

The optical investigation described does not indicate any such difference, and from this and other evidence it must be concluded that there is no essential difference between principal and auxiliary valence.

1. DICOBALT-AMMINES.

(a) *Compounds with One Bridged Linkage.*

Decammino - μ - amino - dicobaltic Salts, $[(NH_3)_5Co—NH_2Co(NH_3)_5]R_5$.—These salts are obtained from the octammino-μ-amino dicobaltic salts. They form the series richest in ammonia of the dicobalt-ammines containing the amino-group.[2]

The salts are characterised by their beautiful reddish-blue colour and the lustre of the crystals. All the normal salts of the series are neutral in solution, and their constitution has been proved by the

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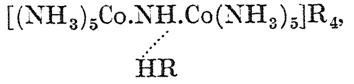
[1] Werner, *Ber.*, 1913, 46, 3674.

[2] Werner, *ibid.*, 1908, 41, 3912.

behaviour of the compounds towards mineral acids. If treated for some time with a mixture of hydrochloric acid and sulphuric acid at 100° C., they are decomposed into a mixture of chloro-pentammino- and hexammino-cobaltic salts. This result points to only one possible arrangement of the ammonia molecules, and the decomposition may be represented by the reaction:

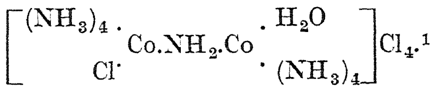
$$[(NH_3)_5Co\cdots CNH_2.Co(NH_3)_5]Cl_5+HCl \longrightarrow [Co(NH_3)_6]Cl_3 + [Co(NH_3)_5Cl]Cl_2.$$

Isomeric with the series are the salts of formula

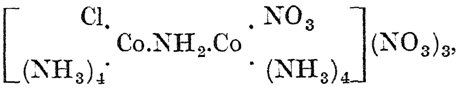

$$\begin{matrix}[(NH_3)_5Co.NH.Co(NH_3)_5]R_4,\\ \vdots\\ HR\end{matrix}$$

which show acidic properties in aqueous solution.

Decammino-μ-amino-dicobaltic Nitrate, $[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)_5$, is prepared from chloro-aquo-octammino-μ-amino-dicobaltic chloride,


$$\left[\begin{matrix}(NH_3)_4. & & .H_2O\\ & Co.NH_2.Co & \\ Cl^{\cdot} & & {}^{\cdot}(NH_3)_4\end{matrix}\right]Cl_4.$$[1]

A freshly prepared solution of this compound is decomposed by concentrated nitric acid, and a greyish-violet precipitate of chloro-nitrato-μ-amino-dicobaltic nitrate,


$$\left[\begin{matrix}Cl. & & .NO_3\\ & Co.NH_2.Co & \\ (NH_3)_4^{\cdot} & & {}^{\cdot}(NH_3)_4\end{matrix}\right](NO_3)_3,$$

is formed.

The precipitate is dried and mixed with liquid ammonia, in which it dissolves, giving a brown solution. The excess of ammonia is allowed to evaporate and the residue heated with water at 100° C. until no more dissolves. The insoluble residue of the decammino-salt is filtered and recrystallised from boiling water containing a little acetic acid.

The salt crystallises in long shining needles of a bluish-red colour. It is sparingly soluble in water and the solution is neutral. It may be precipitated from aqueous solution with nitric acid, and it is not decomposed on heating with concentrated nitric acid.

Decammino-μ-amino-dicobaltic Chloride, $[(NH_3)_5.CoNH_2Co(NH_3)_5]Cl_5.H_2O$, is obtained from the nitrate by dissolving it in water and adding an excess of ammonium chloride; the treatment with ammonium chloride is repeated, and the product is then carefully recrystallised from water. It crystallises in fine rose-red needles. It is more soluble in water than the nitrate, and the solution is deep red in colour and neutral in reaction. Neither dilute nor concentrated hydrochloric acid, even on heating, decomposes the salt, but if it be dissolved in concentrated sulphuric acid, and an equal volume of concentrated hydrochloric acid added and the mixture heated, it gradu-

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[1] Werner, *Ber.*, 1908, **41**, 3916.

ally decomposes into a mixture of hexammino-salt and chloro-pentammino-salt.

The **bromide,** $[(NH_3)_5Co.NH_2.Co(NH_3)_5]Br_5.H_2O$, is prepared in the same manner, using ammonium bromide in place of the chloride.

The **sulphate,** $[(NH_3)_5Co.NH_2.Co(NH_3)_5]_2(SO_4)_5.3H_2O$, may be obtained by decomposing the bromide with sodium sulphate. It is slightly soluble in water, giving a pale red solution, and it crystallises in small shining needles.

Decammino-μ-oxy-dicobaltic Salts, $[(NH_3)_5Co'''.O_2.Co'''(NH_3)_5]R_4$, and **Decammino-$\mu$-anhydroxy-dicobaltic Salts,** $[(NH_3)_5Co'''.O_2.Co^{IV}(NH_3)_5]R_5$.—The two series of salts are very closely related, the latter being derived from the former. In the first series both cobalt atoms are trivalent; in the second series one cobalt atom is assumed to be tetravalent. The oxy-salts were among the first of the polynuclear compounds prepared and examined, and in 1898 Werner and Mylius prepared the nitrate of the series and proved the constitution of these salts, showing them to be compounds formed by the union of two pentammino-cobalt nuclei by means of a molecule of oxygen.

Decammino-μ-oxy-dicobaltic Nitrate, $[(NH_3)_5Co.O_2.Co(NH_3)_5](NO_3)_4.2H_2O$, may be prepared by oxidising an ammoniacal solution of cobaltous nitrate by passing through it a stream of air. After allowing the solution to stand for some time a crystalline precipitate separates, which is collected, washed with aqueous ammonia and with alcohol, and dried. The substance crystallises in brown prisms, which become green on drying. It decomposes with explosion if heated to 200° C., and is transformed into ammonium sulphate, cobaltous sulphate, and oxygen on treatment with cold sulphuric acid. Hot concentrated hydrochloric acid decomposes the salt, chlorine being evolved and cobaltous chloride and ammonium chloride left as a residue.

If heated to 100° C. for some time until there is no further change in weight, the salt is completely decomposed, and on treating the residue with water, filtering, and mixing the filtrate with concentrated hydrochloric acid, a mixture of hexammino-cobaltic chloride, chloro-pentammino-cobaltic chloride is obtained.[1]

The **sulphate,** $[(NH_3)_5Co.O_2.Co(NH_3)_5](SO_4)_2.3H_2O$, is formed in the same way as the nitrate from cobaltous sulphate, ammonia, and air. It crystallises in olive-green leaflets, is more stable than the nitrate, but has the same general reactions.

The **chloride,** $[(NH_3)_5Co.O_2Co(NH_3)_5]Cl_4.H_2O$, is formed by the oxidation of an ammoniacal solution of cobaltous chloride. From dilute alcohol it may be obtained in greenish-brown iridescent leaflets. It is unstable, and decomposes both in solution and in the dry state.

Decammino-μ-anhydroxo-dicobaltic Salts, $[(NH_3)_5Co^{III}.O_2.Co^{IV}(NH_3)_5]R_5$.—In 1833 Maquenne [2] obtained a green sulphate by the action of sulphuric acid on the oxy-salt, which he believed to be the acid sulphate. Vortmann, later, showed that the compound belonged to a new series of salts, and by an erroneous interpretation assumed that the salt was formed by replacing a hydroxyl group in the complex by an acid radicle. Hence he gave the salts the name anhydroxy-dicobaltic salts. In 1898, however, Werner and Mylius succeeded in proving that these

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[1] Werner and Mylius, *Zeitsch. anorg. Chem.*, 1898, 16, 261.

[2] Maquenne, *Compt. rend.*, 1883, 96, 344.

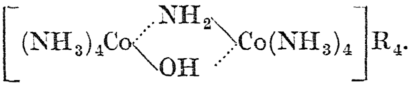
[3] Vortmann, *Monatsh.*, 1885, 6, 437.

compounds are formed by uniting a pentammino-cobalto^{III} radicle with a pentammino-cobaltic^{IV} radicle by means of a molecule of oxygen.[1]

Decammino-μ-anhydroxy-dicobaltic Nitrate, $[(\mathrm{NH_3})_5\mathrm{Co^{III}O_2Co^{IV}(NH_3)_5}](\mathrm{NO_3})_5$.—The salt is obtained from cobaltous carbonate by treating it with nitric acid, ammonium nitrate, and ammonia.[2] It crystallises in dark green needles and is very quickly decomposed by water. The salts of this series are all dark green in colour and are unstable in aqueous solution.

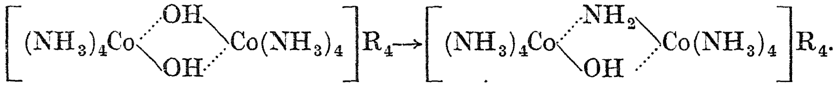
(b) *Compounds with Two Bridged Linkages.*

Octammino-μ-amino-ol-dicobaltic Salts,



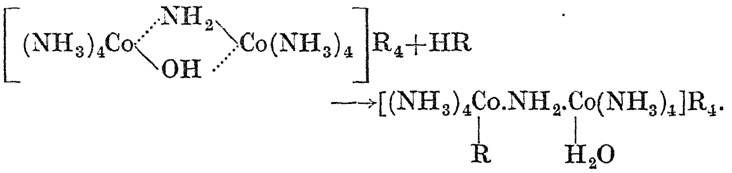
$$\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]\mathrm{R_4}.$$

The sulphate of the series is the chief constituent of the so-called Vortmann's salt,[3] obtained by the oxidation of an ammoniacal solution of cobaltous nitrate and cautious neutralisation with sulphuric acid. Two compounds can be isolated, one red, the other green. The red salt was regarded by Werner and Baselli as imino-octammino-dicobaltic salt of formula $[(\mathrm{NH_3})_4\mathrm{Co.NH.Co}(\mathrm{NH_3})_4]\mathrm{R_4}$. Werner, however, proved that the red salt is analogous to the octammino-diol-dicobaltic salts, and to be derived from these by the substitution of a hydroxyl group by $(\mu)(\mathrm{NH_2})$ group thus :



$$\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]\mathrm{R_4}\rightarrow\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]\mathrm{R_4}.$$

The hydroxyl group in this series is easily removed by acids ; the amino-group, on the other hand, is much more stable, and is only split off from one of the cobalt atoms by the action of concentrated acids. Cold concentrated hydrochloric acid, hydrobromic acid, or nitric acid cause the removal of the hydroxyl group in the following way :—

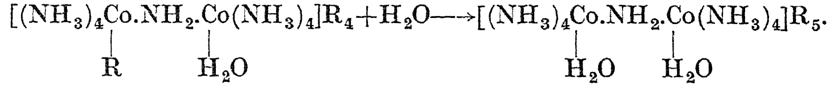


$$\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]\mathrm{R_4}+\mathrm{HR}$$
$$\longrightarrow[(\mathrm{NH_3})_4\underset{\mathrm{R}}{\mathrm{Co}}.\mathrm{NH_2}.\underset{\mathrm{H_2O}}{\mathrm{Co}}(\mathrm{NH_3})_4]\mathrm{R_4}.$$

Acido-aquo-octammino-μ-amino-cobaltic salt.

The salts are transformed into the decammino-salts on treatment with liquid ammonia.

These aquo-derivatives are typical aquo-salts, and behave like the aquo-salts of the single cobalt-ammines. In aqueous solution they are further hydrated thus :



$$[(\mathrm{NH_3})_4\underset{\mathrm{R}}{\mathrm{Co}}.\mathrm{NH_2}.\underset{\mathrm{H_2O}}{\mathrm{Co}}(\mathrm{NH_3})_4]\mathrm{R_4}+\mathrm{H_2O}\longrightarrow[(\mathrm{NH_3})_4\underset{\mathrm{H_2O}}{\mathrm{Co}}.\mathrm{NH_2}.\underset{\mathrm{H_2O}}{\mathrm{Co}}(\mathrm{NH_3})_4]\mathrm{R_5}.$$

Diaquo-octammino-μ-amino-dicobaltic salt.

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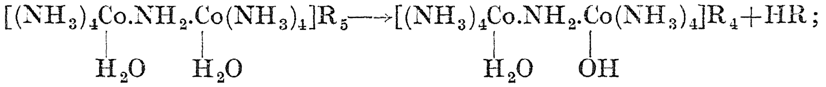
[1] Werner and Mylius, *Zeitsch. anorg. Chem.*, 1898, 16, 261.

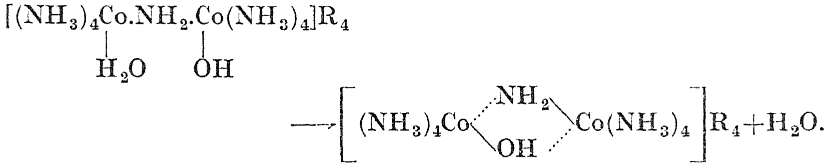
[2] Jörgensen, *ibid.*, 1894, 5, 185.

[3] Werner, *Ber.*, 1907, 40, 4609.

The diaquo-salts then undergo further reaction, and may be transformed again into octammino-μ-amino-ol-dicobaltic salts thus :

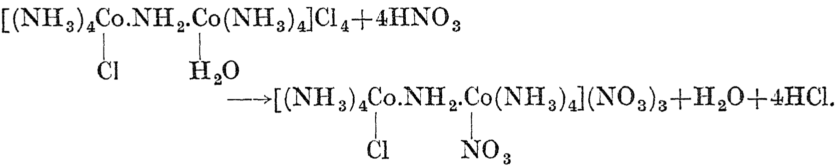


$$[(NH_3)_4\underset{H_2O}{Co}.NH_2.\underset{H_2O}{Co}(NH_3)_4]R_5 \longrightarrow [(NH_3)_4\underset{H_2O}{Co}.NH_2.\underset{OH}{Co}(NH_3)_4]R_4 + HR;$$



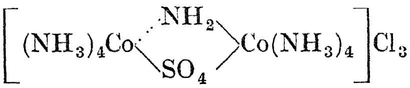
Therefore, if the acido-aquo-octammino-μ-amino-cobaltic salts in solution be left to stand for some time, they are converted into the less soluble octammino-μ-amino-ol-salts, which then crystallise from the solution.

The acido-aquo-salts can change into diacido-salts on treatment with acid. For example, if chloro-aquo-octammino-μ-amino-dicobaltic chloride be treated with concentrated nitric acid the molecule of water is replaced by the nitrate radicle, giving chloro-nitrato-octammino-μ-amino-dicobaltic nitrate,

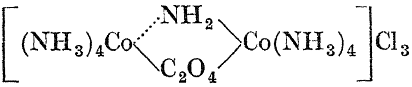


$$[(NH_3)_4\underset{Cl}{Co}.NH_2.\underset{H_2O}{Co}(NH_3)_4]Cl_4+4HNO_3 \longrightarrow [(NH_3)_4\underset{Cl}{Co}.NH_2.\underset{NO_3}{Co}(NH_3)_4](NO_3)_3+H_2O+4HCl.$$

Dibasic acids, on the other hand, replace the hydroxyl group by acidic radicle, giving rise to compounds such :

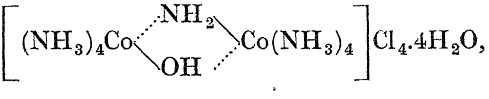


with sulphuric acid, and



with oxalic acid.[1]

Octammino-μ-amino-ol-dicobaltic Chloride,



is prepared from a mixture of cobaltous nitrate in aqueous solution and ammonia. The mixture is oxidised by means of air at a temperature of 30° C., and then carefully neutralised with sulphuric acid at low temperature. After standing for some time a reddish-brown precipitate separates, which was originally named "Vortmann's sulphate." This is washed with water and then rubbed with concentrated nitric

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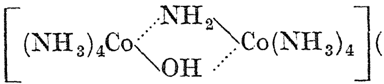
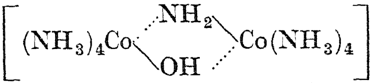
[1] Werner and Baselli, *Zeitsch. anorg. Chem.*, 1898, **16**, 11.

acid until it solidifies again, and the residue washed free from acid. The residue, composed of a red and a green compound, is then treated with water until the green salt goes into solution. The remaining red salt, octammino-μ-amino-sulphato-dicobaltic nitrate, is shaken with concentrated hydrochloric acid and allowed to stand until the colour changes to brown, when it is collected, washed with water and alcohol, and dried. The crude chloride so produced is dissolved in water and reprecipitated with concentrated hydrochloric acid. It may be recrystallised from water at ordinary temperature by evaporating the solution in a desiccator.

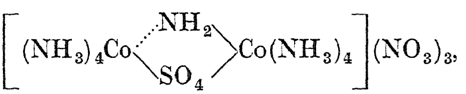
The compound is slightly soluble in cold water and easily soluble in hot water. If heated with hydrochloric acid for a considerable time it decomposes into chloro-pentammino-cobaltic chloride and dichloro-tetrammino-cobaltic chloride. It crystallises in glistening brownish-red prisms.

The **sulphate**,  $\left[(NH_3)_4Co\begin{matrix}NH_2\\ OH\end{matrix}Co(NH_3)_4\right](SO_4)_2.2H_2O$, is obtained by decomposing the chloride, dissolved in very dilute acetic acid, with silver nitrate, filtering the solution and decomposing the filtrate with dilute sulphuric acid. It forms brownish-red prismatic crystals. It is insoluble in water, and loses two molecules of water if left over phosphorus pentoxide, and is decomposed by concentrated sulphuric acid.

The **nitrate**,  $\left[(NH_3)_4Co\begin{matrix}NH_2\\ OH\end{matrix}Co(NH_3)_4\right](NO_3)_4$, is also obtained from the chloride. It is only slightly soluble in water, and crystallises in dark red needles.

Many derivatives of this series of salts have been prepared. For example, the chloride, if freshly prepared, yields in aqueous solution crystalline salts with chloroplatinic acid, potassium iodide, and mercuric chloride,[1] and numerous acido-derivatives have been prepared.

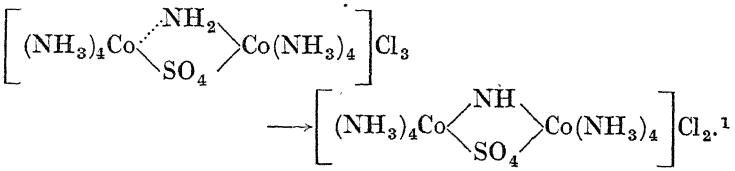
Octammino-μ-amino-sulphato-dicobaltic Nitrate,



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_3,$$

is formed by adding concentrated nitric acid to the corresponding sulphate solution, prepared by heating octammino-μ-amino-ol-dicobaltic salts with sulphuric acid. It crystallises in violet-red prisms.

The **bromide** crystallises in leaflets containing one molecule of water. The **chloride** loses one molecule of hydrochloric acid on heating, and passes into octammino-μ-imino-sulphato-dicobaltic chloride thus :



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ SO_4\end{matrix}Co(NH_3)_4\right]Cl_3 \longrightarrow \left[(NH_3)_4Co\begin{matrix}NH\\ SO_4\end{matrix}Co(NH_3)_4\right]Cl_2.^1$$

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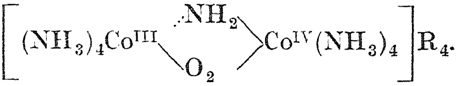
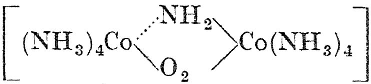
[1] Werner and Salzer, *Annalen*, 1910, 375, 51.

Octammino-μ-amino-peroxo-dicobaltic Salts,

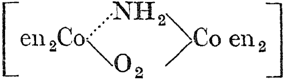


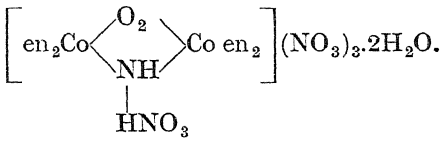
$$\left[(NH_3)_4Co^{III}\begin{matrix}NH_2\\O_2\end{matrix}Co^{IV}(NH_3)_4\right]R_4.$$

Salts of this type show oxidising properties, and if treated with reducing agents, such as hydriodic acid, are transformed into the octammino-μ-amino-diol-salts. They are decomposed on warming with concentrated sulphuric acid, and from the amount of oxygen evolved it is assumed that the tetravalent cobalt atom is transformed into trivalent cobalt. For every two atoms of cobalt one and a half atoms of oxygen are liberated. The nitrogen evolved when the salts are more strongly heated with sulphuric acid supports this view.

The **nitrate** of the series,  $\left[(NH_3)_4Co\begin{matrix}NH_2\\O_2\end{matrix}Co(NH_3)_4\right](NO_3)_4$, is obtained from Vortmann's green sulphate by treating it with nitric acid.[1] It crystallises in dark green prisms. The aqueous solution of this salt is unstable and rapidly decomposes.

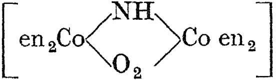
The **sulphate** crystallises in grey-green prisms, and is formed by treating the nitrate with dilute sulphuric acid. Other salts of the series are known.

Ammonia groups in the salts of the series may be replaced by ethylenediamine. Thus, tetraethylenediamino-μ-amino-peroxo-dicobaltic nitrate,  $\left[en_2Co\begin{matrix}NH_2\\O_2\end{matrix}Co\ en_2\right](NO_3)_4$, is formed when the octammino-nitrate is warmed with 10 per cent. ethylenediamine and the solution neutralised with nitric acid. It separates as a green crystalline salt. If neutralisation takes place at low temperature a red salt is obtained, which is tetraethylenediamino-μ-ammonium peroxo-dicobaltic nitrate,

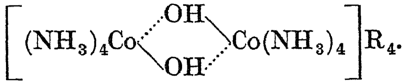


$$\left[en_2Co\begin{matrix}O_2\\\underset{\displaystyle HNO_3}{\underset{|}{NH}}\end{matrix}Co\ en_2\right](NO_3)_3.2H_2O.$$

Sodium iodide reduces these green salts to tetraethylenediamino-μ-amino-ol-dicobaltic iodide, and both the red and the green salts are easily reduced by hydriodic acid, with formation of the corresponding μ-amino-ol-salts.

Ammonia causes the loss of a molecule of acid from both series of salts with production of tetraethylenediamino-μ-imino-peroxo-dicobaltic salts. For instance, the **iodide,**  $\left[en_2Co\begin{matrix}NH\\O_2\end{matrix}Co\ en_2\right]I_2.5H_2O$, may be readily obtained from the amino-peroxo-bromide by triturating it with ammonia and sodium iodide. It crystallises in small brown needles.

Octammino-diol-dicobaltic Salts,



$$\left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]R_4.$$

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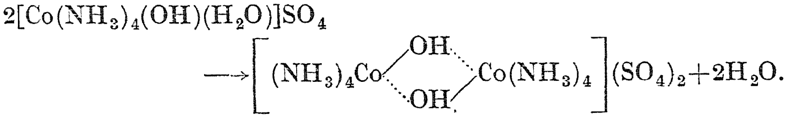
[1] Werner and Grün, *Annalen*, 1910, 375, 61.

These salts are easily obtained from hydroxo-aquo-tetrammino-cobaltic salts, $[Co(NH_3)_4(OH)(H_2O)]R_2$.

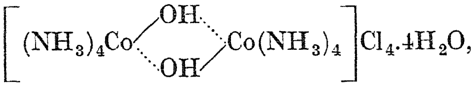
Hydroxo-aquo-tetrammino-cobaltic sulphate, if heated, loses two molecules of water, and is transformed into octammino-μ-diol-dicobaltic sulphate thus :



$$2[Co(NH_3)_4(OH)(H_2O)]SO_4 \longrightarrow \left[(NH_3)_4Co\begin{matrix}OH\\ OH\end{matrix}Co(NH_3)_4\right](SO_4)_2+2H_2O.$$

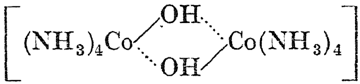
The diol-compounds are readily decomposed by concentrated hydrochloric and hydrobromic acids, yielding a mixture of *cis*-diaquo-tetrammino-cobaltic and *cis*-diacido-tetrammino-cobaltic salts, a reaction which has proved useful in determining the configuration of stereoisomeric cobalt-ammines.

Octammino-μ-diol-dicobaltic Chloride,

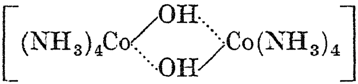


$$\left[(NH_3)_4Co\begin{matrix}OH\\ OH\end{matrix}Co(NH_3)_4\right]Cl_4.4H_2O,$$

is prepared from the sulphate, which is almost insoluble in water, by rubbing it with ammonium chloride. It forms dark red crystals which are soluble in water and neutral in reaction.[1]

The **bromide**,  $\left[(NH_3)_4Co\begin{matrix}OH\\ OH\end{matrix}Co(NH_3)_4\right]Br_4.4H_2O$, is prepared from the chloride by treating the cold solution with potassium bromide, when a dark red crystalline precipitate of the bromide separates.

The **nitrate** is also obtained from the chloride by acting upon it with sodium nitrate, when double decomposition takes place and a light carmine-red precipitate is formed. This is recrystallised from water on the further addition of sodium nitrate. The salt is anhydrous.

The **iodide**,  $\left[(NH_3)_4Co\begin{matrix}OH\\ OH\end{matrix}Co(NH_3)_4\right]I_4.2H_2O$, forms dark violet crystals, and the **chlorate**, $[(NH_3)_4Co : (OH)_2 : Co(NH_3)_4](ClO_3)_4$, crystallises in crimson prisms.

The salts of the series are bright red crystalline bodies. They are soluble in water, neutral in reaction, and dilute mineral acids do not transform them into aquo-salts. The least soluble member of the series is the **sulphate** $[(NH_3)_4Co : (OH)_2 : Co(NH_3)_4](SO_4)_2.2H_2O$, which is prepared by heating hydroxo-aquo-tetrammino-cobaltic sulphate at 100° C. till it is constant in weight. The mass is extracted with water and the sparingly soluble sulphate collected and dried. The crude product so obtained is converted into the chloride and an aqueous solution of this then treated with a solution of sodium sulphate, when a crystalline precipitate of the diol-sulphate is obtained. It is collected, washed with water, alcohol, and finally with ether. It forms small red needle-shaped crystals which contain two molecules of water of hydration.

Belonging to the series are the tetraethylenediamino-μ-diol-

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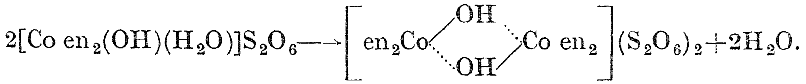
[1] Werner, *Ber.*, 1907, 40, 4434.

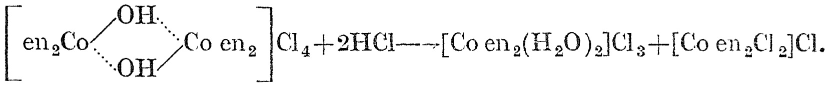
dicobaltic salts, $\left[\mathrm{en_2Co}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co\,en_2}\right]R_4$. These are obtained from hydroxo-aquo-diethylenediamino-cobaltic salts, $[\mathrm{Co\,en_2(OH)(H_2O)}]R_2$.[1]

Thus, hydroxo-aquo-diethylenediamino-cobaltic dithionate, $[\mathrm{Co\,en_2(OH)(H_2O)}]\mathrm{S_2O_6}$, if heated, loses water, as in the case of the corresponding tetrammino-salts, with formation of tetraethylenediamino-cobaltic dithionate,



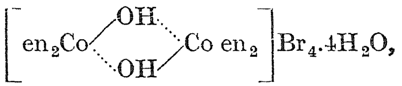
$$2[\mathrm{Co\,en_2(OH)(H_2O)}]\mathrm{S_2O_6}\longrightarrow\left[\mathrm{en_2Co}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co\,en_2}\right](\mathrm{S_2O_6})_2+2\mathrm{H_2O}.$$

The dithionate, like the sulphate of the corresponding ammino-salts, is very sparingly soluble in water, and the other salts may be obtained from it by decomposing it with ammonium salts of the acid. They decompose on treatment with concentrated hydrochloric acid thus :



$$\left[\mathrm{en_2Co}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co\,en_2}\right]\mathrm{Cl_4}+2\mathrm{HCl}\longrightarrow[\mathrm{Co\,en_2(H_2O)_2}]\mathrm{Cl_3}+[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}.$$

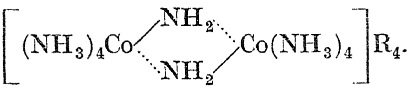
Tetraethylenediamino-μ-diol-dicobaltic Bromide,



$$\left[\mathrm{en_2Co}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co\,en_2}\right]\mathrm{Br_4}.4\mathrm{H_2O},$$

is obtained by rubbing the dithionate with water and ammonium bromide. The reaction mass is dissolved in water and precipitated by the addition of ammonium bromide. It crystallises with four molecules of water, two of which are removed when the substance is heated to 100° C. It is easily soluble in water, and the violet solution obtained is neutral in reaction.

Octammino-μ-diamino-dicobaltic Salts,



$$\left[\mathrm{(NH_3)_4Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{smallmatrix}\mathrm{Co(NH_3)_4}\right]R_4.$$

Several members of this series have been prepared. The methods of preparation are not satisfactory, and it is difficult to obtain the salts pure.

The **dithionate,** $\left[\mathrm{(NH_3)_4Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{smallmatrix}\mathrm{Co(NH_3)_4}\right](\mathrm{S_2O_6})_2$, has been obtained as a by-product in the preparation of *cis*-dichloro-tetrammino-cobaltic chloride, $[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$, from octammino-μ-diol-dicobaltic chloride. A red substance is produced when the crude tetrammino-salt is dried, and if the substance be dissolved in water and sodium dithionate added, yellow-orange crystals separate which have the composition of the diamino-salt, $\left[\mathrm{(NH_3)_4Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{smallmatrix}\mathrm{Co(NH_3)_4}\right](\mathrm{S_2O_6})_2$. The salt crystallises in shining leaflets which are almost insoluble in water.

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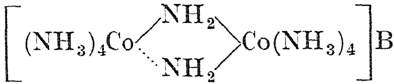
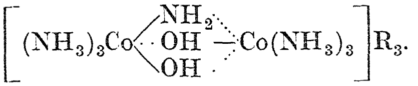
[1] Werner, *Ber.*, 1907, 40, 284.

The **bromide,**  $\left[(NH_3)_4Co\begin{array}{c}NH_2\\ \\NH_2\end{array}Co(NH_3)_4\right]Br_4.4H_2O$, may be prepared from the dithionate by rubbing it with successive quantities of ammonium bromide and water till almost completely dissolved.

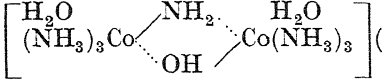
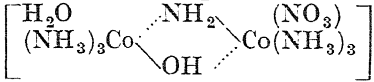
On filtering the liquid the bromide is obtained from the filtrate by precipitation with ammonium bromide. It crystallises in brownish-red leaflets.

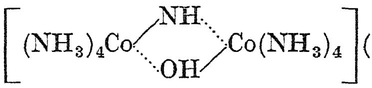
(c) *Compounds with Three Bridged Linkages.*

Hexammino-μ-amino-diol-dicobaltic Salts,



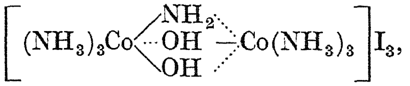
$$\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right]R_3.$$

Compounds of this series are derived from the so-called "melano-chloride," a substance formed by oxidising an ammoniacal solution of cobaltous chloride with air and precipitating a solid by means of concentrated hydrochloric acid. From the mixed solid obtained the sparingly soluble **diaquo-hexammino-μ-amino-ol-dicobaltic nitrate,**  $\left[\begin{array}{c}H_2O\\(NH_3)_3Co\end{array}\begin{array}{c}NH_2\\ \\OH\end{array}\begin{array}{c}H_2O\\Co(NH_3)_3\end{array}\right](NO_3)_4$, is precipitated on the addition of silver nitrate. This salt forms the starting material for the preparation of the μ-amino-diol salts. If diaquo-hexammino-μ-amino-ol-dicobaltic nitrate is dissolved in warm water containing a few drops of nitric acid and the cold solution mixed with concentrated nitric acid, yellowish-brown needles of **nitrato-aquo-hexammino-μ-amino-ol-dicobaltic nitrate,**  $\left[\begin{array}{c}H_2O\\(NH_3)_3Co\end{array}\begin{array}{c}NH_2\\ \\OH\end{array}\begin{array}{c}(NO_3)\\Co(NH_3)_3\end{array}\right](NO_3)_3$, are precipitated, and this, on treatment with liquid ammonia, changes into **octammino-μ-amino-ol-dicobaltic nitrate,**



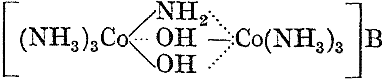
$$\left[(NH_3)_4Co\begin{array}{c}NH\\ \\OH\end{array}Co(NH_3)_4\right](NO_3)_4.^1$$

Hexammino-μ-amino-diol-dicobaltic iodide,



$$\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right]I_3,$$

is prepared by treating an aqueous solution of the diaquo-salt with solid potassium iodide. It is precipitated in brownish needles which are sparingly soluble in cold water yielding a neutral solution. It is difficult to purify as it is easily decomposed.

The **bromide,**  $\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right]Br_3.H_2O$, is obtained by treating a concentrated aqueous solution of the diaquo-salt with ammonium bromide. It is precipitated from solution in dark red needles. The salt may also be prepared from the iodide by rubbing it with moist

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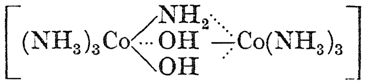
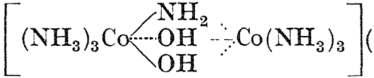
[1] Werner, *Annalen*, 1910, 375, 89.

silver bromide, filtering from the precipitated silver iodide, and treating the filtrate with alcohol. It crystallises in small needles and is sparingly soluble in water.

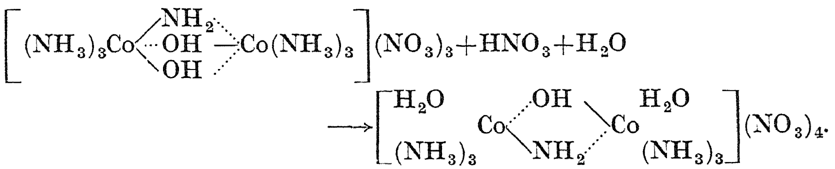


The **chloride**, $\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right]Cl_3.H_2O$, may be obtained from the iodide or the bromide by treating with moist silver chloride and precipitation from the filtrate with alcohol. It crystallises in pale red needles and is easily soluble in water.



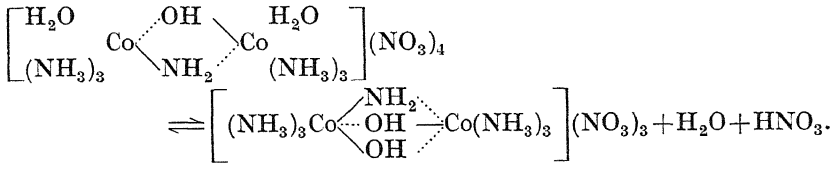
The **nitrate**, $\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right](NO_3)_3.2H_2O$, is produced by decomposition of the iodide by rubbing a concentrated solution with silver nitrate and precipitating the salt, after removal of silver iodide, with alcohol. It separates in small red crystals which are easily soluble in water.[1]

In this series of compounds one of the hydroxo-groups of the bridged linking is much more easily split off than the other, hence they readily pass into the diaquo-hexammino-μ-amino-ol-dicobaltic salts. For example, if the nitrate is crystallised from water containing nitric acid, the hydroxo linkage is broken and the substance passes into the diaquo-μ-amino-olsalt thus :



$$\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right](NO_3)_3+HNO_3+H_2O$$
$$\longrightarrow\left[\begin{array}{ccccc}H_2O & & OH & & H_2O\\ & Co & & Co & \\ (NH_3)_3 & & NH_2 & & (NH_3)_3\end{array}\right](NO_3)_4.$$

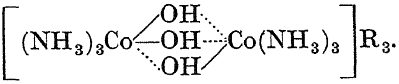
The isolation of the diaquo-nitrate depends on its sparing solubility, on account of which it may be precipitated from a solution in which there is equilibrium between the μ-amino-ol and the μ-amino-diol compounds, by means of nitric acid thus :



$$\left[\begin{array}{ccccc}H_2O & & OH & & H_2O\\ & Co & & Co & \\ (NH_3)_3 & & NH_2 & & (NH_3)_3\end{array}\right](NO_3)_4$$
$$\rightleftharpoons\left[(NH_3)_3Co\begin{array}{c}NH_2\\OH\\OH\end{array}Co(NH_3)_3\right](NO_3)_3+H_2O+HNO_3.$$

From the same solution, therefore, ammonium nitrate is capable of forming the diaquo-μ-amino-ol salt, whereas ammonium bromide and ammonium iodide yield respectively the bromide and the iodide of the μ-amino-diol salt.[2]

Hexammino-triol-dicobaltic Salts,



$$\left[(NH_3)_3Co\begin{array}{c}OH\\OH\\OH\end{array}Co(NH_3)_3\right]R_3.$$

These salts are obtained from the dichloro-aquo-triammino-cobaltic salts.[3]

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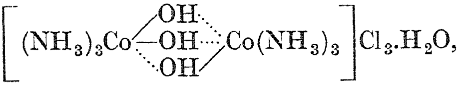
[1] Werner, *Annalen*, 1910, 375, 91.

[2] Werner, *ibid.*, 1910, 375, 25.

[3] Werner, *Ber.*, 1906, 39, 2674 ; Werner and Grün, *ibid.*, 1907, 40, 4834.

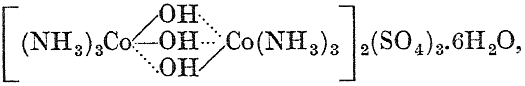
Hexammino-triol-dicobaltic Chloride,



$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]Cl_3.H_2O,$$

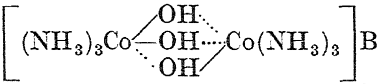
is obtained by acting upon a solution of dichloro-aquo-triammino-cobaltic chloride, $[Co(NH_3)_3H_2O.Cl_2]Cl$, with sodium hydroxide. It may also be prepared from the sulphate of the series by rubbing it with ammonium chloride and water. It crystallises in brownish-red needles from dilute alcohol, and is decomposed on heating to 100° C.

Hexammino-triol-dicobaltic Sulphate,



$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]_2(SO_4)_3.6H_2O,$$

is prepared by the action of sodium hydroxide on dichloro-aquo-triammino-cobaltic sulphate. It crystallises in pale red prisms containing six molecules of water of hydration. It loses five molecules of water if kept over phosphorus pentoxide, and if heated to 77° C. it is obtained anhydrous.

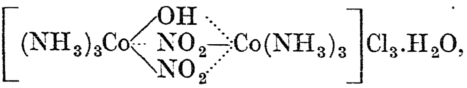
The **bromide,**  $\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]Br_3$, is formed when chloro-bromo-aquo-triammino-cobaltic bromide, $[Co(NH_3)_3ClBr.H_2O]Br$, is heated with water at 60° C.

This series of compounds, if decomposed by the halogen acids, gives quantitative yields of triammino-cobaltic salts; hence three ammonia molecules are attached to each cobalt atom. The acid residues in the salts are readily ionised, and each salt may be transformed into the other by double decomposition. These compounds are not aquo-salts, and their aqueous solutions are neutral in reaction.

Isomeric with the series are the black dodecammino-hexol-tetracobaltic salts, $[Co(OH)_6(Co(NH_3)_4)_3]R_6$, which may be regarded as polymers of the hexammino-triol-dicobaltic salts.

A series of compounds has been prepared where two of the hydroxyl linkages of the triol-series are replaced by nitro-groups. These are the hexammino-μ-dinitro-ol-dicobaltic salts.[1]

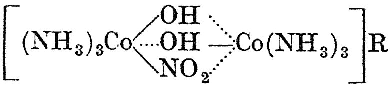
Hexammino-μ-dinitro-ol-dicobaltic Chloride,



$$\left[(NH_3)_3Co\begin{matrix}OH\\NO_2\\NO_2\end{matrix}Co(NH_3)_3\right]Cl_3.H_2O,$$

is obtained from dichloro-hexammino-μ-nitro-ol-dicobaltic salts by treating them in acetic-acid solution with nitrous acid. It crystallises in orange-red needles, and is sufficiently stable to allow of its being recrystallised from hydrochloric acid without decomposition.

Hexammino-μ-nitro-diol-dicobaltic Salts,



$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\NO_2\end{matrix}Co(NH_3)_3\right]R_3,$$

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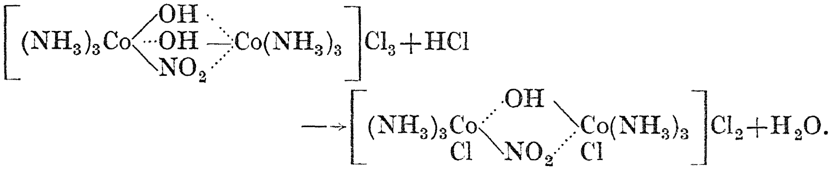
[1] Werner and Welti, *Annalen*, 1910, 375, 130.

are formed by treating an acetic-acid solution of hexammino-triol-dicobaltic salt with nitrous acid. They are orange-coloured salts. The nitro-group in these salts is stable, but one of the hydroxyl linkages is easily broken, and on warming with hydrochloric acid one hydroxyl linkage is broken and two chlorine atoms enter the complex radicle thus :

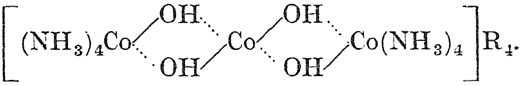


$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\NO_2\end{matrix}Co(NH_3)_3\right]Cl_3+HCl \longrightarrow \left[\begin{matrix}(NH_3)_3Co\\Cl\end{matrix}\begin{matrix}OH\\NO_2\end{matrix}\begin{matrix}Co(NH_3)_3\\Cl\end{matrix}\right]Cl_2+H_2O.$$

Hence it is possible to pass from the dicobalt-ammines containing three bridged linkages to those containing two bridges.

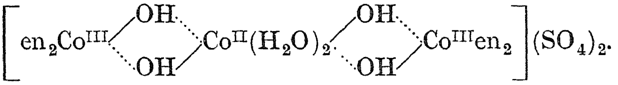
2. TRICOBALT-AMMINES.

(a) *Compounds with Four Bridged Linkages,*



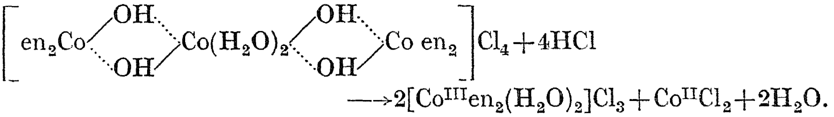
$$\left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]R_4.$$

This series is represented by the tetraethylenediamino-diaquo-tetrol-cobalto-dicobaltic salts. For example,



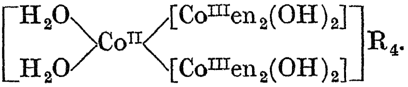
$$\left[en_2Co^{III}\begin{matrix}OH\\OH\end{matrix}Co^{II}(H_2O)_2\begin{matrix}OH\\OH\end{matrix}Co^{III}en_2\right](SO_4)_2.$$

The compounds are obtained by oxidising an aqueous solution of cobaltous salt containing ethylenediamine by means of air. They contain two [Co en$_2$(OH)$_2$] nuclei united by a cobaltous atom which is itself associated with two molecules of water. The constitution of the salts has been investigated by Werner [1] by examining the decomposition products obtained on treatment with hydrochloric acid. Cold hydrochloric acid decomposes the substance with formation of one molecule of cobaltous chloride and two molecules of *cis*-diaquo-diethylenediamino-cobaltic chloride thus :



$$\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Co(H_2O)_2\begin{matrix}OH\\OH\end{matrix}Co\,en_2\right]Cl_4+4HCl \longrightarrow 2[Co^{III}en_2(H_2O)_2]Cl_3+Co^{II}Cl_2+2H_2O.$$

The salts contain four hydroxyl groups employed in linking the cobalt atoms in the complex. The water molecules represented as united to the cobaltous cobalt are retained even when the salts are dried, but the function of these is not clearly understood. From the above formula and the decomposition products obtained it is assumed that the cobaltous cobalt has co-ordinated with it two molecules of water and two [Co en$_2$(OH)$_2$] radicles thus :



$$\left[\begin{matrix}H_2O\\H_2O\end{matrix}Co^{II}\begin{matrix}[Co^{III}en_2(OH)_2]\\[Co^{III}en_2(OH)_2]\end{matrix}\right]R_4.$$

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[1] Werner, *Ber.*, 1907, 40, 4426.

Werner suggests that it may be a derivative of cobaltous cobaltic hydroxide, $Co_3(OH)_8$.

Tetraethylenediamino-diaquo-tetrol-cobalto-dicobaltic Sulphate, $\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ \\ [(OH)_2Co\,en_2]_2\end{matrix}\right](SO_4)_2.5H_2O$, is prepared by treating the corresponding chloride with sodium sulphate. It separates in bright red microscopic needles which are sparingly soluble in water.

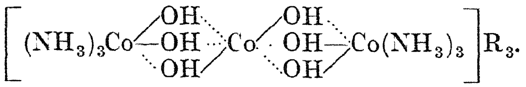
The **chloride,** $\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ \\ [(OH)_2Co\,en_2]_2\end{matrix}\right]Cl_4$, is prepared directly from cobaltous chloride and ethylenediamine on oxidation with air and subsequent treatment with sodium chloride to precipitate the compound. The crude salt contains a little triethylenediamino-cobaltic chloride, which is removed from the sparingly soluble tetraethylenediamino-diaquo-tetrol-chloride by washing with water. It is a bright red microcrystalline powder.

The **iodide,** $\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ \\ [(OH)_2Co\,en_2]_2\end{matrix}\right]I_4.2H_2O$, resembles the chloride, but is brownish red in colour.

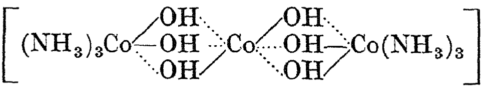
The **dithionate,** $\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ \\ [(OH)_2Co\,en_2]_2\end{matrix}\right]_2(S_2O_6)_2.2H_2O$, is obtained from the chloride by double decomposition with sodium dithionate. It forms a bluish-red crystalline powder.

The **chloroplatinite,** $\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ \\ [(OH)_2Co\,en_2]_2\end{matrix}\right](PtCl_4)_2.2H_2O$, is a light brownish-red crystalline powder.

(b) *Compounds containing Six Bridged Linkages,*



Whilst preparing hexammino-triol-dicobaltic sulphate from chloro-diaquo-triammino-cobaltic sulphate, Werner [1] obtained a reddish-brown mother-liquor, and on cooling this he obtained from it a green precipitate on the addition of concentrated hydrochloric acid. On dissolving this in water containing a little acetic acid and adding sodium sulphate, the impure hexammino-hexol-tricobaltic sulphate separates. This is collected, treated with ammonium chloride, and greenish-brown crystals of the pure chloride obtained.



The **chloride,** $Cl_3.3H_2O$, is easily soluble in water, giving an intensely yellowish-green solution.

The **bromide** may be obtained from the chloride by double decomposition with ammonium bromide, and by the action of sodium dithionate, the **dithionate,**

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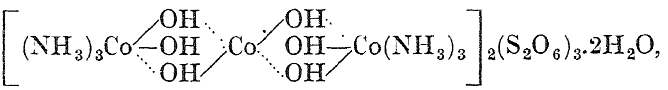
[1] Werner, *Ber.*, 1907, 40, 4834; Werner, *Annalen*, 1910, 375, 40.

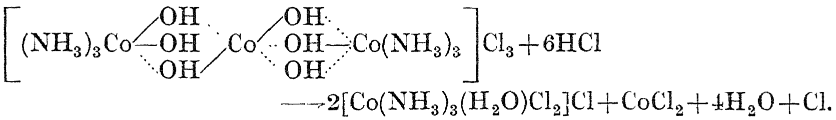


$$\left[(\mathrm{NH_3})_3\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_3\right]_2(\mathrm{S_2O_6})_3.2\mathrm{H_2O},$$

separates in brown crystals.

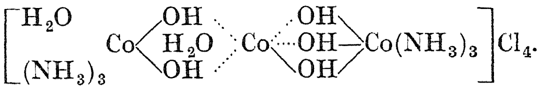
The salts of this series decompose on treatment with hydrochloric acid, giving dichloro-aquo-triammino-cobaltic chloride, cobaltous chloride, and chlorine.

The formation of the triammino-salt indicates that two of the cobalt atoms are united with three molecules of ammonia, and the evolution of chlorine shows that one cobalt atom has been reduced from trivalent to divalent state. The reaction may be represented thus :



$$\left[(\mathrm{NH_3})_3\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_3\right]\mathrm{Cl_3}+6\mathrm{HCl}$$
$$\longrightarrow 2[\mathrm{Co}(\mathrm{NH_3})_3(\mathrm{H_2O})\mathrm{Cl_2}]\mathrm{Cl}+\mathrm{CoCl_2}+4\mathrm{H_2O}+\mathrm{Cl}.$$

When solutions of these salts are treated with concentrated hydrochloric acid, green crystals of diaquo-hexammino-pentol-tricobaltic chloride are formed by the breaking of one ol-linkage thus :

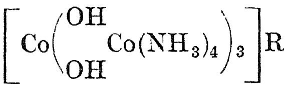


$$\left[\begin{matrix}\mathrm{H_2O}\\ \\ (\mathrm{NH_3})_3\end{matrix}\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{H_2O}\\ \mathrm{OH}\end{matrix}\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_3\right]\mathrm{Cl_4}.$$

It is not quite certain whether all the chlorine is outside the complex or not.

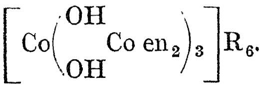
3. TETRACOBALT-AMMINES.

Two series of salts are known containing four cobalt atoms in the molecule, namely, **dodecammino-hexol-tetracobaltic salts,**



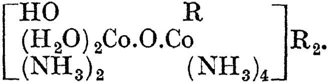
$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right)_3\right]\mathrm{R_6},$$

and **hexaethylenediamino-hexol-tetracobaltic salts,**



$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Co\ en_2}\right)_3\right]\mathrm{R_6}.$$

These salts are easily obtained from tetrammino- and diethylenediamino-cobaltic salts respectively. The ammino-series were first prepared by Jörgensen[1] in 1898. He gave them the name anhydrobasic-tetrammino-diaquo-diammino-salts, and the formula



$$\left[\begin{matrix}\mathrm{HO} & & \mathrm{R}\\ (\mathrm{H_2O})_2\mathrm{Co.O.Co} & & \\ (\mathrm{NH_3})_2 & & (\mathrm{NH_3})_4\end{matrix}\right]\mathrm{R_2}.$$

This was rejected by Werner,[2] as it did not agree with the properties of the substances. Thus, the salts do not yield aquo-salts on heating with dilute mineral acids, therefore the hydroxyl group cannot be directly united to cobalt as in the hydroxo-salts. The chloride of the series cannot have chlorine in the complex, otherwise the salt could not

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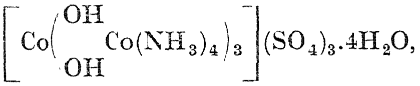
[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1898, 16, 186.

[2] Werner, *Ber.*, 1907, 40, 2103.

be transformed into halogen-free sulphate by the action of soluble sulphates. Also, the decomposition products obtained on treatment with hydrochloric acid contradict Jörgensen's formula.

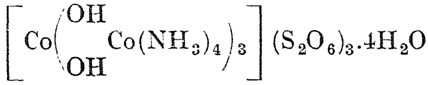
If the formula given above be adopted it conforms to the reactions of the salts.

Dodecammino-hexol-tetracobaltic Sulphate,



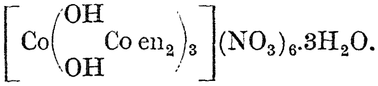
$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right)_3\right](\mathrm{SO_4})_3\cdot 4\mathrm{H_2O},$$

is obtained by heating dibromo-tetrammino-cobaltic bromide with water until bromine is evolved, and subsequent treatment of the liquid with a solution of ammonium sulphate. Or it may be prepared by adding pyridine to a solution of diaquo-tetrammino-cobaltic sulphate dissolved in warm dilute acetic acid. It crystallises in dark violet leaflets which are almost insoluble in water. On heating for some time with water the salt is decomposed and cobalt oxide precipitated.



The **dithionate,** $\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right)_3\right](\mathrm{S_2O_6})_3\cdot 4\mathrm{H_2O}$, is obtained by adding sodium dithionate and pyridine to a solution of diaquo-tetrammino-cobaltic chloride dissolved in very dilute acetic acid and heating the mixture to boiling. It crystallises in glistening brownish crystals.

Hexaethylenediamino-hexol-tetracobaltic Salts.—The most easily prepared salt of the series is the nitrate,



$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Co\,en_2}\right)_3\right](\mathrm{NO_3})_6\cdot 3\mathrm{H_2O}.$$

When a solution of cobaltous nitrate containing ethylenediamine is submitted to atmospheric oxidation, the nitrate is produced in long brown needles which are soluble in water.

It is transformed into *cis*-diaquo-diethylenediamino-cobaltic chloride on treatment with concentrated hydrochloric acid; dilute hydrochloric acid reacts with the compound, with formation of *cis*-dichloro-diethylenediamino-cobaltic chloride; and potassium hydroxide transforms the salt into *cis*-hydroxo-aquo-diethylenediamino-cobaltic nitrate.

The **chloride** may be prepared in similar manner to the nitrate from cobaltous chloride, and the other salts from the nitrate by double decomposition with soluble salts of the respective acids. All the salts of the series are soluble in water, neutral in reaction, and have a yellowish-brown colour.

C. Cobalt-ammines of Unknown Constitution.

There are still some complex polynuclear cobalt-ammines to which satisfactory constitutional formulæ have not yet been assigned. These are, for example, the "Fusko salts" described by Frémy;[1] a class of compounds containing sulphur prepared by Hofmann[2] by the action

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[1] Frémy, *Ann. Chim. Phys.*, 1852, **35**, 257.

[2] Hofmann, *Zeitsch. anorg. Chem.*, 1898, **16**, 382.

of ammonia and sulphur dioxide on cobaltous acetate; and the salts of Sörensen containing oxalato-groups, prepared by the action of ammonia on potassium cobaltioxalate. These latter are dark red insoluble substances which most probably belong to the diol-class of compounds.[1]

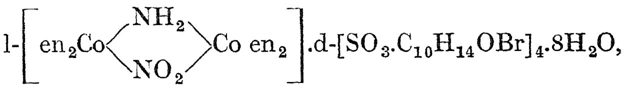
Optical Activity in the Polynuclear Cobalt-ammines.

As in the case of the mononuclear cobalt salts, the configuration of the compounds suggests that some should exist in optically active forms. Several cobalt-ammines of the polynuclear series have been resolved into their optically active isomers.

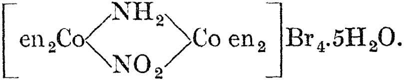
In 1913 Werner[2] described a new series of optically active cobalt compounds containing two asymmetric cobalt atoms in the molecule, the tetraethylenediamino-μ-amino-nitro-dicobaltic salts. The resolution is effected by treating tetraethylenediamino-μ-amino-nitro-dicobaltic bromide with silver d-bromo-camphor sulphonate and fractionally crystallising the product.

Three different d-bromo-camphor sulphonates are obtained, namely, (1) an inactive crystalline salt containing eight molecules of water of hydration, from which a series of lævo-salts can be prepared; (2) an active crystalline form with seven molecules of water of hydration, yielding a series of meso-salts; and (3) another active form with six molecules of hydration, yielding a series of dextro-salts.

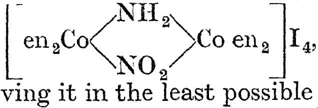
(1) **l-Tetraethylenediamino-μ-amino-nitro-dicobaltic d-bromo-camphor Sulphonate,**

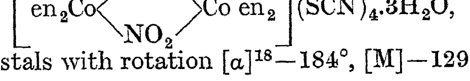


$$\mathrm{l}\text{-}\left[\mathrm{en_2Co}{<}^{\mathrm{NH_2}}_{\mathrm{NO_2}}{>}\mathrm{Co\ en_2}\right]\mathrm{.d\text{-}[SO_3.C_{10}H_{14}OBr]_4.8H_2O},$$

crystallises in glistening orange-red crystals. It is optically inactive, as the two complex radicles compensate one another, but on treatment with the calculated quantity of cold concentrated hydrobromic acid yields **lævo-rotatory tetraethylenediamino-μ-amino-nitro-dicobaltic bromide,**  $\left[\mathrm{en_2Co}{<}^{\mathrm{NH_2}}_{\mathrm{NO_2}}{>}\mathrm{Co\ en_2}\right]\mathrm{Br_4.5H_2O}$.

It crystallises from water in lance-shaped reddish-orange crystals which effloresce in air and have rotation $[\alpha]^{17} - 162°$, $[M] - 1344{\cdot}6°$.

The **iodide,**  $\left[\mathrm{en_2Co}{<}^{\mathrm{NH_2}}_{\mathrm{NO_2}}{>}\mathrm{Co\ en_2}\right]\mathrm{I_4}$, is obtained from the bromide by dissolving it in the least possible quantity of water, filtering the solution and adding to it sodium iodide. It separates as a red powder and crystallises from water in dark red octahedra with the following rotation: $[\alpha]^{17} - 136°$, $[M] - 1262{\cdot}1°$.

The **thiocyanate,**  $\left[\mathrm{en_2Co}{<}^{\mathrm{NH_2}}_{\mathrm{NO_2}}{>}\mathrm{Co\ en_2}\right]\mathrm{(SCN)_4.3H_2O}$, forms orange-red columnar crystals with rotation $[\alpha]^{18} - 184°$, $[M] - 1299°$.

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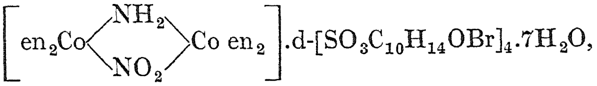
[1] Sörensen, *Studier over Kobaltidoxalater* (Kopenhagen, 1899), p. 161.

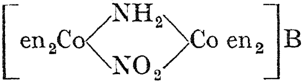
[2] Werner, *Ber.*, 1913, 46, 3674.

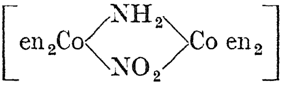
(2) **Tetraethylenediamino-μ-amino-nitro-dicobaltic d-bromo-camphor Sulphonate,**


$$\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right].\mathrm{d\text{-}[SO_3C_{10}H_{14}OBr]_4.7H_2O},$$

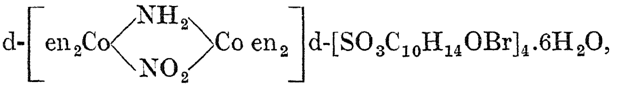
crystallises in felted orange needles with rotation $[\alpha]^{17}+72°$, $[M]+1285{\cdot}9°$.

On treatment with acids the corresponding salts of tetraethylenediamino-μ-amino-nitro-dicobalt are obtained. These salts are inactive in every case, and are the meso-salts.

Meso-tetraethylenediamino-μ-amino-nitro-dicobaltic Bromide,  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_4.6H_2O}$, is obtained in short prismatic yellowish-red crystals by treating the above compound with concentrated hydrobromic acid followed by the addition of alcohol.

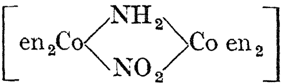
The **iodide,**  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{I_4.H_2O}$, separates as a finely crystalline powder.

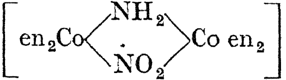
(3) **d-Tetraethylenediamino-μ-amino-nitro-dicobaltic d-bromo-camphor Sulphonate,**


$$\mathrm{d\text{-}}\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{d\text{-}[SO_3C_{10}H_{14}OBr]_4.6H_2O},$$

is the least soluble of the three bromo-camphor sulphonates, and crystallises in shining rectangular leaflets with rotation $[\alpha]^{17}+160°$, $[M]+2828{\cdot}6°$. On treatment with acids it yields the corresponding dextro-salts.

d-Tetraethylenediamino-μ-amino-nitro-dicobaltic Bromide separates in the same crystalline form as the l-salt, and contains five molecules of water. The rotation in this case is $[\alpha]^{16}+164°$, $[M]+1361{\cdot}2°$.

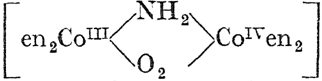
The **iodide,**  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{I_4.H_2O}$, crystallises in deep red octahedra with rotation $[\alpha]^{17}+138°$, $[M]+1280{\cdot}6°$.

The **thiocyanate,**  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{(SCN)_4.3H_2O}$, has a rotation of $[\alpha]^{18}+182°$, $[M]+1284{\cdot}9°$.

On mixing equal quantities of d- and l-bromide the racemic salt crystallises in cubes.

The **iodide** crystallises in prisms and the **thiocyanate** in dark red prisms.

On prolonged boiling of aqueous solutions of the active bromo-camphor sulphonates change takes place, and only inactive dicobaltic salts of the meso series are obtained.

Optical Activity in the Tetraethylenediamino-μ-amino-peroxo-dicobaltic Salts,  $\left[\mathrm{en_2Co^{III}}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co^{IV}en_2}\right]\mathrm{R_4}$.[1]

From the configuration of these salts four optically active forms are possible, represented by the following :—

1. [+A+B],
2. [−A−B],
3. [+A−B],
4. [−A+B],

and racemic forms made up of 1+2 and 3+4 (where A represents ($\mathrm{en_2Co^{III}}$) and B ($\mathrm{en_2Co^{IV}}$)).

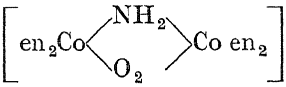
Two optically active forms have been prepared, namely, those represented by 1 and 2. Also the racemic form by mixing 1 and 2. Those corresponding to 3 and 4 are still doubtful.

The starting material is prepared by the action of ethylenediamine on octammino-μ-amino-peroxo-dicobaltic nitrate, which gives the racemic inactive nitrate.

The nitrate is transformed into the bromide, and this is then treated with active silver bromo-camphor sulphonate. A dark green solution is formed, and a difficultly soluble bromo-camphor sulphonate mixed with silver salt. This mixture is extracted with hot water and the solution so obtained fractionally crystallised. The resolution is tedious and the yield is not good.

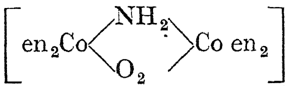
The d-Series.

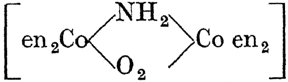
The bromo-camphor sulphonate of the d-series,



$$\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co\,en_2}\right][\mathrm{SO_3C_{10}H_{14}OBr}]_4.9\mathrm{H_2O},$$

crystallises from warm water and separates from a concentrated solution in grass-green crystals. On heating to 100° C. the sulphonate undergoes decomposition and becomes brown in colour. Rotation of the salt is $[\alpha]^{20^\circ}+520^\circ$, $[M]+9734{\cdot}4^\circ$.

The **d-bromide**,  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_4.5H_2O}$, is obtained by dissolving the sulphonate in a small quantity of water and rubbing with solid sodium bromide. It crystallises in black glistening prisms which have rotation $[\alpha]^{17}+840^\circ$, $[M]+6854{\cdot}4^\circ$, and from this salt other d-salts are prepared. Thus, on treatment of an aqueous solution with solid sodium dithionate, the *dithionate* is precipitated in greenish-black crystals of rotation $[\alpha]^{17}+848^\circ$, $[M]+6919{\cdot}6^\circ$.

The **d-nitrate**,  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co\,en_2}\right](\mathrm{NO_3})_4.2\mathrm{H_2O}$, is prepared by dissolving the bromo-camphor sulphonate in a little concentrated nitric acid and precipitating the cold solution with alcohol. It is easily soluble in water and separates as a light green crystalline powder. The rotation of the salt is $[\alpha]^{17}+920^\circ$, $[M]+6348^\circ$.

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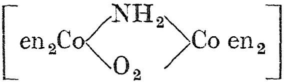
[1] Werner, *Ber.*, 1914, 47, 1961.

The l-Series.

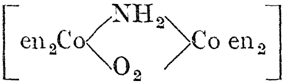
d-Bromo-camphor sulphonate of the l-series may be separated from the fourth or fifth extraction of the crude product. It crystallises in olive-green needles which are sparingly soluble in cold water but easily soluble in hot water. Perfectly pure l-salts are best obtained from the mother-liquor of the resolution of the bromide with l-bromo-camphor sulphonate.



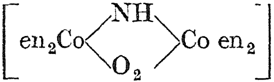
The **bromide,** $\left[\mathrm{en_2Co}\begin{matrix}\diagup\mathrm{NH_2}\diagdown\\ \diagdown\mathrm{O_2}\diagup\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br_4.5H_2O}$, separates in grass-green leaflets or in dark green prisms of rotation $[\alpha]^{19}-840°$, [M] $-6854{\cdot}4°$. These active salts are fairly stable in aqueous solution, but the activity diminishes on keeping.

It is suggested that the extremely high rotations of these salts is due to tetravalent cobalt in the molecule, a suggestion which is supported by the marked diminution in rotation when the tetravalent cobalt is reduced to trivalent cobalt, as shown in the dicobaltic salts described.

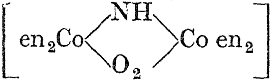
Racemic Salts.



The **bromide,** $\left[\mathrm{en_2Co}\begin{matrix}\diagup\mathrm{NH_2}\diagdown\\ \diagdown\mathrm{O_2}\diagup\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br_4.6H_2O}$, crystallises in dark green regular crystals.



Optically Active Tetraethylenediamino - μ - imino - peroxo-dicobaltic Salts, $\left[\mathrm{en_2Co}\begin{matrix}\diagup\mathrm{NH}\diagdown\\ \diagdown\mathrm{O_2}\diagup\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{R_3}$.

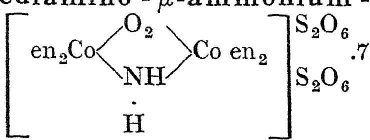


The **iodide,** $\left[\mathrm{en_2Co}\begin{matrix}\diagup\mathrm{NH}\diagdown\\ \diagdown\mathrm{O_2}\diagup\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{I_3.4H_2O}$, is prepared by treating d-tetraethylenediamino-μ-amino-peroxo-dicobaltic bromide with concentrated aqueous ammonia and decomposing the filtered solution with ammonium iodide. The l-salt obtained crystallises in glistening brown needles with rotation $[\alpha]^{17}-160°$, $[\mathrm{M}]-1372{\cdot}81°$.

The d-iodide is prepared from l-tetraethylenediamino-μ-amino-peroxo-dicobaltic bromide by the same reaction. It separates in dark brown needles which are easily soluble in water and have rotation $[\alpha]^{17}+160°$, $[\mathrm{M}]-1372{\cdot}8°$.

Tetraethylenediamino-μ-ammonium-peroxo-dicobaltic salts, which are isomeric with the amino-peroxo-salts, may also be obtained in optically active forms.

The preparation of salts of this series in the pure state is difficult. The dithionates are most easily prepared, and from these pure bromides are obtained.



l - Tetraethylenediamino - μ-ammonium - peroxo-dicobaltic Dithionate, $\left[\mathrm{en_2Co}\begin{matrix}\diagup\mathrm{O_2}\diagdown\\ \diagdown\underset{\overset{\cdot}{\mathrm{H}}}{\mathrm{NH}}\diagup\end{matrix}\mathrm{Co\ en_2}\right]\begin{matrix}\mathrm{S_2O_6}\\ \mathrm{S_2O_6}\end{matrix}\mathrm{.7H_2O}$, crystallises in red shining needles which are somewhat sparingly soluble in water and have rotation $[\alpha]^{18}-192°$, $[\mathrm{M}]-1625{\cdot}8°$.

The d-compound crystallises in red felted needles which are sparingly soluble in water and have rotation $[\alpha]^{18}+192°$, $[M]+1625\cdot8$. The pure l- and d-bromides are also red crystalline bodies containing no water of hydration. The rotation of these is higher than the value obtained when the salts are prepared directly from the amino-peroxo-compound, where some of the valency isomer is mixed with the ammonium salts. The rotations obtained are $[\alpha]^{19}\pm208°$, $[M]\pm1510°$.

Optically active peroxo-salts may be transformed into μ-amino-ol-cobaltic salts. Thus, l-tetraethylenediamino-μ-amino-peroxo-dicobaltic salts yield d-tetraethylenediamino-μ-amino-ol-salts and d-tetraethylenediamino-μ-amino-nitro-dicobaltic salts. In each case there is a change in sign from the μ-peroxo-salts to the μ-amino-ol or μ-amino-nitro-dicobaltic salts, and a distinct diminution in rotation.

Optically Active Dodecammino-hexol-tetra-cobaltic Salts.[1]—These salts may be resolved by means of bromo-camphor sulphonic acid. Dodecammino-hexol-tetracobaltic chloride is mixed with silver bromo-camphor sulphonate, whereby all the chlorine is precipitated as silver chloride and the solution treated with dilute acetic acid. The first crop of d-bromo-camphor sulphonate is lævo-rotatory, that from l-bromo-camphor sulphonate dextro-rotatory.

The highest rotation obtained is $[\alpha]-620°$ in aqueous acetone. The active bromides are prepared by dissolving these salts in 50 per cent. acetone, adding small quantities of sodium bromide and diluting the solution with absolute alcohol.

d- and l-bromides crystallise in reddish-grey powders with two molecules of water. The salts exhibit abnormal rotation dispersion. The highest rotations observed are $[\alpha]+4446°$ and $-4500°$.

AMMINO-DERIVATIVES OF NICKEL SALTS.

Nickel, although closely resembling cobalt, shows much less tendency to form complex radicles, and there is no long series of stable ammino-nickel salts as in the case of cobalt. Further, the stable series of ammino-derivatives of cobalt are those in which the metal is trivalent, whereas in the case of nickel the nickelic salts are unknown, and the complex ammino-derivatives are additive compounds of nickelous salts.

The ammino-derivatives of nickel salts are therefore comparable with ammino-cobaltous salts.

Nickel salts in aqueous solution are partially precipitated as basic salts on the addition of aqueous ammonia. The precipitate so formed, however, dissolves in excess of ammonia, yielding a blue liquid containing complex ammino-salts. In the dry state the salts rapidly absorb ammonia gas, with formation of ammino-compounds.

Ammino-derivatives of Nickel Nitrate.

Tetrammino-nickel Nitrate, $[Ni(NH_3)_4](NO_3)_2.H_2O$, is obtained by the addition of ammonia to a solution of nickel nitrate and the addition of alcohol to the well-cooled liquid. The precipitated ammine crystallises in large transparent octahedra of a blue colour. It decomposes in air with loss of ammonia, and falls to a bluish-white powder. On heating it melts, loses water and ammonia, leaving a residue of

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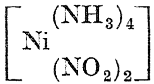
[1] Werner, *Ber.*, 1914, 47, 3087.

nickel oxide. It is easily soluble in water, and the solution decomposes on warming.[1]

Hexammino-nickel Nitrate, $[Ni(NH_3)_6](NO_3)_2$, is prepared by the action of dry ammonia gas on anhydrous nickel nitrate.[2] It is decomposed by water.

If finely divided nickel is mixed with silver nitrate in presence of liquid ammonia at low temperature and ammonia allowed to evaporate spontaneously in absence of moisture, pale violet crystals of composition $Ni(NO_3)_2.9NH_3$ separate. The substance decomposes on treatment with water, with formation of metallic hydroxide and evolution of ammonia.[3]

Tetrammino-nickel Nitrite, $[Ni(NH_3)_4](NO_2)_2$, is formed by the action of ammonia on a mixture of aqueous nickel sulphate and sodium nitrite at 22° C. After standing for some time a crystalline precipitate is deposited. The substance crystallises in small cherry-red monoclinic crystals which dissolve in cold water, forming a green solution. The solution soon becomes cloudy owing to decomposition of the salt. Even in moist air the salt decomposes, loses ammonia, and changes in colour. The colour of the compound is peculiar to this one salt, a fact remarked upon by Ephraim, who assumes for the compound a different constitution from the other nickel ammino-salts. He suggests the formula



$\left[\mathrm{Ni}\begin{matrix}(NH_3)_4\\ \\ (NO_2)_2\end{matrix}\right]$

for the substance.[4]

Pentammino-nickel Nitrite, $[Ni(NH_3)_5](NO_2)_2$, is produced by the treatment of the tetrammino-salt with dry ammonia gas. It is blue in colour like the other ammino-derivatives of nickel salts.

Trihydrazino-nickel Nitrate, $[Ni(N_2H_4)_3](NO_3)_2$.—Hydrazine may take the place of ammonia, yielding a derivative with properties resembling those of the ammines.[5]

The substance is prepared by treating the tetrammino-derivative with 50 per cent. hydrazine hydrate on a water-bath; ammonia is copiously evolved and the hydrazino-derivative is precipitated. The precipitate is blue in colour, but the last of the precipitate is almost colourless. After washing with alcohol and ether it is obtained as a reddish-violet powder which is insoluble in water. It is more difficult to decompose with hot water than the corresponding cobaltous compound.

Ammino-derivatives of Nickel Fluoride.

A compound of composition $5NiF_2.6NH_3.8H_2O$ is produced when nickel carbonate is dissolved in hydrofluoric acid and the liquid treated with concentrated aqueous ammonia. The filtrate from the reaction is evaporated over potassium hydroxide, and on standing for several weeks a thick oil is formed, from which on dilution with water and slight warming light green crystals separate. It is insoluble in cold water but decomposed by warm water.[6]

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[1] Erdmann, *J. prakt. Chem.*, 1866, **97**, 395.

[2] Andrée, *Compt. rend.*, 1888, **106**, 938; Ephraim, *Ber.*, 1913, **46**, 3101.

[3] Guntz and Martin, *Bull. Soc. chim.*, 1910, **7**, 313.

[4] Soret and Robineau, *ibid.*, 1889, **2**, 138; Ephraim, *Ber.*, 1913, **46**, 3101.

[5] Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1908, **60**, 266.

[6] Böhm, *ibid.*, 1905, **43**, 334.

Ammino-derivatives of Nickel Chloride.

Biltz and Fetkenheuer [1] report the existence of three ammino-compounds, namely, hexammino-nickel chloride, $[Ni(NH_3)_6]Cl_2$, di ammino-nickel chloride, $[Ni(NH_3)_2]Cl_2$, and monammino-nickel chloride, $[Ni(NH_3)]Cl_2$. Triammino-nickel chloride, $[Ni(NH_3)_3]Cl_2$, is also described.

Hexammino-nickel Chloride, $[Ni(NH_3)_6]Cl_2$.—Nickel chloride absorbs ammonia gas at ordinary temperature. Rise in temperature occurs and increase in volume. The hexammine is best prepared, however, from an aqueous solution of the salt, as when prepared from the dry salt and ammonia gas it is exceedingly bulky. Aqueous ammonia is added to a solution of pure nickel chloride until the nickel hydroxide first precipitated is almost dissolved. The liquid is filtered and a saturated aqueous solution of ammonium chloride containing ammonia added, and air drawn through the liquid. On the addition of a further quantity of ammonium chloride a precipitate forms, which is collected, washed with ammonium chloride and ammonia, and finally with alcohol containing ammonia.

The hexammine prepared from the dry salt is almost white in colour, and on heating loses ammonia, leaving a residue of nickel chloride and metallic nickel. It dissolves in water, yielding a blue solution, from which is precipitated nickel hydroxide. Prepared in aqueous solution the substance forms a light blue powder, which may be crystallised from water containing ammonia in opaque violet octahedra. It is almost insoluble in concentrated aqueous ammonia and in ammonium-chloride solution containing ammonia. On heating to 120° C. it loses four molecules of ammonia.[2]

The same ammine containing a half molecule of water, $[Ni(NH_3)_6]Cl_2.\frac{1}{2}H_2O$, may be obtained by slightly warming the anhydrous compound with aqueous ammonium chloride through which is passing a stream of gaseous ammonia, or by leading ammonia gas through a well-cooled suspension of nickel hydroxide in aqueous ammonium chloride. It crystallises in transparent violet-coloured octahedra. The hexammine is stable in cold water, but decomposes when the solution is heated.

Triammino-nickel Chloride, $[Ni(NH_3)_3]Cl_2.2H_2O$, is obtained in large octahedral crystals on dissolving the hexammine in water and slightly warming the solution.[3]

Diammino-nickel Chloride, $[Ni(NH_3)_2]Cl_2$, is formed on heating hexammino-nickel chloride to 120° C.

Monammino-nickel Chloride, $[Ni(NH_3)]Cl_2$, is also known, and is produced by the thermal decomposition of the hexammine. It is yellow in colour and decomposes completely at 373° C.[4]

Ammino-derivatives of Nickel Bromide.

Hexammino-nickel Bromide, $[Ni(NH_3)_6]Br_2$, is the best known of the ammino-derivatives of nickel bromide. It is obtained either by the action of dry ammonia gas on dry powdered nickel bromide, or by

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[1] Biltz and Fetkenheuer, *Zeitsch. anorg. Chem.*, 1913, 83, 163.

[2] Sörensen, *ibid.*, 1894, 5, 363.

[3] Andrée, *Compt. rend.*, 1888, 106, 937.

[4] Biltz and Fetkenheuer, *Zeitsch. anorg. Chem.*, 1913, 83, 163.

treating a concentrated aqueous solution of the salt with excess of concentrated aqueous ammonia. A blue liquid is formed, from which a violet-coloured crystalline powder is precipitated on cooling. It crystallises in small, shining, violet octahedra, which lose ammonia on exposure to air. It is soluble in water, but if left in contact with excess of water, nickel hydroxide is precipitated and the liquid becomes deep blue in colour.

The formation of the hexammino-derivative of nickel bromide is characteristic, and gives a method for the purification of nickel compounds, for the corresponding cobaltous salt is much more soluble. The salt is almost insoluble in cold aqueous ammonia but soluble on heating the solution.[1]

Diammino-nickel Bromide, $[Ni(NH_3)_2]Br_2$, is produced during the thermal decomposition of the hexammino-derivative.

Ammino-derivatives of Nickel Iodide.

Hexammino-nickel Iodide, $[Ni(NH_3)_6]I_2$, may be prepared by passing ammonia gas into a saturated aqueous solution of nickel iodide. A light blue precipitate is formed, which on warming almost dissolves, yielding a blue liquid. From this on cooling and addition of alcohol the hexammino-derivative is precipitated as a light blue crystalline powder.[2] It crystallises in glistening blue octahedra and loses ammonia on exposure to air, becoming greenish brown in colour. It is soluble in water, with formation of nickel hydroxide.

Tetrammino-nickel iodide is claimed to be formed when slightly heated nickel iodide is exposed to the action of ammonia gas. The substance swells up and a yellowish-white powder is left.[3]

Diammino-nickel Iodide, $[Ni(NH_3)_2]I_2$, is produced by the thermal decomposition of the hexammino-derivative. From the researches of Biltz and Fetkenheuer,[4] by thermal decomposition of the hexammino-derivative only the existence of the hexammine and the diammino-derivative are indicated.

By preparing ammino-derivatives of nickel iodide in presence of mercuric iodide, complex substances containing mercuric iodide are formed. Depending on the proportions of mercuric iodide to nickel salt and the amount of ammonia present, four different compounds are formed, namely, $[Ni(NH_3)_4]I_2.HgI_2.4H_2O$; $[Ni(NH_3)_6]I_2.HgI_2.8H_2O$; $[Ni(NH_3)_4]I_2.2HgI_2.2H_2O$; and $[Ni(NH_3)_6]I_2.2HgI_2.8H_2O$.

The first two compounds are produced when excess of nickel salt is used, the two latter substances when excess of mercuric iodide is used. The tetrammino-derivatives are produced if only a small quantity of free ammonia is used, and the hexammino-salts when a more concentrated solution of ammonia is employed.

The first two compounds are greenish blue, the latter are light violet in colour. All are crystalline, and separate in star-like crystals. In concentrated solution the separation of the compounds is almost quantitative.[5]

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[1] Rammelsberg, *Pogg. Annalen*, 1842, 55, 69; Richards and Cushman, *Zeitsch. anorg. Chem.*, 1898, 16, 175.

[2] Erdmann, *J. prakt. Chem.*, 1840, 19, 445.

[3] Rammelsberg, *Pogg. Annalen*, 1839, 48, 119.

[4] Biltz and Fetkenheuer, *Zeitsch. anorg. Chem.*, 1913, 83, 163.

[5] Ephraim and Mosimann, *Ber.*, 1921, 54, 398.

Dihydrazino-nickel Chloride, $[Ni(N_2H_4)_2]Cl_2$, is produced by mixing a hot aqueous solution of nickel chloride with 50 per cent. hydrazine hydrate, when a bluish-white precipitate separates which is washed with water and dried *in vacuo.* The substance is a bluish-white powder which is soluble in ammonia and in dilute acids.[1]

Trihydrazino-nickel Chloride, $[Ni(N_2H_4)_3]Cl_2$, is obtained by treating hexammino-nickel chloride with 50 per cent. aqueous hydrazine hydrate. On heating the mixture ammonia is evolved, and the hydrazino-salt precipitated as a violet crystalline powder which dissolves in dilute acids, giving a blue solution. The corresponding hydrazino-compounds of nickel bromide are prepared in the same manner from nickel bromide and hexammino-nickel bromide. They are crystalline substances, and resemble the chlorides in appearance and in reactions.

Ammino-derivatives of Nickel Sulphate.

Hexammino-nickel Sulphate, $[Ni(NH_3)_6]SO_4$.—Anhydrous nickel sulphate rapidly absorbs ammonia gas, heat is developed, and a bulky white powder produced of composition $NiSO_4.6NH_3$. It is soluble in water, forming a blue solution and a precipitate of green nickel hydroxide. The solid when heated decomposes with loss of ammonia.[2]

Two other ammino-derivatives are known, namely, pentammino-dinickel sulphate and tetrammino-nickel sulphate.

Pentammino-dinickel Sulphate, $[Ni_2(NH_3)_5](SO_4)_2.7H_2O$, is produced when a stream of ammonia gas is passed through a cooled aqueous solution of nickel sulphate. A bulky precipitate forms, which goes into solution on slight warming, and separates on cooling in large pale violet needles which deliquesce on exposure to moist air.[3]

Tetrammino-nickel Sulphate, $[Ni(NH_3)_4]SO_4.2H_2O$, is deposited from the deep blue solution obtained by dissolving nickel sulphate in concentrated aqueous ammonia on cooling or on standing *in vacuo* over sulphuric acid. It crystallises in transparent dark blue rectangular prisms which decompose on exposure to air, yielding a light blue powder, and on heating lose ammonia and sulphur dioxide, leaving basic nickel sulphate. The substance is soluble in water, forming a deep blue solution, which on heating loses ammonia. It is insoluble in alcohol.[4]

Hexammino-nickel Sulphate Potassium Iodide, $[Ni(NH_3)_6]SO_4.2KI$, is produced when a 20 per cent. aqueous solution of nickel sulphate is gradually added to concentrated aqueous ammonia saturated with potassium iodide. The substance separates as a violet microcrystalline powder. The corresponding potassium bromide and potassium chloride additive products are obtained on saturating the aqueous ammonia solution with potassium bromide or iodide respectively. The salts are hygroscopic, and tend to lose ammonia with substitution of water, and subsequent change in colour from violet to green. In the case of the nickel halides such additive compounds are not obtained, but instead the simple hexammino-nickel halide is formed, thus giving a further method for the preparation of these ammines.[5]

Hexahydroxylamino-nickel Sulphate, $[Ni(NH_2OH)_6]SO_4$, is pro-

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[1] Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1908, 60, 262.
[2] Rose, *Pogg. Annalen*, 1830, 20, 151.
[3] Andrée, *Compt. rend.*, 1888, 106, 937.
[4] Erdmann, *J. prakt. Chem.*, 1836, 7, 264.
[5] Poma, *Atti R. Accad. Lincei*, 1910, 19, 223.

duced by the addition of hydroxylamine to a cold saturated aqueous solution of nickel sulphate. A red solution is obtained from which crystals separate on standing or on the addition of alcohol. The red compound loses colour on moistening with water and a white powder is produced. On heating, the substance swells up, turns blue, then red, and finally becomes almost white.[1]

Trihydrazino-nickel Sulphate, $[Ni(N_2H_4)_3]SO_4$, is formed by adding hydrazine hydrate to an aqueous solution of nickel sulphate to which ammonia has been added. On warming the clear liquid on a water-bath the hydrazino-derivative gradually separates as a reddish-violet powder. This is washed with water and dried *in vacuo*. From analysis the compound appears to contain some water of hydration.[2]

Other salts of nickel also absorb ammonia. The hexammine of nickel perchlorate, $[Ni(NH_3)_6](ClO_4)_2$, may be mentioned, as this substance has been suggested as a delicate test for nickel.[3]

It is obtained as a violet precipitate when ammonium perchlorate is added to an aqueous ammoniacal solution of a nickel salt. The compound is fairly stable but decomposes on heating above 110° C. It is soluble in concentrated aqueous ammonia and decomposes slightly on washing with water or with alcohol. Used as a qualitative test for nickel, it is capable of detecting one part of the metal in 7700 parts of water, so that it is not such a delicate test for nickel as the dimethylglyoxime test.[4]

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[1] Uhlenhuth, *Annalen*, 1899, 307, 334.

[2] Franzen and Mayer, *Zeitsch. anorg. Chem.*, 1908, 60, 265.

[3] Salvadori, *Gazzetta*, 1912, [1], 42, 458; Neusser, *Oesterr. Chem. Zeit.*, 1924, 27, 54.

[4] See Vol. IX., Part II., p. 134, of this series.

CHAPTER XII.

THE METAL-AMMINES OF RUTHENIUM, RHODIUM, AND PALLADIUM.

ALL three metals of this group give rise to ammino-derivatives the compositions of which, however, differ considerably. The ammino-derivatives of ruthenium mostly contain a nitroso-group as well as ammonia; the ammino-derivatives of rhodium salts closely resemble the cobalt-ammines; and the ammino-derivatives of palladium salts correspond to the ammino-derivatives of platinum salts.

AMMINO-DERIVATIVES OF RUTHENIUM SALTS.

Ammino-derivatives of ruthenium salts are of two classes, namely, those formed by the addition of ammonia to simple ruthenium salts, and those formed where ruthenium, ammonia, and nitroso-group constitute the basic radicle. The first class is small, the second contains a series of derivatives comparable with the ammino-derivatives of platinum.

Class I. Ammino-derivatives of Ruthenium Halides.

Heptammino-diruthenium Chloride, $[Ru_2(NH_3)_7]Cl_6$, is produced when anhydrous ruthenium chloride is exposed to the action of dry ammonia gas at ordinary temperature. Heat is developed during absorption, and increase in volume takes place. Absorption takes place most readily if the reacting substances are kept at 0° C. The substance is a deep violet-coloured powder which is partially soluble in water, giving an intense violet-red liquid; solution is only complete, however, if the solvent is saturated with ammonia. Apparently decomposition takes place during solution, for if finely divided anhydrous ruthenium chloride be added in successive small quantities to aqueous ammonia at 0° C. and the mixture heated for some little time at 40° C., a deep red solution is obtained from which separate, when sufficiently concentrated, small crystalline leaflets of composition $2RuCl_2(OH)_2.7NH_3.2H_2O$. The *hydroxy-chloride* so formed is brown, with a somewhat metallic lustre. One part of the substance in 10,000 parts of water yields an intense red colour. The dry salt is stable in dry air, but the aqueous solution decomposes slowly on exposure to light, with precipitation of brown ruthenium sesquioxide, the decomposition being more rapid on heating.[1]

The corresponding *heptammino-diruthenium bromide*, $[Ru_2(NH_3)_7]Br_6$, and *heptammino-diruthenium iodide*, $[Ru_2(NH_3)_7]I_6$, are prepared in the same way by the action of ammonia gas on the bromide and iodide

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[1] Joly, *Compt. rend.*, 1893, 115, 1299.

respectively. They are insoluble in alcohol, and have similar properties to the chloride.[1]

Class II. The Ammino-derivatives of Ruthenium Salts containing a Nitroso-group.

The first research on these compounds was carried out by Claus,[2] who described two classes of ammino-derivatives obtained from ruthenium dichloride, namely, those obtained from the hydroxide, $Ru(NH_3)_4(OH)_2$, and those from the hydroxide of composition $Ru(NH_3)_2(OH)_2$. These compounds were examined later by Joly,[3] who showed that they contained, besides ammonia and hydroxyl group, a nitroso-group linked to ruthenium, giving rise to the trivalent group (RuNO). He termed them ruthenium nitroso-ammonium compounds. These containing two molecules of ammonia were represented by the formula $Ru(NH_3)_2NO(OH)_3.H_2O$, and those containing four molecules of ammonia in the molecule by the formula $Ru(NH_3)_4NO.OH.R_2$ (where R represents a monovalent acidic radicle).

The first group is small, and no crystalline derivatives have been obtained from it.

The second group was further divided into:

(1) Derivatives containing the divalent group, $[OH.Ru.NO(NH_3)_4]''$.
(2) Derivatives containing the trivalent group, $[Ru.NO(NH_3)_4]'''$.

From these groups numerous crystalline derivatives have been prepared.

In 1907 Werner[4] confirmed Joly's views that the substances contain a nitroso-group, and regarded them as derived from tetravalent ruthenium. They are hydroxo-nitroso-tetrammino-ruthenium salts of general formula $\left[\begin{matrix}OH. & \\ & Ru(NH_3)_4 \\ NO. & \end{matrix}\right]R_2$.

The co-ordination number of the substances is six, and they may be compared with the ammino-platinum compounds of formula $[R_2Pt(NH_3)_4]R_2$.

A series of ruthenium compounds has been obtained by replacing ammonia by ethylenediamine in the complex. These bring ruthenium completely into line with the other metals of the platinum group as far as co-ordination number is concerned.

The nitroso-derivatives of ruthenium may be divided into five classes:

1. **Hydroxo-nitroso-tetrammino-ruthenium salts.**

General formula $\left[\begin{matrix}OH. & \\ & Ru(NH_3)_4 \\ NO. & \end{matrix}\right]R_2$.

2. **Hydroxo-nitroso-diethylenediamino-ruthenium salts.**

General formula $\left[\begin{matrix}OH. & \\ & Ru\ en_2 \\ NO. & \end{matrix}\right]R_2$.

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[1] Gutbier and Trenkner, *Zeitsch. anorg. Chem.*, 1905, 45, 166.
[2] Claus, *Annalen*, 1856, 98, 317.
[3] Joly, *Compt. rend.*, 1889, 108, 1300; 1890, 111, 969.
[4] Werner, *Ber.*, 1907, 40, 2614.

3. **Acido-nitroso-tetrammino-ruthenium salts.**

General formula $\left[\begin{matrix}\mathrm{R.} & \\ & \mathrm{Ru(NH_3)_4} \\ \mathrm{NO.} & \end{matrix}\right]\mathrm{R_2}.$

4. **Diacido-nitroso-tetrammino-ruthenium salts.**

General formula $\left[\begin{matrix}\mathrm{R_2:} & \\ & \mathrm{Ru(NH_3)_4} \\ \mathrm{NO.} & \end{matrix}\right]\mathrm{R}.$

5. **Aquo-nitroso-tetrammino-ruthenium salts.**

General formula $\left[\begin{matrix}\mathrm{H_2O.} & \\ & \mathrm{Ru(NH_3)_4} \\ \mathrm{NO.} & \end{matrix}\right]\mathrm{R_3}.$

The starting material for the preparation of these salts is ammonium or potassium nitroso-pentachlororuthenate, $\left[\mathrm{Ru}\begin{matrix}\mathrm{Cl_5} \\ \mathrm{NO}\end{matrix}\right](\mathrm{NH_4})_2$ or $\left[\mathrm{Ru}\begin{matrix}\mathrm{Cl_5} \\ \mathrm{NO}\end{matrix}\right]\mathrm{K_2}$. The latter is most conveniently prepared by evaporating ruthenium chloride with concentrated nitric acid, dissolving the residue in hydrochloric acid, and precipitating with potassium chloride, when reddish-blue crystals of potassium nitroso-pentachlororuthenate separate.

1. Hydroxo-nitroso-tetrammino-ruthenium Salts.

Hydroxo-nitroso-tetrammino-ruthenium Bromide,[1]

$$\left[\begin{matrix}\mathrm{OH} & \\ & \mathrm{Ru(NH_3)_4} \\ \mathrm{NO} & \end{matrix}\right]\mathrm{Br_2},$$

is obtained by dissolving potassium nitroso-pentachlororuthenate in cold water, mixing with concentrated aqueous ammonia, and heating the resulting reddish-violet solution on a water-bath till the colour of the liquid changes to brownish yellow. Thereafter a concentrated aqueous solution of potassium bromide is added and a yellow crystalline precipitate of the bromide separates, or the substance may be separated from solution by mixing the well-cooled ammoniacal solution with an equal volume of concentrated hydrobromic acid, when the reaction product separates in golden-yellow leaflets. These contain some aquo-salt, which is transformed into the hydroxo-salt by washing with water. The crude product is recrystallised from 15 per cent. acetic acid. The bromide is somewhat sparingly soluble in pure water with neutral reaction, more easily soluble in water containing mineral acids, and less soluble in acetic acid than in pure water.

The *iodide*, $\left[\begin{matrix}\mathrm{OH.} & \\ & \mathrm{Ru(NH_3)_4} \\ \mathrm{NO.} & \end{matrix}\right]\mathrm{I_2}$, is prepared from the bromide by mixing a saturated aqueous solution with half its volume of saturated aqueous potassium iodide. The salt is precipitated as a yellow-brown crystalline powder, which is filtered and washed with alcohol and ether. It is more sparingly soluble in water than the bromide, and again less soluble in acetic acid than in pure water.

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[1] Werner, *Ber.*, 1907, 40, 2614.

The *chloride*, $\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{Cl_2}$, may be prepared by the direct action of ammonia on ammonium nitroso-pentachlororuthenate,[1] or from aquo-nitroso-tetrammino-ruthenium chloride, $\left[\begin{array}{l}\mathrm{H_2O.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{Cl_3}$, by shaking it with alcohol. The red colour of the aquo-salt changes to lemon yellow, and from this the chloride is separated as a yellow crystalline powder which is more soluble in water than the bromide.

The *nitrate*, $\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{(NO_3)_2}$, is obtained by rubbing aquo-nitroso-tetrammino-ruthenium nitrate with alcohol, whereby the reddish-yellow aquo-salt is transformed into a yellow crystalline powder. It is then filtered and treated with more alcohol. The transformation is complete when the alcohol washings are no longer acid in reaction.

The *sulphate*, $\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{SO_4}$, and the *carbonate*, $\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{CO_3}$, have also been prepared.

These hydroxo-salts are all sulphur-yellow crystalline substances. The acid residues are hydrolysable and hence outside the co-ordination complex, and the aqueous solutions, unlike the hydroxo-salts of chromium- and cobalt-ammines, are neutral to litmus, a fact which Werner suggests is due to the smaller tendency of the hydroxo-radicle attached to ruthenium to combine with hydrogen ions. This tendency is much less than in the case of the ammines of cobalt and chromium, but that it still exists is indicated by the increased solubility of these hydroxo-compounds in water acidified with mineral acids, and from such solutions aquo-nitroso-tetrammino-ruthenium salts are obtained thus :

$$\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{R_2}+\mathrm{HR}\longrightarrow\left[\begin{array}{l}\mathrm{H_2O.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{R_3}.$$

The true nature of the hydroxo-compounds is further proved by the fact that the halogen salts are less soluble in acetic acid than in pure water, hence acetic acid is not a sufficiently strong acid to form aquo-salts.

On treating the halogen salts with silver oxide an aqueous solution of the free base of the series, $\left[\begin{array}{l}\mathrm{OH.}\\ \qquad\mathrm{Ru(NH_3)_4}\\ \mathrm{NO.}\end{array}\right]\mathrm{(OH)_2}$, is obtained. The liquid is very strongly basic, and on evaporation it decomposes, leaving a brown residue which is probably *nitroso-trihydroxo-diammino-ruthenium*,

$$\left[\begin{array}{l}\mathrm{(OH)_3\!:}\\ \qquad\mathrm{Ru(NH_3)_2}\\ \mathrm{NO.}\end{array}\right].$$

The properties of this substance have not been investigated.[2]

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[1] Joly, *Compt. rend.*, 1889, 108, 1301.

[2] Joly, *ibid.*, 1889, 108, 1300; Werner, *Ber.*, 1907, 40, 2616; see also Vol. IX., Part I, p. 150, of this series.

2. Hydroxo-nitroso-diethylenediamino-ruthenium Salts.

Hydroxo-nitroso-diethylenediamino-ruthenium Iodide,

$$\left[\begin{matrix}\text{OH.} & \\ & \text{Ru en}_2 \\ \text{NO.} & \end{matrix}\right]\text{I}_2,$$

is prepared from hydroxo-nitroso-tetrammino-ruthenium bromide by warming it with 10 per cent. ethylenediamine solution, cooling the liquid, and then mixing it with potassium iodide. The crude diethylenediamino-iodide separates, mixed with some colloidal ruthenium. The salt is purified by dissolving in water and partly precipitating with silver nitrate to remove impurity. The filtrate is then treated with potassium iodide and the iodide thereby precipitated. It crystallises in golden-yellow leaflets.[1]

The *bromide*, $\left[\begin{matrix}\text{OH.} & \\ & \text{Ru en}_2 \\ \text{NO.} & \end{matrix}\right]\text{Br}_2$, crystallises in thin yellow prisms; the *chloride*, $\left[\begin{matrix}\text{OH} & \\ & \text{Ru en}_2 \\ \text{NO} & \end{matrix}\right]\text{Cl}_2$, in yellow needles; and the *nitrate*, $\left[\begin{matrix}\text{OH.} & \\ & \text{Ru en}_2 \\ \text{NO.} & \end{matrix}\right](\text{NO}_3)_2$, in dark yellow prisms.

Salts have been prepared with optically active camphor sulphonic acids. These also are yellow crystalline bodies, but no resolution of the base has been effected. d-Camphoric acid, d-tartaric acid, and d-nitrocamphor compounds were also prepared, and again no resolution was effected. Hence it is concluded that the hydroxo- and nitroso-groups are probably in the 1-, 6-, or *trans*-position.

3. Acido-nitroso-tetrammino-ruthenium Salts.

Chloro-nitroso-tetrammino-ruthenium Chloride,

$$\left[\begin{matrix}\text{Cl.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{matrix}\right]\text{Cl}_2.$$

Hydroxo-nitroso-tetrammino-ruthenium bromide is dissolved in hot water, an equal volume of concentrated hydrochloric acid added, and the mixture evaporated on a water-bath. After some time a pale flesh-coloured, sparingly soluble powder separates.

The *chloroplatinite*, $\left[\begin{matrix}\text{Cl} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO} & \end{matrix}\right]\text{PtCl}_4$, which is sparingly soluble, is precipitated from a solution of the chloride on the addition of chloroplatinous acid.[2]

The *iodide*, $\left[\begin{matrix}\text{Cl.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{matrix}\right]\text{I}_2$, is precipitated in almost quantitative

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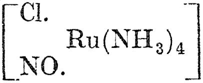
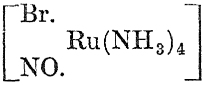
[1] Werner and Smirnoff, *Helv. Chim. Acta.*, 1920, 3, 737.

[2] Joly, *Compt. rend.*, 1890, III, 970.

yield by dissolving the chloride in warm water and filtering the solution into a concentrated aqueous solution of potassium iodide. It separates in fine yellow crystalline leaflets.

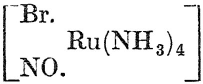
The *nitrate*,  $\begin{bmatrix} \text{Cl.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{bmatrix}(NO_3)_2$, is obtained from a concentrated aqueous solution of the chloride on treatment with concentrated acid as a finely crystalline orange-yellow precipitate. It is sparingly soluble in water, and the cold aqueous solution gives no precipitate of silver chloride on the addition of silver nitrate. Thus showing that the chlorine in the compound is within the complex and therefore not ionised in solution.

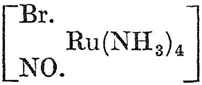
Bromo-nitroso-tetrammino-ruthenium Bromide,

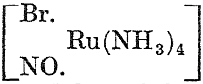


$$\begin{bmatrix} \text{Br.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{bmatrix}Br_2,$$

is prepared from aquo-nitroso-tetrammino-ruthenium bromide on heating with excess of hydrobromic acid for several hours. The reddish-yellow aquo-salt changes to flesh colour, and a sparingly soluble crystalline powder separates. This is filtered from the liquid and the filtrate cooled, when small orange-red crystals of the bromide separate. The salt is sparingly soluble in water, yielding a slightly red solution. The bromine atom in the complex is very firmly held, for, even on warming for several hours with silver nitrate, only a little more bromide than the amount corresponding to the two ionisable bromide atoms is precipitated as silver bromide.

The *iodide*,  $\begin{bmatrix} \text{Br.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{bmatrix}I_2$, is obtained on decomposing the bromide with a concentrated solution of potassium iodide. It separates as a yellowish-orange crystalline powder which is sparingly soluble in water.

The *nitrate*,  $\begin{bmatrix} \text{Br.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{bmatrix}(NO_3)_2$, is produced by rubbing the bromide with concentrated nitric acid. It is a glistening brownish-red crystalline substance, and is more soluble in water than the bromide.

The *sulphate*,  $\begin{bmatrix} \text{Br.} & \\ & \text{Ru(NH}_3)_4 \\ \text{NO.} & \end{bmatrix}SO_4$, is very soluble in water and cannot be precipitated by sulphuric acid. It is therefore prepared by the addition of the calculated quantity of a saturated aqueous solution of silver sulphate to a cold saturated solution of the bromide. The silver bromide is filtered from the liquid and the filtrate concentrated till separation of the salt takes place. It is a brownish-yellow crystalline powder.

Nitrato-salts of the same type as the chloro- or bromo-salts have also been prepared.[1] The salts of the acido-nitroso-tetrammino-ruthenium type are typical acido-ammino-derivatives.

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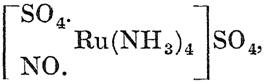
[1] Joly, *Compt. rend.*, 1890, III, 971.

4. Diacido-nitroso-tetrammino-ruthenium Salts.

These are represented by the sulphato-nitroso-tetrammino-ruthenium salts.

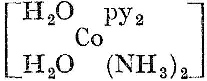
Sulphato-nitroso-tetrammino-ruthenium Sulphate,

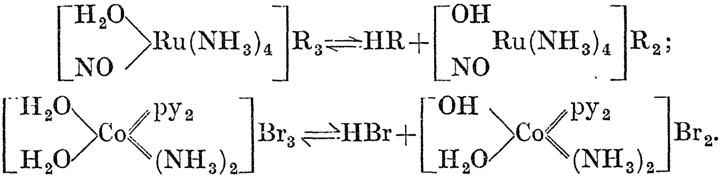


$$\left[\begin{matrix}SO_4. & \\ & Ru(NH_3)_4 \\ NO. & \end{matrix}\right]SO_4,$$

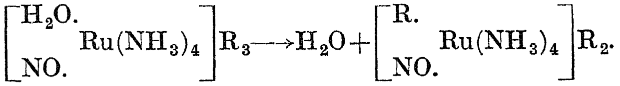
is obtained from chloro-nitroso-tetrammino-ruthenium chloride by evaporation with a slight excess of sulphuric acid. The compound separates in small orange needles and decomposes on addition of water, giving a sparingly soluble residue. On dissolving this in warm water a neutral solution is obtained, from which long needle-shaped crystals of composition $[NORu(NH_3)_4]_2(SO_4)_3.10H_2O$, separate on cooling.

5. Aquo-nitroso-tetrammino-ruthenium Salts.

The aquo-salts are extremely easily hydrolysed, and even moistening with water causes them to decompose, with formation of the less soluble hydroxo-salts. Alcohol also causes hydrolysis of the compounds. The behaviour of the salts towards water resembles that of the diaquo-dipyridino-diammino-cobaltic salts. Thus, the bromide,  $\left[\begin{matrix}H_2O & & py_2 \\ & Co & \\ H_2O & & (NH_3)_2\end{matrix}\right]Br_3$, is almost as easily transformed into the hydroxo-salt as are these aquo-nitroso-tetrammino-ruthenium salts. The two reactions may be represented thus :

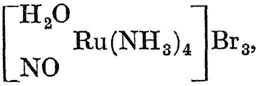


Aquo-ruthenium salts, therefore, cannot be washed with alcohol or water, as both reagents cause hydrolysis. They may, however, be washed with absolute ether or with acetone without causing any change. Like all aquo-ammino-metallic salts, these compounds may be caused to lose water, passing thereby into acido-tetrammino-salts, where one acidic radicle enters the complex thus :



$$\left[\begin{matrix}H_2O. & \\ & Ru(NH_3)_4 \\ NO. & \end{matrix}\right]R_3 \longrightarrow H_2O + \left[\begin{matrix}R. & \\ & Ru(NH_3)_4 \\ NO. & \end{matrix}\right]R_2.$$

Aquo-nitroso-tetrammino-ruthenium Bromide,



$$\left[\begin{matrix}H_2O & \\ & Ru(NH_3)_4 \\ NO & \end{matrix}\right]Br_3,$$

is produced from hydroxo-nitroso-tetrammino-ruthenium bromide by treating it in aqueous solution with concentrated hydrobromic acid. On cooling and adding a further quantity of acid, reddish-yellow crystalline leaflets separate. The crystals effloresce quickly in air, and become opaque on treatment with water or alcohol due to hydrolysis. They dissolve in water, yielding a strongly acid solution, and in excess the substance is completely transformed into the hydroxo-salt again.

The *nitrate*, $\left[\begin{matrix} H_2O & \\ & Ru(NH_3)_4 \\ NO & \end{matrix}\right](NO_3)_3$, is prepared from the hydroxo-bromide by mixing a saturated solution slowly with concentrated nitric acid. On standing, a crystalline precipitate of fine golden-yellow leaflets is produced. This is filtered and washed free from acid with acetone and ether. If shaken with water a yellow precipitate of the hydroxo-salt separates, and at the same time the water becomes strongly acid in reaction.

The *chloride*, $\left[\begin{matrix} H_2O & \\ & Ru(NH_3)_4 \\ NO & \end{matrix}\right]Cl_3.H_2O$, is produced in the same way by treating hydroxo-nitroso-bromide with concentrated hydrochloric acid. If potassium bromide or iodide or ammonium nitrate be added to a solution of this salt, the corresponding pure hydroxo-nitroso-tetrammino-salt is precipitated. On heating it loses water and hydrochloric acid, and yields a mixture of chloro-nitroso-tetrammino-ruthenium chloride and hydroxo-nitroso-tetrammino-ruthenium chloride.

Complex ruthenium salts containing pyridine have been prepared.[1] They are very stable, and have been resolved into their optical isomerides.

Potassium dioxalato-nitroso-pyridino-Ruthenate,

$$\left[\begin{matrix} py & & C_2O_4 \\ & Ru & \\ NO & & C_2O_4 \end{matrix}\right]K.4H_2O,$$

is formed by the action of potassium oxalate and pyridine on potassium nitroso-pentachlororuthenate. It crystallises in large red triclinic prisms. If treated with hydrochloric acid at 100° C. the oxalato-groups are replaced by chlorine, yielding the salt, $\left[\begin{matrix} py & & Cl_2 \\ & Ru & \\ NO & & Cl_2 \end{matrix}\right]K$, and this on treatment with more pyridine passes into nitroso-pyridino-dichloro-hydroxo-ruthenium, $\left[\begin{matrix} py & & Cl_2 \\ & Ru & \\ NO & & OH \end{matrix}\right]$, which may be transformed by means of hydrochloric acid into the trichloro-derivative, $\left[\begin{matrix} py & & Cl \\ & RuCl & \\ NO & & Cl \end{matrix}\right]$.

Potassium dioxalato-nitroso-pyridino-ruthenate yields with quinine hydrochloride two isomeric quinine salts, a dextro- and a lævo-modification, which differ in solubility. The isomers are separated by fractional crystallisation. The dextro-salt is the less soluble, and crystallises in long needles with rotation of $[\alpha]_D +252$ in a solution of equal volumes of alcohol and chloroform. The lævo-salt is more soluble,

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[1] Charonnat, *Compt. rend.*, 1924, 178, 1423.

and crystallises in smaller needles with rotation of $[\alpha]_D - 346$. The active salts may be kept at ordinary temperature for some time without racemisation.

The corresponding ammonium salts are obtained from the quinine salts by treating them with ammonia in an alcoholic chloroform solution. They are viscous substances with rotation of $\alpha_D \pm 425$. On mixing equivalent quantities of the two active salts in solution a crystalline racemate is produced. Alkali or alkali carbonates decompose the salts, so that the sodium or potassium salt cannot be produced by decomposing the quinine salts with these reagents.

Other active salts have been prepared, such as the pyridine salts and the quinidine salts.

Ruthenium may therefore be placed among the elements which form optically active compounds due to asymmetry of the molecule.

AMMINO-DERIVATIVES OF RHODIUM SALTS.

The ammino-rhodium compounds resemble closely the corresponding cobalt and chromium derivatives.

The first compound of the ammino-rhodium series examined was chloro-pentammino-rhodium chloride, $[Rh(NH_3)_5Cl]Cl_2$, which was prepared by treating rhodium trichloride with ammonia. Claus [1] investigated the composition of the substance and prepared from it, by means of moist silver oxide, a strongly basic substance, which proved to be the corresponding hydroxide, $[Rh(NH_3)_5Cl](OH)_2$.

Jörgensen, to show the analogy of the compounds with those of cobalt and chromium, suggested the names luteo-rhodium, purpureo-rhodium, and roseo-rhodium compounds, although the ammino-derivatives of rhodium are colourless.

The nomenclature now adopted is the same as that of the other metal-ammines, and denotes the number of ammino-groups, acidic, water, or other groups in the molecule.

The substances may be classified into three main groups :

(1) *Hexammino-rhodium salts, luteo-salts,* $[Rh(NH_3)_6]R_3$.
(2) *Acido-pentammino-rhodium salts, purpureo-salts,* $[Rh(NH_3)_5R]R_2$.
(3) *Aquo-pentammino-rhodium salts, roseo-salts,* $[Rh(NH_3)_5H_2O]R_3$.

1. *Hexammino-rhodium Salts,* $[Rh(NH_3)_6]R_3$.

The salts of this series are colourless crystalline bodies which are soluble in water. They are stable compounds, and resemble in many respects the aquo-pentammino-salts. They may be distinguished from the latter by the ease with which they react with sodium pyrophosphate, forming a very sparingly soluble pyrophosphate. Also, they do not form acido-pentammino-salts on heating.

Hexammino-rhodium Chloride, $[Rh(NH_3)_6]Cl_3$, may be obtained by heating chloro-pentammino-rhodium chloride in a closed vessel at 100° C. for some time, when, on addition of hydrochloric acid to the cooled mixture, the anhydrous salt is precipitated. It crystallises from hot concentrated hydrochloric acid in the anhydrous form, or, from hot dilute acid, with two molecules of water of hydration. The anhydrous salt crystallises in colourless rhombic plates or compact

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[1] Claus, *J. prakt. Chem.*, 1854, 63, 99.

needle-shaped crystals. The hydrated salt separates in large efflorescent prisms. Both salts are soluble in water and insoluble in hydrochloric acid, and treatment for a long period with concentrated acid on a water-bath gradually converts the salt into chloro-pentammino-rhodium chloride. It forms characteristic salts with mercuric chloride, potassium dichromate, and platinic chloride, which resemble those formed with cobalt and chromium hexammines.[1]

The *bromide*, $[Rh(NH_3)_6]Br_3$, is prepared by the addition of concentrated hydrobromic acid to a solution of the chloride or the nitrate. It crystallises in thin hexagonal plates, and is less soluble than the chloride, which it resembles in reactions.

The *nitrate*, $[Rh(NH_3)_6](NO_3)_3$, may be obtained by dissolving hexammino-rhodium sodium pyrophosphate, $[Rh(NH_3)_6].NaP_2O_7$, in a small quantity of hydrochloric acid and adding dilute nitric acid, when an acid nitrate is precipitated. This reverts to the normal salt on washing with water, giving a snow-white crystalline powder consisting of small rhombic plates. If crystallised from hot water it may be obtained in larger crystals. It is sparingly soluble in water, almost insoluble in nitric acid, and repeated evaporation of the substance with hydrochloric acid transforms it into the chloride.

The *acid nitrate*, $[Rh(NH_3)_6](NO_3)_3.HNO_3$, crystallises in long colourless needles, and is decomposed into the normal salt on treatment with water or alcohol.[2]

The *sulphate*, $[Rh(NH_3)_6]_2(SO_4)_3.5H_2O$, is prepared from the chloride by decomposing it with freshly precipitated silver oxide and water. The strongly alkaline liquid obtained contains the hydroxide, $[Rh(NH_3)_6](OH)_3$, which is made faintly acid with sulphuric acid, evaporated to half its bulk, mixed with 60 per cent. alcohol, and allowed to stand at ordinary temperature for twenty-four hours. The salt crystallises in long lustrous needles and is soluble in water.

The *sodium pyrophosphate*, $[Rh(NH_3)_6]NaP_2O_7.12H_2O$, is obtained as a silky white crystalline precipitate on the addition of sodium pyrophosphate to a dilute solution of neutral hexammino-rhodium salt. It crystallises in small hexagonal prisms or rhombic plates and is almost insoluble in water.

Ammonia may be replaced by ethylenediamine in the hexammino-salts, giving rise to the triethylenediamino-rhodium salts. These are completely analogous to the triethylenediamino-salts of cobalt.

Triethylenediamino-rhodium Chloride, $[Rh\,en_3]Cl_3.2\frac{1}{2}H_2O$, is formed by the interaction of ethylenediamine monohydrate and sodium hexachlor-rhodite thus:

$$3C_2H_4(NH_2)_2+[RhCl_6]Na_3\longrightarrow[Rh(C_2H_4(NH_2)_2)_3]Cl_3+3NaCl.$$

The substance so produced, even after repeated crystallisation from water, still contains sodium chloride, with which it appears to be isomorphous. The pure chloride is best prepared by treating a solution of the crude salt with solid sodium iodide, whereby it is transformed into the iodide. The iodide is recrystallised, and is then converted into the chloride by shaking the aqueous solution with freshly precipitated silver chloride. It crystallises in transparent cubes or in small glistening needles, and loses $2\frac{1}{2}$ molecules of water on heating to 120° C.[3]

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[1] Jörgensen, *J. prakt. Chem.*, 1891, 44, 48.

[2] Jörgensen, *ibid.*, 1891, 44, 63.

[3] Werner, *Ber.*, 1912, 45, 1228.

Jaeger[1] states that the substance crystallises in strongly refractive prisms containing *three* molecules of water.

The *iodide*, $[Rh\,en_3]I_3.1\frac{1}{2}H_2O$, is prepared by the above method from the impure chloride. It is soluble in water, and crystallises from aqueous solution in transparent rhombic crystals.

The *thiocyanate*, $[Rh\,en_3](SCN)_3$, is formed from the iodide by treating it in aqueous solution with potassium thiocyanate. It separates in crystalline aggregates which always contain a little iodide.

This series of compounds, reasoning from analogy with the cobalt- and chromium-ammines, should exist in optical isomers. This has been proved to be the case by the resolution of the chloride.[2] The rotatory power of the rhodium salts is of opposite sign to that of cobalt and chromium salts, and from consideration of the various optically active compounds which have been obtained, Werner draws the conclusion that those asymmetrical isomers which give the less soluble salts with the same active acid have corresponding configurations. Cobalt- and chromium-ammines give sparingly soluble d-isomers, whilst rhodium-ammines give sparingly soluble l-salts, so that rhodium has an optical effect opposite to that of cobalt and chromium. The rotatory power of these triethylenediamino-rhodium salts is of the same order as that of the corresponding chromium or cobalt compounds. The rotation dispersion of the active rhodium salts is small, so that white light may be used in optical measurement.

The resolution of the salts was accomplished by means of sodium d-camphor nitronate or by the action of chloride with tartaric acid. In each case the l-salt separated first, leaving the d-salt in solution in the mother-liquor.

l - Triethylenediamino - rhodium d - camphor Nitronate, $[Rh\,en_3][NO_2.C_{10}H_{14}O]_3$ is prepared by treating an aqueous solution of triethylenediamino-rhodium chloride with a solution of sodium d-camphor nitronate, when a sparingly soluble precipitate of the l-salt separates. From the mother-liquor the d-salt is obtained. These two salts serve as the starting material for the preparation of the optical isomers of the triethylenediamino-rhodium salts.

l - Triethylenediamino - rhodium Iodide, $[Rh\,en_3]I_3.\frac{1}{2}H_2O$, is obtained by rubbing the l-camphor nitronate to a thin paste with water and solid sodium iodide. The iodide so formed is extracted with water and then recrystallised. It crystallises in small glistening cubes, and has rotation of $[\alpha]_D -50°$, $[M]_D -336{\cdot}5°$.

d-Triethylenediamino-rhodium Iodide, $[Rh\,en_3]I_3.\frac{1}{2}H_2O$.—When the mother-liquor from the separation of l-triethylenediamino-rhodium camphor nitronate is precipitated with sodium iodide, a white precipitate containing chiefly inactive iodide is formed. The filtrate from this is evaporated to dryness, the residue is extracted with hot alcohol to remove sodium camphor nitronate and dissolved in water. On the addition of solid sodium iodide pure d-triethylenediamino-rhodium iodide separates in efflorescent cubes. The rotation of the salt is $[\alpha]_D +48°$, $[M]_D +323°$.

l-Triethylenediamino-rhodium Chloride, $[Rh\,en_3]Cl_3.2\frac{1}{2}H_2O$, is prepared from the l-iodide. It crystallises in long efflorescent needles with rotation $[\alpha]_D -80°$, $[M]_D -347{\cdot}6°$.

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[1] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 244.

[2] Werner, *Ber.*, 1912, 45, 1228.

The *d-chloride* crystallises in similar crystals with rotation of $[\alpha]_D + 78°$, $[M]_D + 338{\cdot}9°$.

These active salts are stable, and may be evaporated in aqueous solution without loss of activity. They are also stable towards acids.

Similar active salts are prepared through tartaric acid, in which case a solution of the chloride is treated with silver tartrate.

On concentration **l-triethylenediamino-rhodium d-chloride tartrate,** $[\mathrm{Rh\,en_3}]\mathrm{Cl}(C_4H_4O_6).5H_2O$ or $4H_2O$, separates in transparent monoclinic plates or prisms with rotation of $[\alpha]_D - 50°$, $[M]_D - 278{\cdot}25°$.

The d-isomer separates from the mother-liquor as a non-transparent fibrous mass, and has rotation $[\alpha]_D + 44°$, $[M]_D + 244{\cdot}86°$.

From these compounds the same optically active isomeric salts are obtained as in the case of the camphor nitronates.

Both the racemic salts and the optically active salts appear to be isomorphous with the corresponding cobalt salts when examined crystallographically.[1]

2. *Acido-pentammino-rhodium Salts,* $[\mathrm{Rh(NH_3)_5R}]\mathrm{R_2}$.

Chloro-pentammino-rhodium Chloride, $[\mathrm{Rh(NH_3)_5Cl}]\mathrm{Cl_2}$, was the first salt of the series obtained. It may be prepared by boiling a solution of rhodium trichloride or the double rhodium ammonium chloride with excess of ammonia. The warm solution is filtered, evaporated to dryness, and the residue dissolved in boiling water and cooled when the chloride separates. To obtain the compound free from aquo-salt it is better to precipitate it from aqueous solution with hydrochloric acid, which dissolves the aquo-salt formed. The crystalline salt is washed with acid and dried at 100° C. The compound may also be prepared by dissolving the alloy of rhodium and zinc in aqua-regia and adding to the solution aqueous ammonia.[2] It crystallises in yellowish-white rhombic prisms isomorphous with the corresponding salts of cobalt and chromium. It is sparingly soluble in cold water, much more soluble in boiling water, insoluble in alcohol and in cold hydrochloric acid. It is stable, but begins to decompose on heating to 200° C. On heating in hydrogen gas it is reduced, yielding a deposit of rhodium metal. If heated to 100° C. with sodium hydroxide it is transformed into aquo-pentammino-rhodium chloride without loss of ammonia. This salt forms the starting-point for the preparation of other salts of the series.

The base of the series, **chloro-pentammino-rhodium hydroxide,** $[\mathrm{Rh(NH_3)_5Cl}](\mathrm{OH})_2$, is produced by mixing the chloride with moist silver oxide. Silver chloride is precipitated, and a strongly alkaline liquid produced containing the hydroxide. The base absorbs carbon dioxide from the air, removes ammonia from ammonium salts, and precipitates metallic hydroxides from solutions of the metallic salts. It is only known in solution, and on evaporation of the liquid it is slowly transformed in the cold, more rapidly on heating, into a mixture of aquo-pentammino-rhodium chloride and aquo-pentammino-rhodium hydroxide, thus:

$$3[\mathrm{Rh(NH_3)_5Cl}](\mathrm{OH})_2 + 3\mathrm{H_2O} \longrightarrow [\mathrm{Rh(NH_3)_5.H_2O}]\mathrm{Cl_3} + 2[\mathrm{Rh(NH_3)_5.H_2O}](\mathrm{OH})_3.$$

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[1] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 244.

[2] Claus, *J. prakt. Chem.*, 1854, 63, 99; Jörgensen, *ibid.*, 1882, 25, 346.

The *sulphate*, $[Rh(NH_3)_5Cl]SO_4.2H_2O$, is obtained by exactly neutralising a solution of the hydroxide with sulphuric acid. It crystallises in large yellow prisms which are sparingly soluble in cold water and more soluble in boiling water.

The *acid sulphate*, $[Rh(NH_3)_5Cl]SO_4.3H_2SO_4$, is produced by decomposing the chloride with concentrated sulphuric acid. It separates in long silky prisms of a yellow colour. It is slightly soluble in cold water.

The *nitrate*, $[Rh(NH_3)_5Cl](NO_3)_2$, is precipitated in yellow octahedra when the chloride is treated in concentrated aqueous solution with cold nitric acid. The salt is slowly precipitated, washed with acid and then with alcohol.

Bromo-pentammino-rhodium Bromide, $[Rh(NH_3)_5Br]Br_2$, is prepared in a similar manner to the chloro-salt by heating rhodium-zinc alloy with a mixture of bromine and hydrobromic acid, or by warming aquo-pentammino-rhodium bromide with excess of hydrobromic acid to 100° C.[1, 2] It separates in small orthorhombic yellow crystals which are almost insoluble in cold water and insoluble in alcohol and hydrobromic acid. It has the same constitution as the chloro-compound. Treated with nitric acid, hydrochloric acid, or silver carbonate, it yields the corresponding salts respectively, and with moist silver oxide yields an unstable hydroxide, $[Rh(NH_3)_5Br](OH)_2$. The methods from the preparation of the bromo-salts are like those for the chloro-salts.

Iodo-pentammino-rhodium Iodide, $[Rh(NH_3)_5I]I_2$, is best prepared by warming aquo-pentammino-rhodium hydroxide at 100° C. with excess of hydriodic acid. It forms rhombic crystals which are bright orange-yellow in colour, sparingly soluble in water and insoluble in hydriodic acid and in alcohol.[2]

The *chloride*, $[Rh(NH_3)_5I]Cl_2$, is obtained by treating the iodide with hydrochloric acid, when the salt separates in small chrome-yellow octahedra. It is sparingly soluble in water and insoluble in alcohol.

The *sulphate*, $[Rh(NH_3)_5I]SO_4$, is obtained by treating the chloride with concentrated sulphuric acid. The mixture is diluted with water and left to stand, when orange-yellow efflorescent crystals of composition $[Rh(NH_3)_5I]SO_4.6H_2O$ separate. The anhydrous salt is prepared from this on drying at 100° C., or on precipitation of the mother-liquor from the hydrated salt. It crystallises in quadratic prisms of an orange-yellow colour.

The *nitrate*, $[Rh(NH_3)_5I](NO_3)_2$, crystallises in regular octahedra which are sparingly soluble in water, insoluble in nitric acid and in alcohol. It is prepared by mixing the chloride with dilute nitric acid.

These halogen-pentammino-salts all have the same general chemical characteristics ; all are yellow in colour and are rather sparingly soluble in water.

Nitrito-pentammino-rhodium Nitrate, $[Rh(NH_3)_5NO_2](NO_3)_2$, is prepared from chloro-pentammino-rhodium chloride by dissolving it in dilute aqueous sodium hydroxide and adding pure sodium nitrite and dilute nitric acid. The substance separates as a white crystalline powder which is recrystallised from hot water. It is fairly soluble in cold water, insoluble in alcohol, and the aqueous solution, unlike that of the nitrato-nitrate, is not converted into aquo-nitrite on boiling. It is also unacted on by sodium hydroxide or ammonium sulphide.

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[1] Jörgensen, *J. prakt. Chem.*, 1883, **27**, 461.

[2] Thopsöe, *ibid.*, 1883, **27**, 441.

The *chloride*, $[Rh(NH_3)_5NO_2]Cl_2$, is prepared by the same method as the nitrate, adding dilute hydrochloric acid, after the addition of sodium nitrite. The salt separates as a white powder. It may also be obtained by filtering a concentrated aqueous solution of the nitrate into dilute hydrochloric acid and then adding alcohol, which precipitates the chloride from solution. When heated the chloride decomposes, leaving a residue of pure rhodium. The base of the series, nitrito-pentammino-rhodium hydroxide, $[Rh(NH_3)_5NO_2](OH)_2$, is produced by treating the chloride with silver oxide and water. The filtrate, after removal of silver chloride, is strongly alkaline, and very stable even on boiling. It is capable of liberating ammonia from ammonium salts and precipitating hydroxides of metallic salts. Acids transform it into the corresponding nitrito-salts.

Nitrito-pentammino-rhodium Chloroplatinate, $[Rh(NH_3)_5NO_2]PtCl_6$, separates as a buff-coloured precipitate on the addition of chloroplatinic acid to an aqueous solution of the nitrate. It crystallises in small needles.

The *bromide*, $[Rh(NH_3)_5NO_2]Br_2$, is obtained as a white crystalline precipitate on the addition of hydrobromic acid to cold aqueous solutions of the nitrate. It is easily soluble in water.

The *sulphate*, $[Rh(NH_3)_5NO_2]SO_4$, crystallises in flat shining needles and explodes on heating.

The *acid sulphate*, $[Rh(NH_3)_5NO_2]SO_4.H_2SO_4$, crystallises in long white needles. These decompose on heating, leaving a residue of rhodium. The nitrito-salts, like all the rhodium salts, resemble those of cobalt and chromium, but are more stable, the nitrate being particularly stable. This fact Jörgensen attributes partly to the nature of the central atom.[1]

Nitrato-pentammino-rhodium Nitrate, $[Rh(NH_3)_5NO_3](NO_3)_2$, may be prepared by heating aquo-pentammino-rhodium nitrate, or by dissolving the aquo-nitrate in hot water and adding an equal volume of concentrated nitric acid. After heating for some time, on cooling, the salt separates in small octahedral crystals of greenish-yellow colour. It is only sparingly soluble in water, and on heating the dry salt over a small flame it explodes.[2]

The *chloride*, $[Rh(NH_3)_5NO_3]Cl_2$, separates as a pale greenish-yellow precipitate when a cold aqueous solution of the nitrate is filtered into a mixture of three volumes of hydrochloric acid and one volume of water at 0° C.

The *dithionate*, $[Rh(NH_3)_5NO_3]S_2O_6.H_2O$, is precipitated from a saturated solution of the nitrate or chloride on the addition of a solution of sodium dithionate. It crystallises in white silky needles resembling the corresponding cobalt salt, and is insoluble in water.

3. *Aquo-pentammino-rhodium Salts*, $[Rh(NH_3)_5H_2O]R_3$.

Aquo-pentammino-rhodium Nitrate, $[Rh(NH_3)_5H_2O](NO_3)_3$, is prepared by the addition of nitric acid to a concentrated solution of aquo-pentammino-rhodium hydroxide, when the salt is precipitated in microscopic quadratic plates. It is easily soluble in water, and the dry salt loses water at 100° C., being converted into nitrato-pentammino-rhodium nitrate thus :

$$[Rh(NH_3)_5H_2O](NO_3)_3 \longrightarrow [Rh(NH_3)_5NO_3](NO_3)_2 + H_2O.$$

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[1] Jörgensen, *J. prakt. Chem.*, 1886, 34, 410.

[2] Jörgensen, *ibid.*, 1886, 34, 406.

On the addition of chloroplatinic acid to a solution of the salt, the sparingly soluble nitrate chloroplatinate, $[Rh(NH_3)_5H_2O]NO_3.PtCl_6.2H_2O$, separates as an orange-yellow crystalline precipitate. It easily loses two molecules of water at 100° C., the other molecule being given off more slowly with formation of nitrato-pentammino-rhodium chloroplatinate, $[Rh(NH_3)_5NO_3]PtCl_6$. On heating with dilute hydrochloric acid the substance is transformed into a solution of chloroplatinic chloride and a heavy white precipitate of nitrato-pentammino-rhodium chloride.

Aquo-pentammino-rhodium Chloride, $[Rh(NH_3)_5H_2O]Cl_3.H_2O$, may be prepared by digesting chloro-pentammino-rhodium chloride for several days with moist silver oxide and dissolving the base so formed in hydrochloric acid. It crystallises in yellowish-white octahedra.[1]

The *bromide*, $[Rh(NH_3)_5H_2O]Br_3$, is formed when concentrated hydrobromic acid is added to a solution of aquo-pentammino-rhodium hydroxide. It crystallises in small octahedra or six-sided plates. At 100° C. it loses water and passes into bromo-pentammino-rhodium bromide. It is easily soluble in water.

The *sulphate*, $[Rh(NH_3)_5H_2O]_2(SO_4)_3.2H_2O$, is produced from the hydroxide on treatment with dilute sulphuric acid and precipitation with alcohol. It separates in small white octahedra, and, unlike the other aquo-salts, is not converted into the sulphato-salt on boiling with water. It crystallises in large quadratic prisms, and at 100° C. rapidly loses water.

A chloroplatinate of composition $[Rh(NH_3)_5H_2O]_2PtCl_6(SO_4)_2$ is produced on the addition of chloroplatinic acid to a solution of the sulphate. It crystallises in silky, yellowish six-sided plates.

A series of ammino-rhodium compounds has also been prepared which correspond to the tetrammino-series of salts. These contain pyridine in place of ammonia.[2]

Dichloro-tetrapyridino-rhodium Chloride, $[Rh\,py_4Cl_2]Cl$, is prepared by dissolving rhodium zinc in aqua-regia, and, after removal of acid, heating the aqueous solution with pyridine. On cooling, the pyridino-salt is deposited in yellow prisms. It melts when heated, yielding a black oil, and on further heating, metallic rhodium.

Dichloro-tetrapyridino-rhodium Hydroxide, $[Rh\,py_4Cl_2](OH)$, may be obtained from the chloride by grinding it with freshly precipitated silver oxide. The liquid so produced absorbs carbon dioxide from the air and liberates ammonia from ammonium salts.

The *nitrate*, $[Rh\,py_4Cl_2]NO_3$, is obtained by filtering a solution of the chloride into dilute nitric acid.

The *bromide*, $[Rh\,py_4Cl_2]Br$, is prepared in similar manner to the nitrate.

The *sulphate*, $[Rh\,py_4Cl_2]_2SO_4$, and the *chloroplatinate*, $[Rh\,py_4Cl_2]_2PtCl_6$, have also been prepared.

AMMINO-DERIVATIVES OF PALLADIUM SALTS.

Ammonia combines with palladium salts, yielding ammino-compounds. These are, however, mostly derivatives of the stable palladous salts. Thus the two principal groups of the ammino-derivatives of palladium are the pallados-ammines or diammino-palladium compounds,

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[1] Jörgensen, *J. prakt. Chem.*, 1886, 34, 396.

[2] Jörgensen, *ibid.*, 1883, 27, 478.

$[Pd(NH_3)_2R_2]$, and the pallado-diammines or tetrammino-palladium salts, $[Pd(NH_3)_4]R_2$. These are analogous to two of the series of the ammino-derivatives of the platinous salts, the platos-ammines and the plato-diammines.

They are more conveniently classified into two groups, each containing palladium with a co-ordination number of four thus :

(1) Those containing two molecules of ammonia, *diacido-diammino-palladium compounds*, of general formula $[Pd(NH_3)_2R_2]$.

(2) Those containing four molecules of ammonia, the *tetrammino-palladous salts*, of general formula $[Pd(NH_3)_4]R_2$.

Ammino-derivatives of the unstable palladic salts are unknown, but a series of compounds have been prepared where pyridine takes the place of ammonia in the complex, and these appear to be derivatives of palladic salts. Unlike the platinic salts, however, the co-ordination number in these substances is four instead of six.

The first ammino-derivative of palladium was prepared by Vauquelin in 1813.[1] Vauquelin's salt, the chloropalladite of tetrammino-palladium, $[Pd(NH_3)_4]PdCl_4$, corresponds to the green salt of Magnus, the first known compound of the ammino-platinum salts.

The ammino-derivatives of palladium have been investigated principally by Fischer, Fehling, and Müller.[2]

1. *Diacido-diammino-palladium, the Pallados-ammines,* $[Pd(NH_3)_2R_2]$.

Palladous salts on treatment with excess of ammonia yield tetrammino-palladous salts, from which on the addition of acid the corresponding diacido-diammino-compounds are precipitated. This method may be employed for the preparation of the chloro-, bromo-, and iodo-compounds, which are sparingly soluble in water, and the other members of the series are prepared from these by double decomposition. Ammonia transforms the compounds into tetrammino-palladous salts.

Dichloro-diammino-palladium, $[Pd(NH_3)_2Cl_2]$, is produced by the addition of ammonia to an aqueous solution of palladous chloride until the red precipitate at first formed just dissolves. The liquid is either evaporated to dryness and extracted with water, or it may be heated, to remove excess of ammonia, cooled, and acidified with a slight excess of hydrochloric acid. A yellow powder is obtained which is washed with water and dried at 100° C. The same substance is formed by warming tetrammino-palladous chloride, $[Pd(NH_3)_4]Cl_2$, with palladous chloride. It crystallises in yellow quadratic prisms, is sparingly soluble in water, and is decomposed on heating to redness, yielding ammonia, ammonium chloride, and a porous mass of metallic palladium. Hot concentrated hydrochloric acid or nitric acid reacts with the ammine, forming the corresponding palladous salt. The formation of this ammine is made use of in the separation and purification of palladium.[3]

A *hydrated* compound, $[Pd(NH_3)_2Cl_2]H_2O$, is obtained by treating an alcoholic suspension of the anhydrous body with concentrated aqueous ammonia and evaporating the mixture on a water-bath. The

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[1] Vauquelin, *Ann. Chim. Phys.*, 1813, 88, 184.

[2] Fischer, *Ann. Phys. Chim.*, 1847, 71, 431; Fehling, *Annalen*, 1841, 39, 110; Müller, *ibid.*, 1853, 86, 341; *J. prakt. Chem.*, 1853, 59, 29.

[3] Gutbier, *J. prakt. Chem.*, 1909, 79, 235.

hydrated compound is precipitated, after separation of some tetrammino-palladous chloride and anhydrous diammino-compound. It crystallises in transparent yellow quadratic prisms which are soluble in water and insoluble in alcohol. The crystals effloresce in air, and lose water at 90° C., yielding the insoluble anhydrous compound.[1]

Dibromo-diammino-palladium, $[Pd(NH_3)_2Br_2]$, is prepared by dissolving pure palladium in a mixture of hydrobromic and nitric acids, expelling the nitric acid by repeated evaporation with hydrobromic acid, and dissolving the residue in a small quantity of hydrobromic acid. The palladous bromide solution so obtained is filtered into excess of ammonium hydroxide, when a brown precipitate of the double salt, $[Pd(NH_3)_4]Br_2.PdBr_2$, is produced. This on prolonged treatment with ammonium hydroxide dissolves, with formation of $[Pd(NH_3)_2Br_2]$. The crystalline compound is obtained by filtering the liquid into excess of hydrobromic acid. It crystallises in small yellow octahedra which are insoluble in cold water. Prolonged boiling with water decomposes it with loss of ammonia, and hydrochloric acid transforms it slowly into the chloro-compounds. It is insoluble in sulphuric acid and in potassium hydroxide, although the chloro-compound is soluble.[2]

Di-iodo-diammino-palladium, $[Pd(NH_3)_2I_2]$.—Two compounds are known having the same composition, one yellow, the other red. Both these substances have been described as the di-iodo-compound. It is probable that the yellow substance is the true iodo-derivative, and the other the iodo-palladite of the tetrammino-compound.

A solution of tetrammino-palladium iodide is first prepared, and on evaporation or treatment with acid it partially decomposes, and deposits a substance which is sometimes an orange crystalline body and sometimes a yellow amorphous substance, both of which have the same composition.

The **hydroxo-compound,** $[Pd(NH_3)_2(OH)_2]$, is obtained on treating the chloro-derivative with moist silver oxide, or by precipitation from a solution of the sulphato-compound with the calculated quantity of barium hydroxide. The solution is filtered and evaporated *in vacuo* or in air free from carbon dioxide, when a yellow residue of microscopic octahedra is obtained. The aqueous solution is strongly alkaline, rapidly absorbs carbon dioxide from the air, and combines with evolution of heat with acids, forming the corresponding acido-derivatives. In the dry state it may be heated to 105° C. without decomposition. Prolonged boiling with water causes it to lose ammonia, as in the case of the dibromo-derivative, leaving a brown residue. It precipitates the hydroxides of the metals copper and silver from solutions of their salts, and liberates ammonia from ammonium salts.[2]

The **sulphato-derivative,** $[Pd(NH_3)_2SO_4]$, crystallises in orange-yellow octahedra, is soluble in cold water, and is precipitated from aqueous solution by hydrochloric acid. It is obtained by treating the hydroxo-compound with sulphuric acid, or by the double decomposition of the chloride with silver sulphate.[2]

The **carbonato-derivative,** $[Pd(NH_3)_2CO_3]$, is produced by saturating the hydroxo-compound with carbon dioxide, or by treating an aqueous solution of the sulphato-derivative with barium carbonate. It crystallises from solution, after removal of barium sulphate, in

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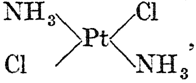
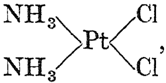
[1] Fischer, *Pogg. Annalen*, 1847, 71, 431.

[2] Müller, *J. prakt. Chem.*, 1853, 59, 29.

yellow octahedra. It is soluble in water, has an alkaline reaction, and precipitates the carbonates of barium, calcium, and iron from solutions of their salts.

The nitrato-derivative of the series is unknown. Treatment of palladous nitrate with ammonia does not yield the corresponding nitrato-derivative, which appears to be unstable. A liquid is, however, obtained by treating the chloro-derivative with silver nitrate, but on evaporation a brown substance separates which detonates on heating.

Only one series of diacido-diammino-palladous compounds is known, although, reasoning from analogy with the corresponding platinous compounds, a symmetrical series corresponding to the platos-ammines, , and an unsymmetrical series corresponding to the plato-semi-diammines, , should exist.

Ammonia in the series may be replaced by organic bases, giving rise to such compounds as the hydroxylamino-, the pyridino-, the quinolino-derivatives.

Dichloro-dihydroxylamino-palladium, $[Pd(NH_2OH)_2Cl_2]$, is one of the products isolated when hydroxylamine hydrochloride, sodium carbonate, and palladous chloride interact. It appears to exist in two forms, and separates in long, slender, yellow needles or as a yellow granular powder. Owing to its instability the investigation of the series to which it belongs is difficult.[1]

Dichloro-dipyridino-palladium, $[Pd\,py_2Cl_2]$, is produced by the addition of pyridine to an aqueous solution of palladous chloride or potassium chloropalladite. A red precipitate is first obtained, which dissolves on heating with excess of pyridine. From the liquid the substance is precipitated on the addition of concentrated hydrochloric acid as a bright yellow crystalline powder. If heated with ammonia, pyridine is eliminated and dichloro-diammino-palladium formed.[2]

The *bromo-derivative,* $[Pd\,py_2Br_2]$, is formed in a similar manner and separates as a yellow microcrystalline precipitate. It also is decomposed on heating with ammonia, forming dibromo-diammino-palladium. The corresponding *nitrate,* $[Pd\,py_2(NO_3)_2]$, has also been described.[3]

Dichloro-diquinolino-palladium, $[Pd(C_9H_7N)_2Cl_2]$, is prepared in the same way from quinoline, and separates as a yellow precipitate which is readily soluble in aqueous ammonia.

The *bromo-derivative,* $[Pd(C_9H_7N)_2Br_2]$, crystallises in small reddish brown leaflets, and when heated with aqueous ammonia till dissolved, and then treated with hydrochloric or hydrobromic acid, the corresponding ammino-compounds are produced.[4]

Dichloro-dibenzylamino-palladium, $[Pd(C_6H_5CH_2NH_2)_2Cl_2]$, is produced by treating an aqueous solution of potassium chloropalladite with benzylamine. A red precipitate is first obtained, which dissolves, giving a colourless liquid with excess of the base. After filtering, the

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[1] Zeisel and Novack, *Annalen,* 1907, 351, 439.

[2] Rosenheim and Maas, *Zeitsch. anorg. Chem.,* 1898, 18, 331; Gutbier and Krell, *Ber.,* 1906, 39, 620.

[3] Gutbier and Fellner, *Zeitsch. anorg. Chem.,* 1916, 95, 129.

[4] Rosenheim and Maas, *ibid.,* 1898, 18, 331.

palladium derivative is precipitated by the addition of concentrated hydrochloric acid in yellow crystalline leaflets. The corresponding *bromo-derivative*, $[Pd(C_6H_5CH_2NH_2)_2Br_2]$, is prepared in a similar manner and crystallises in golden-yellow leaflets.[1] Derivatives containing isopropylamine and dipropylamine are also known. These have the same general characteristics.[2]

Tetrammino-palladous Salts, $[PdNH_3)_4]R_2$.—These are formed by exposing anhydrous palladium salts to the action of ammonia, or by treating an aqueous solution of the palladous salt, or the corresponding diammino-palladium derivative, with excess of ammonia. The solution formed is unstable and readily loses ammonia on evaporation, passing into the more stable series mentioned above. If, however, evaporation takes place in an atmosphere of ammonia the salts may be separated. In the dry state they slowly lose ammonia in air, more rapidly on heating or *in vacuo*. This series of compounds are almost colourless and are soluble in water. Acids transform them easily into the diammino-compounds.

Tetrammino-palladous Chloride, $[Pd(NH_3)_4]Cl_2$, is prepared by heating palladous chloride with dry gaseous ammonia, or by the same reaction on dichloro-diammino-palladium. It is a white substance which loses ammonia *in vacuo*, leaving dichloro-diammino-palladium.

The *monohydrate*, $[Pd(NH_3)_4]Cl_2.H_2O$, is produced by dissolving dichloro-diammino-palladium in aqueous ammonium chloride and ammonia. It crystallises in colourless rhombic prisms which are very soluble in water, and lose ammonia and water on heating to 120° C. thus :

$$[Pd(NH_3)_4]Cl_2.H_2O \longrightarrow [Pd(NH_3)_2Cl_2]+H_2O+2NH_3.$$

Tetrammino-palladous Hydroxide, $[Pd(NH_3)_4](OH)_2$, may be obtained by decomposing the sulphate with barium hydroxide. It separates as a colourless crystalline substance which is soluble in water and has a strong alkaline reaction. The aqueous solution is capable of precipitating copper, iron, cobalt, and nickel from solutions of their salts, and it also decomposes ammonium salts.

The *bromide*, $[Pd(NH_3)_4]Br_2$, is prepared like the chloride from palladous bromide and excess of ammonia. It crystallises in almost colourless rhombic prisms which are soluble in water and stable in air.

The *iodide*, $[Pd(NH_3)_4]I_2$, is obtained by passing gaseous ammonia over palladous iodide, or on boiling palladous iodide or di-iodo-diammino-palladium with aqueous ammonia till the substance just dissolves and the liquid becomes colourless. Thereafter the liquid is evaporated in an atmosphere of ammonia. It is an unstable, colourless crystalline substance which loses ammonia in air and becomes yellow in colour. *In vacuo* it is transformed first into di-iodo-diammino-palladium, and finally into palladous iodide.

The *sulphate*, $[Pd(NH_3)_4]SO_4.H_2O$, is formed from the base by heating it with sulphuric acid, or by treating the sulphato-diammino-derivative with a large excess of ammonia. It crystallises in colourless silky prisms which are soluble in water and insoluble in alcohol, and easily loses water. Hydrochloric acid precipitates from its solution dichloro-diammino-palladium.

Several double salts are known.

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[1] Rosenheim and Maas, *Zeitsch. anorg. Chem.*, 1898, 18, 331.

[2] Gutbier and Fellner, *ibid.*, 1916, 95, 129.

Tetrammino-palladous Chloro-palladite, $[Pd(NH_3)_4]PdCl_4$, is formed by the addition of ammonia to a solution of palladous chloride, or better, by the addition of palladous chloride to tetrammino-palladous chloride. It crystallises in prismatic needles of a reddish colour and decomposes in boiling water, being transformed into dichloro-diammino-palladium. In the dry state it remains unaltered on heating to 180° C., but at 200° C. it becomes yellow, and undergoes the same transformation as with water. Ammonia in excess yields tetrammino-palladous chloride.

Tetrammino-palladous Chloro-palladate, $[Pd(NH_3)_4]PdCl_6$, is produced by the action of chlorine on cold aqueous dichloro-diammino-palladium, or by the action of aqua-regia on tetrammino-palladous chloride. The substance is a brownish-black crystalline body. It is precipitated and decomposed by hydrochloric acid, with liberation of nitrogen, the formation of ammonium chloride and porous palladium. Boiling water decomposes it into ammonium chloro-palladite. The corresponding *bromo-palladite*, $[Pd(NH_3)_4]PdBr_4$, and *nitrito-palladite*, $[Pd(NH_3)_4]Pd(NO_2)_4$, are also known.

Ethylenediamine and propylenediamine may be substituted for ammonia in the diammino-palladous salts. This series is prepared by the action of ethylenediamine and analogous bases on palladous salts. A double palladous compound is first formed, which is decomposed on addition of excess of the base, yielding the single salt.

Diethylenediamino-palladous Chloride, $[Pd\,en_2]Cl_2$, is a light yellow crystalline substance. The corresponding bromide, $[Pd\,en_2]Br_2$, is dark yellow, and the iodide, $[Pd\,en_2]I_2$, is brownish yellow. The free base corresponding to the salts, $[Pd\,en_2](OH)_2$, has not been isolated, but in solution it is yellow in colour, strongly alkaline, and decomposes ammonium salts with evolution of ammonia.[1]

An optically active derivative of palladium has been prepared by combining potassium chloropalladite with l-propylenediamine. This salt has a rotation $[\alpha]_D+79{\cdot}25°$, $[M]_D+258{\cdot}1°$. It is analogous to the corresponding platinum compound, but the rotation is much greater, thus showing the influence of the central metallic atom in increasing or diminishing the rotation.[2]

Ammino-derivatives of palladic salts are unknown, but pyridine derivatives containing tetravalent palladium have been described. The substances are easily obtained by the oxidation of dichloro-dipyridino-palladium.

Dipyridino-palladic Chloride, $[Pd\,py_2]Cl_4$, is formed by the action of chlorine on dichloro-dipyridino-palladium suspended in chloroform. It crystallises in small orange-coloured prisms, and rapidly loses chlorine on exposure to moist air. If heated with potassium hydroxide a brown precipitate of palladic hydroxide separates, and if this is carefully neutralised with hydrochloric acid, potassium chloro-palladate crystallises out. Treatment with an aqueous solution of potassium iodide decomposes the salt, with formation of the palladous compound thus :

$$[Pd\,py_2]Cl_4+2KI \longrightarrow [Pd\,py_2Cl_2]+2KCl+I_2.$$

Dipyridino-palladic Chloro-bromide, $[Pd\,py_2]Br_2Cl_2$, is pro-

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[1] Gutbier and Woernle, *Ber.*, 1906, 39, 2716.
[2] Tschugaeff, *ibid.*, 1907, 40, 3463.

duced by shaking dichloro-dipyridino-palladium suspended in chloroform with bromine. It separates as a deep orange-red crystalline powder, and is less stable than the tetrachloride. If boiled with potassium hydroxide and then neutralised the chloropalladate is obtained.

Dipyridino-palladic Iodo-chloride, $[\mathrm{Pd\ py_2}]\mathrm{I_2Cl_2}$, crystallises in brown needles and is stable in the dry state in air. On boiling with potassium hydroxide complete decomposition takes place and a residue of palladous iodide remains. If shaken with pure carbon disulphide, two atoms of iodine are removed and dichloro-dipyridino-palladium remains.[1]

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[1] Rosenheim and Maas, *Zeitsch. anorg. Chem.*, 1898, 18, 331.

CHAPTER XIII.

THE METAL-AMMINES OF OSMIUM, IRIDIUM, AND PLATINUM.

ALL three elements form complex ammino-derivatives. Those of osmium have been very little investigated; those of iridium are analogous to the ammino-derivatives of platinum on the one hand and to the ammines of cobalt and chromium on the other; whilst the platinum derivatives resemble those of cobalt, save that the metal in the platinic derivatives is tetravalent and not trivalent as in the cobalt-ammines.

AMMINO-DERIVATIVES OF OSMIUM COMPOUNDS.

Osmium has little tendency to simple salt formation owing to the great affinity which the element has for oxygen. The principal compounds, therefore, are complex in character. The ammino-derivatives appear to be derived from the two ammino-bases, $[OsO(NH_3)_2](OH)_2$ and $[OsO_2(NH_3)_4](OH)_2$.

Diammino-osmo-hydroxide, $[OsO(NH_3)_2](OH)_2$, is prepared from osmium tetroxide and excess of concentrated aqueous ammonia. The yellow liquid obtained is heated in a closed vessel at 50° C. till it becomes dark brown in colour and a black powder is deposited. It is then exposed to the atmosphere and evaporated at low temperature, when a blackish-brown powder is deposited. The dry powder decomposes explosively on heating, with evolution of nitrogen. It dissolves in acids yielding the corresponding salts, and from these the base may be precipitated on the addition of aqueous alkali hydroxide. On boiling with a solution of alkali, however, the base is decomposed, ammonia is liberated, and a precipitate of osmium dioxide remains.[1]

Diammino-osmo-chloride, $[OsO(NH_3)_2]Cl_2$, is obtained by treating the hydroxide with hydrochloric acid. It separates as a brown crystalline powder which is soluble in water, yielding a basic salt. On heating, the salt swells up, loses hydrogen chloride and ammonia, and leaves a residue of osmium.

The *sulphate*, $[OsO(NH_3)_2]SO_4$, and the *nitrate*, $[OsO(NH_3)_2](NO_3)_2$, are also brown crystalline salts.[1]

Tetrammino-osmyl-hydroxide, $[OsO_2(NH_3)_4](OH)_2$, is only known in solution. On treating the chloride, $[OsO_2(NH_3)_4]Cl_2$, with moist silver oxide, or the sulphate, $[OsO_2(NH_3)_4]SO_4$, with barium hydroxide, a strongly alkaline yellow liquid is obtained which absorbs carbon dioxide readily and neutralises acids. All attempts to obtain the

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[1] Claus, *Bull. Acad. Sci. Pétrograd*, 1863, 6, 154; Berzelius, *Ann. Chim. Phys.*, 1829, 42, 91.

base in the solid state have been unsuccessful, as on concentration it decomposes into osmium tetroxide with loss of ammonia. The salts of the base are crystalline compounds, of which the chloride is the best known.

Tetrammino-osmyl-chloride, $[OsO_2(NH_3)_4]Cl_2$, is obtained on mixing a concentrated solution of potassium osmate with ammonium chloride, when an orange-yellow crystalline precipitate is at once obtained. It is sparingly soluble in cold water but decomposes in boiling water, with formation of osmium tetroxide and diammino-osmohydroxide. It is insoluble in alcohol and in water containing ammonium salts, also in concentrated hydrochloric acid.[1] On heating, the substance decomposes, yielding a porous mass of osmium. This reaction has been utilised in preparing metallic osmium. An aqueous solution of the salt gives with potassium ferrocyanide a violet-coloured solution, a reaction which may be used as a delicate test for osmium.

Tetrammino-osmyl-nitrate, $[OsO_2(NH_3)_4](NO_3)_2$, is very unstable. It separates in crystalline granules of an orange-yellow colour.

Tetrammino-osmyl-sulphate, $[OsO_2(NH_3)_4]SO_4$, may be prepared by mixing potassium osmate with ammonium sulphate. It is a yellow crystalline body which is sparingly soluble in cold water and decomposed by boiling water.

The *oxalate*, $[OsO_2(NH_3)_4]C_2O_4$, is prepared in similar manner from potassium osmate and ammonium oxalate. It is a yellow crystalline substance.

By the action of ammonia on potassium osmate a brown liquid is produced which probably contains another base of formula $[Os(NH_3)_2](OH)_2$. The liquid, which has not been fully investigated, is basic in character and yields salts with acids.[2]

AMMINO-DERIVATIVES OF IRIDIUM SALTS.

Ammonia unites readily with iridium salts, giving rise to complex ammino-derivatives. The first compounds described appear to be ammines analogous to those of palladium and platinum, to which they were compared by Berzelius [3] and Skoblikoff.[4] A further series were described by Claus [5] which he represented like those of ammino-rhodium salts, as they bore a marked resemblance to these. After Jörgensen had established the constitution of the ammines of rhodium, cobalt, and chromium salts, Palmaer gave similar constitution to the iridium compounds.

Three different series of ammino-derivatives are known, viz.:

(1) Ammino-derivatives of iridous salts.
(2) Ammino-derivatives of iridic salts.
(3) Ammino-derivatives of iridium sesqui-salts.

In these the metal is divalent, tetravalent, and trivalent respectively. The ammino-iridous and the ammino-iridic salts correspond to the ammino-derivatives of palladium and platinum, whilst those of the sesqui-salts are analogous to the ammino-derivatives of cobalt, chromium, and rhodium.

The third series is by far the largest.

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[1] Gibbs, *Amer. Chem. J.*, 1881, 3, 233.

[2] Frémy, *Ann. Chim. Phys.*, 1844, 12, 521; Gibbs, *Amer. Chem. J.*, 1881, 3, 233.

[3] Berzelius, *Pogg. Annalen*, 1828, 13, 476.

[4] Skoblikoff, *J. prakt. Chem.*, 1853, 58, 31.

[5] Claus, *ibid.*, 1854, 63, 99.

1. *Ammino-derivatives of Iridous Salts.*

The co-ordination number in this series appears to be four.

Dichloro-diammino-iridium, $[Ir(NH_3)_2Cl_2]$, is produced when iridous chloride is warmed with excess of aqueous ammonium carbonate and the reaction mixture neutralised with dilute hydrochloric acid. It is a yellow granular powder which is insoluble in water.[1]

Sulphato-diammino-iridium, $[Ir(NH_3)_2SO_4]$, is prepared by treating the chloride with sulphuric acid, when orange-coloured crystals separate which, unlike the chloro-compound, are soluble in water.

The corresponding *hydroxide*, $[Ir(NH_3)_2(OH)_2]$, has not been prepared.

Tetrammino-iridous Chloride, $[Ir(NH_3)_4]Cl_2$, is obtained by boiling dichloro-diammino-iridium with excess of ammonia. On cooling a yellowish-white precipitate separates, which is decomposed with evolution of ammonia on boiling with water.[1]

Tetrammino-iridous Sulphate, $[Ir(NH_3)_4]SO_4$, crystallises in rhombic prisms which decompose on heating and are easily soluble in water.

The *hydroxide*, $[Ir(NH_3)_4](OH)_2$, has not been prepared.

2. *Ammino-derivatives of Iridic Salts.*

In this series the co-ordination number is six, but the metal itself is tetravalent.

Dichloro-tetrammino-iridic Nitrate, $[Ir(NH_3)_4Cl_2](NO_3)_2$, is formed by the action of concentrated nitric acid on dichloro-diammino-iridium. The salt is soluble in hot water and crystallises in lustrous plates.

Dichloro-tetrammino-iridic Chloride, $[Ir(NH_3)_4Cl_2]Cl_2$, is formed when excess of concentrated hydrochloric acid is added to a solution of the nitrate. It crystallises from boiling water in violet octahedra. Only half of the chlorine in the compound is precipitated by silver nitrate, thus indicating that two chlorine atoms are within the complex.

The *sulphate*, $[Ir(NH_3)_4Cl_2]SO_4$, is also obtained from the nitrate on treatment with sulphuric acid. It crystallises in greenish needles.

3. *Ammino-derivatives of Iridium Sesqui-salts.*

These compounds are much more numerous and have been more thoroughly investigated than the two series already described. Generally speaking they are more stable than the corresponding ammino-cobaltic salts, which they closely resemble.

This series may be divided into the following groups :—

(i) **Hexammino-iridium salts.**
General formula $[Ir(NH_3)_6]R_3$.
(ii) **Aquo-pentammino-iridium salts.**
General formula $[Ir(NH_3)_5H_2O]R_3$.
(iii) **Acido-pentammino-iridium salts.**
General formula $[Ir(NH_3)_5R]R_2$.
(iv) **Hydroxo-pentammino-iridium salts.**
General formula $[Ir(NH_3)_5OH]R_2$.

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[1] Palmaer, *Zeitsch. anorg. Chem.*, 1895, 10, 326.

(v) **Diacido-tetrammino-iridium salts.**
General formula $[Ir(NH_3)_4R_2]R$.

(vi) **Triacido-triammino-iridium compounds.**
General formula $[Ir(NH_3)_3R_3]$.

(i) Hexammino-iridium Salts.

Hexammino-iridium Chloride, $[Ir(NH_3)_6]Cl_3$, is prepared by heating chloro-pentammino-iridium chloride, $[Ir(NH_3)_5Cl]Cl_2$, with 25 per cent. aqueous ammonia in a sealed tube to 140° C. The crude product so obtained is evaporated with hydrochloric acid, the residue dissolved in water, and precipitated by means of sodium pyrophosphate. From this the nitrate is formed by treating with dilute hydrochloric and nitric acids, and finally the nitrate is decomposed by repeated evaporation to dryness with concentrated hydrochloric acid. The residue is then treated with ice-cold hydrochloric acid, when the chloride is precipitated. It crystallises in large six-sided colourless prisms belonging to the monoclinic system, and is soluble in water.[1]

Hexammino-iridium Bromide, $[Ir(NH_3)_6]Br_3$, is formed by treating a solution of the nitrate with hydrobromic acid. It crystallises in colourless six-sided prisms which resemble the chloride, only they are more soluble in water.

Hexammino-iridium Iodide, $[Ir(NH_3)_6]I_3$, is best prepared from the corresponding base, $[Ir(NH_3)_6](OH)_3$, by mixing it with excess of hydriodic acid. It crystallises in yellowish lustrous plates or pyramids, is very soluble in water, and loses iodine on heating.

The *nitrate*, $[Ir(NH_3)_6](NO_3)_3$, crystallises in large quadratic plates belonging to the tetragonal system which are isomorphous with hexammino-cobaltic nitrate. It is soluble in water.

The *hydroxide*, $[Ir(NH_3)_6](OH)_3$, is obtained in solution by treating the chloride with moist silver oxide. The solution is strongly alkaline, displaces ammonia from ammonium salts, and precipitates the hydroxides of some metallic salts. If exposed to air containing carbon dioxide it quickly absorbs the gas, being transformed into the carbonate, $[Ir(NH_3)_6]_2(CO_3)_3$, which crystallises in microscopic plates.

Several more complex salts belonging to the series are known.

Hexammino-iridium Ferricyanide, $[Ir(NH_3)_6][Fe(CN)_6]$, is precipitated when potassium ferricyanide is added to a solution of the chloride. It crystallises in orange-red prisms and is sparingly soluble in water.

Hexammino-iridium Chloro-iridite, $[Ir(NH_3)_6][IrCl_6]$, is precipitated as an amorphous yellow powder on the addition of potassium chloro-iridite to hexammino-iridium chloride. From dilute solution it crystallises in small quadratic plates. It is soluble in cold water, and fairly stable towards concentrated sulphuric acid, which only attacks it above 190° C.

The hexammino-salts are all soluble in water and their solutions are neutral in reaction.[1]

(ii) Aquo-pentammino-iridium Salts, $[Ir(NH_3)_5H_2O]R_3$.

These, unlike the aquo-pentammino-cobaltic salts, are almost colourless. The method of preparation is similar to that given by

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[1] Palmaer, *Zeitsch. anorg. Chem.*, 1895, 10, 320.

Jörgensen for the aquo-pentammino-rhodium salts. They are not so easily formed, however, as the corresponding rhodium compounds.[1]

Aquo-pentammino-iridium Chloride, $[Ir(NH_3)_5H_2O]Cl_3$, is obtained by treating chloro-pentammino-iridium chloride with a concentrated solution of potassium hydroxide for several hours. The liquid is then filtered, cooled, and mixed with concentrated hydrochloric acid, and the precipitate which forms collected and washed with cold concentrated hydrochloric acid and with alcohol. It is thereafter redissolved in water and again precipitated with hydrochloric acid. It separates from solution in crystalline aggregates resembling ammonium chloride in appearance, and on heating to 100° C. it loses water and yields the corresponding chloro-chloride. It is sparingly soluble in water, and the aqueous solution reacts with chloroplatinic acid, forming a yellow crystalline precipitate of the chloroplatinate, $[Ir(NH_3)_5H_2O]_2[(PtCl_6)]_3$. Chlorine water added to the salt in solution gives an intense violet coloration, which gradually changes to dark blue, pale blue, and green, and turns brown on the addition of ammonia.

Aquo-pentammino-iridium Bromide, $[Ir(NH_3)_5H_2O]Br_3$, is produced in the same way as the chloride, using hydrobromic acid instead of hydrochloric acid. It is a crystalline substance and, like the chloride, loses water at 100° C., yielding the bromo-bromide.

Aquo-pentammino-iridium Nitrate, $[Ir(NH_3)_5H_2O](NO_3)_3$, is formed when the corresponding base, $[Ir(NH_3)_5H_2O](OH)_3$, produced by boiling an acido-pentammino-iridium salt with aqueous potassium hydroxide, is treated with nitric acid. It is precipitated in colourless microscopic plates, and on heating to 100° C. it is transformed into nitrato-pentammino-iridium nitrate. An aqueous solution of the salt is transformed into the nitrato-salt on boiling, and the reverse reaction takes place when an aqueous solution of nitrato-pentammino-iridium nitrate is boiled. The same reaction is observed with the corresponding pentammino-rhodium compound.

Aquo-pentammino-iridium Chloroplatinate, $[Ir(NH_3)_5H_2O]_2(PtCl_6)_3$, is produced by the addition of chloroplatinic acid to any of the aquo-salts. It separates as a yellow crystalline precipitate.

Aquo-pentammino-iridium Ferricyanide, $[Ir(NH_3)_5H_2O][Fe(CN)_6]$, is precipitated as a reddish-brown crystalline powder on the addition of potassium ferricyanide to the aquo-pentammino-salts. All the aquo-salts yield violet-coloured solutions with chlorine, due probably to the formation of iridic compounds.

(iii) Acido-pentammino-iridium Salts, $[Ir(NH_3)_5R]R_2$.

Chloro-pentammino-iridium Chloride, $[Ir(NH_3)_5Cl]Cl_2$, is formed by the action of ammonia on iridium trichloride, iridium tetrachloride, or the chloro-double salts. It may also be prepared from chloro-pentammino-iridium sulphate by treating it with barium chloride. Prepared by the first method it separates in wine-coloured crystals, whilst by the second method it is yellow. The red colour of the first product is due to a small quantity of iridium trichloride, which separates with the chloro-chloride and may be removed by heating the hot aqueous solution with hydrogen sulphide. It crystallises in

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[1] Jörgensen, *J. prakt. Chem.*, 1886, 34, 394; Palmaer, *Ber.*, 1891, 24, 2090.

yellowish-white octahedra, and is isomorphous with the corresponding cobalt and rhodium salts. It is soluble in water, and remains unaltered even on heating to 275° C. Above this temperature it decomposes, yielding iridium, ammonium chloride, and ammonia. As in the case of other chloro-pentammino-salts, the chlorine atom within the complex is much more firmly bound than the other two atoms, and is not removed by cold aqueous silver nitrate nor by sulphuric acid.[1]

Chloro-pentammino-iridium Bromide, $[Ir(NH_3)_5Cl]Br_2$, is obtained by decomposing chloro-pentammino-iridium sulphate with the theoretical quantity of barium bromide. It separates in pale yellow rhombic crystals and is soluble in water.

Chloro-pentammino-iridium Iodide, $[Ir(NH_3)_5Cl]I_2$, is obtained by the same method as the bromide, substituting barium iodide for barium bromide. It crystallises in brownish-yellow rhombic prisms, and is less soluble in water than the bromide.

The *sulphate*, $[Ir(NH_3)_5Cl]SO_4.2H_2O$, crystallises in short yellow prisms.

The *nitrate*, $[Ir(NH_3)_5Cl](NO_3)_2$, is obtained from the above compound by treating it with barium nitrate. It is a light yellow crystalline substance.

The *dithionate*, $[Ir(NH_3)_5Cl]S_2O_6$, is formed by treating a cold saturated aqueous solution of the chloride with barium dithionate. It crystallises in long six-sided prisms.

The *oxalate*, $[Ir(NH_3)_5Cl]C_2O_4$, crystallises in slender white needles.[2]

Chloro-pentammino-iridium Hydroxide, $[Ir(NH_3)_5Cl](OH)_2$, may be obtained by decomposition of the chloride with freshly precipitated silver oxide, or by warming the chloride with sodium hydroxide on a water-bath. The base is stable, absorbs carbon dioxide from the air, and only slowly decomposes on boiling with water.

Chloro-pentammino-iridium Chloro-iridite, $[Ir(NH_3)_5Cl]_3(IrCl_6)_2$, is formed when the chloro-chloride is mixed with iridium trichloride. It separates as a flocculent yellow powder, and on recrystallising separates as a yellow crystalline powder. It is slowly attacked by sulphuric acid at 110° C., and is decomposed on heating, yielding iridium, ammonium chloride, and hydrochloric acid.

The *chloro-nitrite*, $[Ir(NH_3)Cl](NO_2)_2$, is obtained from the chloride by treating it with the theoretical quantity of silver nitrite. It crystallises in yellow rhombic prisms.[3]

These pentammino-salts are mostly soluble in water, neutral in reaction, with the exception of the nitrite, which is alkaline.

Bromo-pentammino-iridium Bromide, $[Ir(NH_3)_5Br]Br_2$, is prepared by boiling chloro-pentammino-iridium chloride with potassium hydroxide for five hours to form the hydroxide, and then adding excess of 50 per cent. hydrobromic acid. A white crystalline precipitate of aquo-pentammino-iridium bromide, $[Ir(NH_3)_5H_2O]Br_3$, is obtained, and on heating a solution of this it is converted into the bromo-bromide. The salt separates in yellow rhombic prisms and is soluble in water.[4]

Bromo-pentammino-iridium Nitrite, $[Ir(NH_3)Br](NO_2)_2$, is prepared in the same manner as the chloro-nitrite. It crystallises in

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[1] Palmaer, *Ber.*, 1890, 23, 3810; *Zeitsch. anorg. Chem.*, 1895, 10, 320.

[2] Palmaer, *Ber.*, 1890, 23, 3810; *Zeitsch. anorg. Chem.*, 1895, 10, 326.

[3] Palmaer, *Ber.*, 1890, 23, 3815.

[4] Palmaer, *Zeitsch. anorg. Chem.*, 1895, 10, 320.

pale yellow prisms which are soluble in water and have an alkaline reaction.

Bromo-pentammino-iridium Sulphate, $[Ir(NH_3)_5Br]SO_4.H_2O$, is produced by triturating the nitrite with excess of sulphuric acid. On the addition of water slender needle-shaped crystals separate on cooling. They appear to be the acid sulphate, but are converted into the normal salt by redissolving in water and precipitating with alcohol. The substance crystallises in shining yellowish plates which lose their water of hydration at 100° C.[1]

Iodo-pentammino-iridium Iodide, $[Ir(NH_3)_5I]I_2$, crystallises in short six-sided prisms and octahedra belonging to the rhombic system. It is obtained by heating aquo-pentammino-iridium iodide to 100° C.

Nitrato-pentammino-iridium Nitrate, $[Ir(NH_3)_5NO_3](NO_3)_2$, is also produced by heating the corresponding aquo-salt to 100° C. It separates in microscopic quadratic plates, is soluble in water, and explodes on heating.[2]

Nitrito-pentammino-iridium Chloride, $[Ir(NH_3)_5NO_2]Cl_2$, may be produced by treating dinitrito-tetrammino-iridium chloride with ammonia, or, in better yield, by acting upon aquo-pentammino-iridium chloride with excess of silver nitrite. It separates from aqueous solution on addition of hydrochloric acid in small colourless needles which are very soluble in water and sparingly soluble in hydrochloric acid. It is stable, and scarcely acted on by boiling nitric acid or aqua-regia or moderately strong hydrochloric acid.

The *iodide*, $[Ir(NH_3)_5NO_2]I_2$, is produced by the addition of potassium iodide to a warm solution of the chloride, when it is precipitated in needle-shaped crystals which are usually yellowish brown, but on recrystallisation from water and the further addition of potassium iodide may be obtained colourless. It may be heated to 100° C. without change.

The *sulphate*, $[Ir(NH_3)_5NO_2]SO_4$, is formed on mixing a concentrated warm aqueous solution of the chloride with sodium sulphate. It is sparingly soluble in water and stable on heating to 100° C.

The *nitrite*, $[Ir(NH_3)_5NO_2](NO_2)_2$, crystallises in colourless plates, and is prepared from the chloride and silver nitrite.

The nitro-pentammino-iridium salts resemble those of chromium, cobalt, and rhodium, and react similarly towards reagents, but they are more stable towards acids. They give on long heating with hydrochloric acid chloro-pentammino-derivatives, but are not decomposed by concentrated nitric acid nor by aqua-regia, and only slowly decompose on heating with concentrated sulphuric acid at 100° C.[3]

(iv) Hydroxo-pentammino-iridium Salts.

These salts have not been investigated. They are represented by the hydroxo-hydroxide, $[Ir(NH_3)_5OH](OH)_2$, described by Claus.[4]

(v) Diacido-tetrammino-iridium Salts, $[Ir(NH_3)_4R_2]R$.

Dinitrito-tetrammino-iridium Chloride, $[Ir(NH_3)_4(NO_2)_2]Cl$, is prepared by heating sodium iridio-tetranitrito dichloride, $[IrCl_2(NO_2)_4]$

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[1] Palmaer, *Ber.*, 1890, 23, 3810.

[2] Palmaer, *Zeitsch. anorg. Chem.*, 1895, 10, 320.

[3] Werner and Vries, *Annalen*, 1909, 364, 108.

[4] Claus, *Jahresber.*, 1855, 435.

$Na_3.2H_2O$, with 27 per cent. aqueous ammonia in a closed tube at 170° C. for nine hours. The mixture becomes colourless, and on evaporation transparent light yellow needles or leaflets separate. These are mixed with nitrite, and are purified by dissolving in water and repeated recrystallisation from dilute hydrochloric acid. It is soluble in water and stable towards concentrated hydrochloric acid and nitric acid. On heating with sodium-nitrite solution in presence of acetic acid no change takes place, and the dinitro-salt is recovered unchanged. If heated strongly the salt becomes brown and decomposes suddenly, leaving a grey mass of metallic iridium. The other salts of the series are obtained from this by double decomposition with alkali salts.[1]

Dinitrito - tetrammino - iridium Bromide, $[Ir(NH_3)_4(NO_2)_2]Br.H_2O$, separates in long, colourless, flat prisms, and may be obtained anhydrous by recrystallisation from hydrobromic-acid solution. The hydrated salts lose water on heating but not over phosphorus pentoxide.

The *iodide*, $[Ir(NH_3)_4(NO_2)_2]I$, crystallises in colourless leaflets or prisms, and is prepared by mixing a solution of the chloride with potassium iodide.

The *sulphate*, $[Ir(NH_3)_4(NO_2)_2]_2SO_4.\frac{1}{2}H_2O$, is obtained by decomposing the chloride with potassium sulphate or sulphuric acid. On cooling the solution needle-shaped crystals separate. It is somewhat sparingly soluble in both hot and cold water, but dissolves on the addition of a small quantity of sulphuric acid. With large quantities of sulphuric acid an acid salt is formed.

The *nitrite*, $[Ir(NH_3)_4(NO_2)_2]NO_2.H_2O$, is easily soluble in water, and on addition of sodium nitrite to a solution of the chloride is only partially formed. It is best prepared by heating the chloride with silver nitrite for some time on a water-bath, filtering from silver chloride and concentrating the filtrate. It crystallises in colourless glistening leaflets.

The dinitrito-salts do not decompose with concentrated acids; the salts are mostly soluble in water, and again are more stable than the corresponding cobalt salts, which react easily with acids with replacement of nitro-groups. Ammonia attacks the cobaltic series, forming nitrito-pentammino-salts, whereas very little nitrito-pentammino-iridium salt is produced even on heating the dinitrito-tetrammino-iridium salts with ammonia in a closed tube to 200° C.[2]

Dichloro-tetrammino-iridium Chloride, $[Ir(NH_3)_4Cl_2]Cl.H_2O$, is produced when dinitrito-tetrammino-iridium chloride is heated with ammonium chloride and concentrated hydrochloric acid for several hours. A yellow liquid is obtained, from which on evaporation a yellow crystalline precipitate separates containing the chloro-compound mixed with ammonium chloride. This is collected, dissolved in warm water, filtered, and allowed to crystallise on the addition of hydrochloric acid. It separates in yellow needles and prisms which are impure, but are purified on further recrystallisation from warm water containing acid. It loses water on heating, and finally leaves a residue of iridium. Concentrated hydrochloric acid does not attack the salt.

Dichloro - tetrammino - iridium Sulphate, $[Ir(NH_3)_4Cl_2]_2SO_4.H_2O$, is obtained by rubbing the chloride with concentrated sulphuric acid till no more hydrochloric acid is evolved. The residue

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[1] Werner and Vries, *Annalen*, 1909, 364, 95.
[2] Werner and Vries, *ibid.*, 1909, 364, 101.

is dissolved in water, cooled, and allowed to crystallise. It crystallises in thin glistening yellow leaflets which are sparingly soluble in water. The water of hydration is more firmly bound than in the case of the chloride.

The *bromide*, $[Ir(NH_3)_4Cl_2]Br.H_2O$, is prepared by the addition of concentrated hydrobromic acid to a warm solution of the chloride, when the crystalline compound separates. It is recrystallised from warm water and obtained in yellow needles or prisms which resemble the chloride. It loses water at 80° C.

The *iodide*, $[Ir(NH_3)_4Cl_2]I$, is produced by adding solid potassium iodide to a warm aqueous solution of the chloride. It crystallises in yellow needles which are less soluble than the chloride.

The *chlor-iridite*, $[Ir(NH_3)_4Cl_2]_3[IrCl_6]$, is precipitated from a solution of the dichloro-chloride by iridium trichloride or potassium hexachloridite. It is slightly yellow in colour, sparingly soluble in water, and crystallises from hot water in fine needle-shaped crystals.

The properties of the dichloro-tetrammino-iridium salts are similar to those of the dinitrito-compounds.[1]

(vi) Triacido-triammino-iridium Compounds, $[Ir(NH_3)_3R_3]$.

Trinitrito-triammino-iridium, $[Ir(NH_3)_3(NO_2)_3]$, is obtained by heating sodium tetranitro-dichloro-iridite, $[Ir(NO_2)_4Cl_2]Na_3.2H_2O$, with 27 per cent. aqueous ammonia for eighteen hours in a sealed tube at 140° C. The solution is then evaporated and the salt crystallised repeatedly. It is only freed with difficulty from chloride by boiling with sodium nitrite. It crystallises in pale yellow transparent crystals, is sparingly soluble in cold, and slightly soluble in hot, water. It is unaffected by boiling hydrochloric acid or concentrated nitric acid, and decomposes on heating with concentrated sulphuric acid at 85° C. The aqueous solution is non-conducting. Potassium hydroxide does not attack the substance even on boiling. Warm aqueous silver nitrate causes no decomposition, and concentrated aqueous ammonia acts upon it only in a closed tube at 160° C. It is therefore more stable than the corresponding cobalt compound.

Trichloro-triammino-iridium, $[Ir(NH_3)_3Cl_3]$, appears to be formed when the trinitrito-compound is heated with ammonium chloride and hydrochloric acid at 180° C. for nine hours, but the substance has not been obtained pure. It also is yellow in colour.[2]

Two series of complex iridium salts corresponding to the hexammino- and diacido-iridium salts have been prepared containing ethylenediamine. These have the same general characteristics as the ammino-salts. Both series have been resolved into optically active isomers, the dinitrito-series by means of d- and l-bromo-camphor sulphonic acid, and the triethylenediamino-series by d- and l-nitro-camphor. Attempts have been made to prepare ethylenediamino-derivatives containing tetravalent iridium. Thus, sodium hexachloro-iridate, $[IrCl_6]Na_2$, reacts with ethylenediamine, but the products are syrupy and cannot be purified. Derivatives of trivalent iridium, however, have been prepared. These are crystalline and fairly easily purified. The

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[1] Palmaer, *Zeitsch. anorg. Chem.*, 1896, 13, 211; Werner and Vries, *Annalen*, 1909, 364, 113.

[2] Werner and Vries, *Annalen*, 1909, 364, 91.

starting material is sodium dichloro-tetranitro-iridite, $[IrCl_2(NO_2)_4]Na_3.2H_2O$. The salt is heated in a sealed tube at 170° C. for several hours with ethylenediamine monohydrate. The reaction mixture is treated with hydriodic acid, thus giving a mixture of racemic dinitrito-diethylenediamino-iridium iodide, $[Ir\,en_2(NO_2)_2]I$, and racemic triethylenediamino-iridium iodide, $[Ir\,en_3]I_3$. From these iodides the other salts are prepared.

Racemic Series.

Dinitrito - diethylenėdiamino - iridium Iodide, $[Ir\,en_2(NO_2)_2]I$, crystallises from water in colourless prisms.

Dinitrito-diethylenediamino-iridium Bromide, $[Ir\,en_2(NO_2)_2]Br$, is prepared by transforming the iodide into d-bromo-camphor sulphonate and decomposing it with hydrobromic acid. It crystallises from dilute alcohol in colourless needles.

The *nitrate,* $[Ir\,en_2(NO_2)_2]NO_3$, is obtained from the bromide by decomposition with silver nitrate. It crystallises in prisms.

The *perchlorate,* $[Ir\,en_2(NO_2)_2]ClO_4$, separates as a crystalline powder.

The *bromo-camphor sulphonate,* $[Ir\,en_2(NO_2)_2][d\text{-}C_{10}H_{14}O_4BrS]$, is prepared by treating the iodide with silver bromo-camphor sulphonate. It separates as a vitreous mass.

Theoretically two dinitro-series are possible, but only one has been obtained, and, as the bromo-camphor sulphonate is separable into two optically active components, the series prepared is regarded as the *cis-*, or 1-, 2-series.

d-Dinitro-diethylenediamino-iridium Salts.

d-Dinitrito-diethylenediamino-iridium d-camphor Sulphonate, d-$[Ir\,en_2(NO_2)_2][d\text{-}C_{10}H_{15}O_4S]$, has a rotation of $[\alpha]_D+25{\cdot}6°$.

The *bromide* crystallises in colourless shining polyhedra with rotation $[\alpha]_D+26°$, $[M]_D+126{\cdot}15°$.

The *perchlorate* is a crystalline powder with rotation $[\alpha]_D+24{\cdot}8°$, $[M]_D+125{\cdot}07°$.

The *nitrate* crystallises in flat shining needles with rotation $[\alpha]_D+27{\cdot}2°$, $[M]_D+127{\cdot}10°$.

l-Dinitro-diethylenediamino-iridium Salts.

l-Dinitrito-diethylenediamino-iridium l-camphor Sulphonate gives rotation $[\alpha]_D-26°$.

The *bromide* gives rotation $[\alpha]_D-26°$, $[M]_D-126{\cdot}15°$.

The *perchlorate* gives rotation $[\alpha]_D-25{\cdot}6°$, $[M]_D-129{\cdot}20°$; and the *nitrate* gives rotation $[\alpha]_D-26{\cdot}8°$, $[M]_D-125{\cdot}23°$.

Triethylenediamino-iridium Salts, $[Ir\,en_3]R_3$.—From the mother-liquor after crystallisation of dinitro-diethylenediamino-iridium d-camphor sulphonate, the d-camphor sulphonate of racemic triethylenediamino-iridium crystallises.

The racemic salts prepared are the bromide, $[Ir\,en_3]Br_3.3H_2O$, the nitrate, and the perchlorate. All are colourless crystalline bodies. The bromide yields with sodium d-camphor nitronate, l-triethylenediamino-iridium d-camphor nitronate, and from the filtrate after separating this salt the d-iodide is precipitated by means of potassium iodide.

The d-Series.

Triethylenediamino-iridium Iodide, $[\mathrm{Ir\,en_3}]\mathrm{I_3}$, has rotation $[\alpha]_D+42^\circ$, $[M]_D+316{\cdot}72^\circ$; the *nitrate*, $[\alpha]_D+57{\cdot}2^\circ$, $[M]_D+319{\cdot}07^\circ$; the *perchlorate*, $[\alpha]_D+48{\cdot}5^\circ$, $[M]_D+325{\cdot}8^\circ$.

The l-Series.

l-Triethylenediamino-iridium d-camphor Nitronate is a crystalline powder which is sparingly soluble in water.

The *l-bromide* is readily soluble in water, and has rotation $[\alpha]_D-50^\circ$, $[M]_D-240{\cdot}16^\circ$; the nitrate, $[\alpha]_D-57{\cdot}5^\circ$, $[M]_D-321{\cdot}64^\circ$.

The rotatory power of the triethylenediamino-series is greater than that of the dinitro-series, and of about the same order as that of the corresponding salts of rhodium and platinum.[1]

Several complex iridium compounds containing pyridine have been prepared.

Potassium Pentachloro-pyridino-iridite, $[\mathrm{Ir\,pyCl_5}]\mathrm{K_2}$, is prepared by heating a mixture of potassium hexachloro-iridite, $[\mathrm{IrCl_6}]\mathrm{K_3}$, and pyridine at 100° C. It is a reddish-brown salt which forms an orange-coloured solution in water, and on heating with chlorine yields pentachloro-pyridino-iridic acid, $[\mathrm{Ir^{IV}pyCl_5}]\mathrm{H}$.

Potassium Tetrachloro-dipyridino-iridite, $[\mathrm{Ir'''py_2Cl_4}]\mathrm{K}$, is formed in the same manner as the mono-pyridino-compound, but on longer heating. The substance occurs in two isomeric forms, one orange-yellow, the other red. On oxidation with chlorine or nitric acid, tetrachloro-dipyridino-iridium, $[\mathrm{Ir^{IV}py_2Cl_4}]$, is produced. It is a crystalline body, and with potassium iodide yields potassium tetrachloro-dipyridino-iridite thus:

$$[\mathrm{Ir^{IV}py_2Cl_4}]+\mathrm{KI}\longrightarrow[\mathrm{Ir'''py_2Cl_4}]\mathrm{K}+\mathrm{I}.$$

Ammonia reacts with the compound, yielding two substances:

$$[\mathrm{Ir'''py_2(NH_3)_2Cl_2}][\mathrm{Ir'''py_2Cl_4}] \quad \text{and} \quad [\mathrm{Ir'''py_2(NH_3)_3Cl}][\mathrm{Ir'''py_2Cl_4}]_2.$$

Potassium Dioxalato-dipyridino-iridite, $[\mathrm{Ir'''py_2(C_2O_4)_2}]\mathrm{K}$, may be prepared by the action of pyridine on potassium trioxalato-iridite, $[\mathrm{Ir(C_2O_4)_3}]\mathrm{K_3}$, or potassium dichloro-dioxalato-iridite, $[\mathrm{IrCl_2(C_2O_4)_2}]\mathrm{K_3}$, at 130° C. The substance is crystalline, and on treatment with hydrochloric acid at 130° C. yields a chloro-aquo-derivative, $[\mathrm{Ir'''py_2(H_2O)ClC_2O_4}]$, which crystallises in yellow needles, and a more complex compound, $[\mathrm{Ir'''py_2(H_2O)_2Cl_2}][\mathrm{Ir'''py_2Cl_4}]$, which crystallises in orange-yellow prisms. From the latter substance on treatment with ammonia, ammonium tetrachloro-dipyridino-iridite, $[\mathrm{Ir'''py_2Cl_4}]\mathrm{NH_4}$, is formed, and a hydroxo-compound, $[\mathrm{Ir'''py_2(H_2O)(OH)Cl_2}]$, which separates in yellow crystals.

The dioxalato-dipyridino-iridium compounds cannot be resolved into optical isomers, although the *cis*-form of the compound, $[\mathrm{IrCl_2(C_2O_4)_2}]\mathrm{K_3}$, has been resolved through the strychnine compounds.[2]

Trichloro-tripyridino-iridium, $[\mathrm{Ir\,py_3Cl_3}]$, is produced by heating potassium tetrachloro-dipyridino-iridite to a temperature of 130° C.

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[1] Werner and Smirnov, *Helv. Chim. Acta.*, 1920, 3, 472; *Chem. Zentr.*, 1920, 3, 381.

[2] Delépine, *Compt. rend.*, 1914, 159, 239.

Using the orange modification two isomers can be isolated, whilst only one is obtained from the red form. The orange-coloured salts and their products correspond to the *cis*-form, and may be expected to give optical isomers, whilst the red salt is the *trans*-form.[1]

AMMINO-DERIVATIVES OF PLATINUM SALTS.

Platinum forms both platinous and platinic salts, in which the metal is divalent and tetravalent respectively. Both series of salts are capable of uniting with ammonia, forming complex ammines. The co-ordination number in the platinous series is four and in the platinic series six. The latter series correspond in many respects to the chromic and cobaltic ammino-salts, but as the metal is tetravalent, the maximum number of radicles outside the complex is four instead of three. Also, the ammino-bases from which the salts are derived are much more stable than those of chromium or cobalt.

The first ammino-derivative of platinum was prepared by Magnus in 1828 by the action of ammonia on platinous chloride. It is a green insoluble compound of composition $PtCl_2(NH_3)_2$, and is usually referred to as *Magnus' green salt.* The preparation of this salt led to researches by Gros, Reiset, and Peyronne, who obtained other ammino-compounds and correlated these with Magnus' salt.[2] The ammino-derivatives of platinum salt may be classified according to the following scheme :—

A. Ammino-derivatives of platinous salts.

1. *Tetrammino-platinous salts, plato-diammine salts.*
   General formula $[Pt(NH_3)_4]R_2$.
2. *Acido-triammino-platinous salts, plato-monodiammine salts.*
   General formula $[Pt(NH_3)_3R]R$.
3. *Diacido-diammino-platinous salts, platos-ammines* or *plato-semi-diammines.*
   General formula $[Pt(NH_3)_2R_2]$.
4. *Triacido-ammino-platinous salts, plato-semi-ammine compounds.*
   General formula $[Pt(NH_3)R_3]M$.

B. Ammino-derivatives of platinic salts.

(These derivatives are formed from the platinous series by oxidation.)

1. *Hexammino-platinic salts, Drechsel's base.*
   General formula $[Pt(NH_3)_6]R_4$.
2. *Acido-pentammino-platinic salts,* $[Pt(NH_3)_5R]R_3$.
3. *Diacido-tetrammino-platinic salts, platini-diammine compounds.*
   General formula $[Pt(NH_3)_4R_2]R_2$.
4. *Triacido-triammino-platinic salts, platini-monodiammine compounds.*
   General formula $[Pt(NH_3)_3R_3]R$.

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[1] Delépine, *Compt. rend.*, 1922, 32, 607.

[2] Magnus, *Pogg. Annalen*, 1828, 14, 204; Gros, *Ann. Chim. Phys.*, 1838, 69, 204; Reiset, *ibid.*, 1844, 11, 417; *Compt. rend.*, 1844, 18, 1103; Peyronne, *ibid.*, 1844, 12, 193; 1846, 16, 462.

5. *Tetracido-diammino-platinic compounds, platini-ammines* or *platini-semi-diammines.*
General formula $[Pt(NH_3)_2R_4]$.
6. *Pentacido-ammino-platinic salts, platini-semi-ammine compounds.*
General formula $[Pt(NH_3)R_5]M$.

C. Diplato-ammino-salts.

D. Diplati-ammino-salts.

A. Ammino-derivatives of Platinous Salts.

1. *Tetrammino-platinous Salts,* $[Pt(NH_3)_4]R_2$.[1]

These salts are obtained by treating chloroplatinous acid, $[PtCl_4]H_2$, with ammonia, or by the addition of ammonia to diacido-diammino-platinum. On heating, the salts lose two molecules of ammonia and pass into diacido-diammino-platinum. Halogens oxidise the salts of this series, yielding diacido-tetrammino-platinic salts. Most of the salts are sparingly soluble in water, and can be obtained by treating a solution of the soluble chloride with the corresponding acid.

Tetrammino-platinous Chloride, $[Pt(NH_3)_4]Cl_2.H_2O$, is produced by boiling platinous chloride with excess of ammonia and evaporating the solution with the addition of ammonia till the green salt of Magnus, .$[Pt(NH_3)_4][PtCl_4]$, first formed is redissolved. On cooling and concentrating the liquid the salt crystallises. The substance crystallises in colourless needles which lose water at 110° C. The anhydrous salt dissolves easily in hot water and is precipitated from solution by alcohol. At 250° C. it loses two molecules of ammonia, and is transformed into the sparingly soluble yellow dichloro-diammino-platinum. Sodium hydroxide does not liberate ammonia from the salt, and chlorine oxidises it, yielding dichloro-tetrammino-platinic chloride, $[Pt(NH_3)_4Cl_2]Cl_2$. All the chlorine in the salt is precipitated by aqueous silver nitrate, thus showing the chlorine to be outside the metallic complex. It reacts readily with several of the metallic chlorides with formation of double chlorides; for example, $[Pt(NH_3)_4]Cl_2.SnCl_2$, $[Pt(NH_3)_4]Cl_2.ZnCl_2$, and $[Pt(NH_3)_4]Cl_2.PbCl_2$.[2]

Tetrammino-platinous Chloroplatinite, $[Pt(NH_3)_4]PtCl_4$, Magnus' green salt, is the longest known of the platinous compounds containing ammonia, and forms the starting-point in the preparation of many of the ammino-derivatives of platinum. It may be obtained by heating chloroplatinous acid with aqueous ammonia. It is sparingly soluble, and on cooling separates as a green crystalline compound. The constitution of the substance is established from its formation from tetrammino-platinous chloride and platinous chloride, also from the fact that an aqueous solution of silver nitrate reacts with the salt, yielding a precipitate of silver chloroplatinite and a solution of tetrammino-platinous nitrate thus:

$$[Pt(NH_3)_4]PtCl_4+2AgNO_3\longrightarrow[Pt(NH_3)_4](NO_3)_2+Ag_2PtCl_4.$$

It is insoluble in water but soluble in warm aqueous ammonia, and on

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[1] The older names of the salts are given in the classification, and the names expressing the composition of the salts are used in the text throughout.

[2] Buckton, *Annalen,* 1852, 84, 270.

treatment with nitric acid or chlorine is transformed into a diacido-tetrammino-platinic salt.[1]

The *chloroplatinate*, $[Pt(NH_3)_4]PtCl_6$, is prepared by mixing a cold solution of sodium chloroplatinate with tetrammino-platinous chloride, when the salt separates as a yellow flocculent precipitate. It decomposes slowly at ordinary temperature and more rapidly on boiling, yielding the chloroplatinite.[2]

The *sulphate*, $[Pt(NH_3)_4]SO_4$, may be prepared by treating the chloride with silver sulphate, or by the addition of sulphuric acid to a solution of the chloride. In the latter case an acid salt is first formed which crystallises in nacreous leaflets. This decomposes on boiling with water in presence of ammonia, yielding the neutral sulphate. It is sparingly soluble in water but soluble in sulphuric acid. Chlorine and bromine oxidise it, as in the case of the chloride.

The *bromide*, $[Pt(NH_3)_4]Br_2.1\frac{1}{2}H_2O$, is obtained from the sulphate on treatment with barium bromide. It crystallises in colourless prisms which are very soluble in water and lose water of hydration at 100° C.

The *iodide*, $[Pt(NH_3)_4]I_2$, is prepared like the bromide. It crystallises in pearly leaflets, and a solution of the salt in water loses ammonia on boiling, leaving diodo-diammino-platinum.

Tetrammino-platinous Hydroxide, $[Pt(NH_3)_4](OH)_2$, the base of the series, is isolated by treating a solution of the sulphate with baryta. The liquid is filtered and evaporated *in vacuo*, when the hydroxide separates in white deliquescent needles. It is a strong base, absorbs carbon dioxide from the air, displaces ammonia from its salts, and precipitates metallic hydroxides from solution of their salts. It decomposes at 110° C., and ammonia is not liberated from it by potassium hydroxide.

The *nitrate*, $[Pt(NH_3)_4](NO_3)_2$, is best prepared by precipitation of a solution of the chloride with excess of nitric acid. It crystallises in colourless monoclinic needles which are soluble in boiling water and explode on heating.

The *nitrite*, $[Pt(NH_3)_4](NO_2)_2.2H_2O$, is prepared from the chloride by treating with silver nitrite. It crystallises in short prisms which effloresce in air and are easily soluble in water.

The *carbonate*, $[Pt(NH_3)_4]CO_3.H_2O$, is obtained along with the bicarbonate, $[Pt(NH_3)_4]CO_3.H_2CO_3$, and the sesqui-carbonate, $2\{[Pt(NH_3)_4]CO_3\}.H_2CO_3$, by mixing carbon dioxide with the free base. It is a colourless crystalline compound.

Tetrammino-platinous salts are known containing pyridine in place of ammonia. Thus, diammino-dipyridino-platinous salts have been prepared. These salts are interesting, as they exist in isomeric forms, and through them the configuration of the isomeric diacido-diammino-platinous compounds have been determined. It is well known that diacido-diammino-platinum exists in stereo-isomeric forms. These isomers react with two molecules of pyridine in such a manner that pyridine replaces acidic radicles in the complex with formation of diammino-dipyridino-platinous salts. Depending upon which isomer is treated with pyridine, two different diammino-dipyridino-platinous salts are produced. *Cis-* or unsymmetrical dichloro-diammino-platinum is

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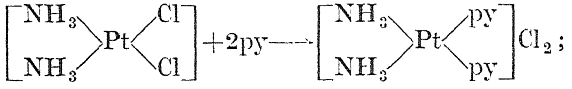
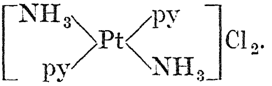
[1] Jörgensen and Sörensen (*Zeitsch. anorg. Chem.*, 1906, 48, 441) describe a red modification of Magnus' green salt, which is probably a polymer of the usual green form.

[2] Cossa, *Gazzetta*, 1890, 20, 725 ; 1895, 25, 505.

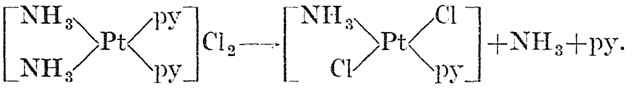
acted upon by pyridine, yielding *cis*-diammino-dipyridino-platinous chloride thus :



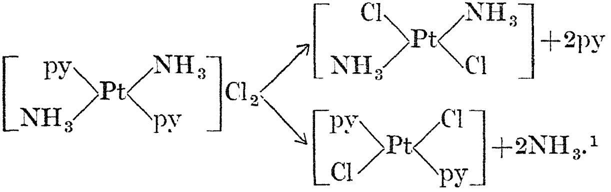
whilst *trans*- or unsymmetrical dichloro-diammino-platinum also reacts with pyridine, yielding *trans*-diammino-dipyridino-platinous chloride,



The two isomers differ in their behaviour towards heat; the *cis*-form loses one molecule of ammonia and one of pyridine, yielding dichloro-ammino-pyridino-platinum,



The *trans*-form loses either two molecules of ammonia or two molecules of pyridine, forming a mixture of dichloro-diammino-platinum and dichloro-dipyridino-platinum,



Ethylenediamine, propylenediamine, and other bases of this type may replace all or part of the ammonia in the tetrammino-salts. The substances are obtained by treating potassium chloroplatinite with the base. The compounds have the same general characteristics as the tetrammino-salts themselves, but are more stable.[2]

Dipropylenediamino-platinous Chloride, $[Pt\,pn_2]Cl_2$, crystallises in greyish-white leaflets, and is prepared by boiling a solution of potassium chloroplatinite with propylenediamine under a reflux until the yellow precipitate first formed dissolves.

Dipropylenediamino-platinous Hydroxide, $[Pt\,pn_2](OH)_2$, is obtained from the chloride by shaking it with freshly precipitated silver oxide. It is strongly alkaline in reaction, absorbs carbon dioxide from the air, and has the properties of an alkali base.

Dipropylenediamino-platinous Bromide, $[Pt\,pn_2]Br_2$, crystallises in colourless leaflets which are easily soluble in water. The *iodide* is also very soluble in water.

Propylenediamino-diammino-platinous Chloride, $[Pt(NH_3)_2pn]Cl_2$, is produced by the cautious addition of ammonia to dichloro-propylenediamino-platinum, $[Pt\,pnCl_2]$, suspended in boiling water.

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[1] Jörgensen, *J. prakt. Chem.*, 1886, 33, 510; Werner, *Zeitsch. anorg. Chem.*, 1893, 3, 310.

[2] Jörgensen, *Zeitsch. anorg. Chem.*, 1906, 48, 374.

It is insoluble in water, microcrystalline, and lilac in colour.[1] Many of these derivatives of platinum containing organic bases have been obtained in optically active forms. Those containing l-propylenediamine will serve as examples. These are easily prepared, and as they are remarkably stable are easily examined for optical properties. The compounds are prepared by the interaction of *cis*-dichloro-l-propylenediamino-platinum, $[Pt\ pnCl_2]$, with the calculated quantity of the corresponding base, l-propylenediamine, ammonia, ethylenediamine, or trimethylenediamine. The liquid obtained is evaporated on a water-bath and precipitated with alcohol. The di-derivative of l-propylenediamine, $[Pt\ pn_2]Cl_2$, has rotation $[\alpha]_D+46{\cdot}37°$, $[M]_D+192{\cdot}0°$.

Diammino-l-propylenediamino-platinous Chloride, $[Pt(NH_3)_2pn]Cl_2$, has rotation $[\alpha]_D+25{\cdot}17°$, $[M]_D+94{\cdot}14°$.

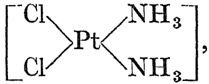
Ethylenediamino-l-propylenediamino-platinous Chloride, $[Pt\ en\ pn]Cl_2$, has rotation $[\alpha]_D+24{\cdot}07°$, $[M]_D+96{\cdot}28°$; and **trimethylenediamino-l-propylenediamino-platinous chloride,** $[Pt\ tr\ pn]Cl_2$, has rotation $[\alpha]_D+23{\cdot}6°$, $[M]_D+97{\cdot}70°$.

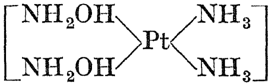
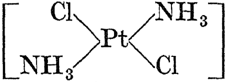
l-Propylenediamine itself has rotation $[\alpha]_D-28{\cdot}04°$, $[M]_D-20{\cdot}79°$.[2]

Derivatives containing Hydroxylamine and Hydrazine in place of Ammonia.

The complete series of compounds containing hydroxylamine in place of ammonia has been obtained thus:

$$[Pt(NH_3)_4]Cl_2 \longrightarrow [Pt(NH_3)_3(NH_2OH)]Cl_2 \longrightarrow [Pt(NH_3)_2(NH_2OH)_2]Cl_2 \longrightarrow [Pt(NH_3)(NH_2OH)_3]Cl_2 \longrightarrow [Pt(NH_2OH)_4]Cl_2.$$

The third member exists in two isomeric forms, namely, a *cis*-form and a *trans*-form. The starting material is *cis*-dichloro-diammino-platinum,  $\left[\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix}\right]$, which is digested with hydroxylamine in aqueous solution.

From the reaction *cis*-**diammino-dihydroxylamino-platinous chloride,**  $\left[\begin{matrix}NH_2OH\\NH_2OH\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix}\right]Cl_2$, is obtained. On treating it with hydrochloric acid it yields a mixed compound, which easily unites with two molecules of hydroxylamine to give **trihydroxylamino-ammino-platinous chloride,** $[Pt(NH_3)(NH_2OH)_3]Cl_2$, or with two molecules of ammonia to give tetrammino-platinous chloride. *Trans*-diammino-dihydroxylamino-platinous chloride is prepared by the action of hydroxylamine on an aqueous solution of *trans*-dichloro-diammino-platinum,  $\left[\begin{matrix}Cl\\NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\Cl\end{matrix}\right]$. These compounds are colourless compounds which are soluble in water; they yield chloroplatinites on treatment with potassium chloroplatinite. The first two are green in colour, as also the salt of *trans*-diammino-dihydroxylamino-platinous chloride, and the others are rose-violet in colour. The different colour of the chloro-

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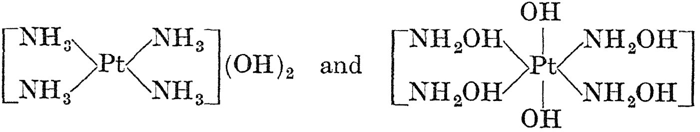
[1] Werner, *Zeitsch. anorg. Chem.*, 1899, 21, 201.

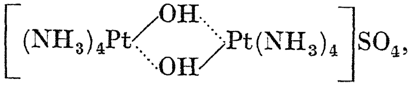
[2] Tschugaeff and Sokoloff, *Ber.*, 1907, 40, 3461. The molecular rotations as quoted by the authors are apparently divided by 100.

platinite of the *trans*- and the *cis*-isomers serves to distinguish these compounds.[1]

Hydroxylamine plays the same part in the molecule as ammonia in ammino-platinum compounds, but the substances differ somewhat in chemical behaviour, for hydroxylamine is more readily eliminated than ammonia from the complex. Also, *cis*-dihydroxylamino-dichloro-platinum is not obtained by the interaction of free hydroxylamine and potassium chloroplatinite, the method used for the preparation of *cis*-dichloro-diammino-platinum. Again, tetrammino-platinous hydroxide, $[Pt(NH_3)_4](OH)_2$, is a very strong base and easily soluble in water, whilst tetrahydroxylamino-platinous hydroxide, $[Pt(NH_2OH)_4](OH)_2$, is almost insoluble in water and a comparatively weak base.[2] For this reason Werner[3] suggested a different formula for the two substances, and indicated that possibly in the tetrahydroxylamino-compound the co-ordination number of the metal is six and not four, as in the tetrammino-compounds thus :



Aquo-triammino-platinous salts have been described of general formula $[Pt(NH_3)_3H_2O]R_2$. These are prepared by passing a current of air through a solution of diammino-dihydroxylamino-platinous chloride, $[Pt(NH_3)_2(NH_2OH)_2]Cl_2$, containing ammonia and ammonium sulphate and a small quantity of any copper salt. Oxidation takes place, and a colourless crystalline precipitate is obtained which is soluble in warm dilute sulphuric acid. Analysis of this product indicates that it is probably a diplatinum derivative of composition



one of the diol-compounds containing metal with co-ordination number of six. On the addition of potassium chloroplatinite to the acid solution a precipitate of aquo-triammino-platinous chloroplatinite, $[Pt(NH_3)_3H_2O]PtCl_4$, separates, which on warming with dilute hydrochloric acid or a soluble chloride yields Cleve's salt, $[Pt(NH_3)_3Cl]PtCl_4$. Aquo-triammino-platinous bromoplatinite, $[Pt(NH_3)_3H_2O]PtBr_4$, is prepared by the addition of potassium bromoplatinite to the acid solution. It crystallises in green needles and, like the chloride, is converted by hydrobromic acid into bromo-triammino-platinous bromoplatinite, $[Pt(NH_3)_3Br]PtBr_4$.[4]

Complex platinous derivatives containing hydrazine are easily prepared by acting upon dichloro-diammino-platinum with hydrazine hydrate in absence of water. The addition of alcohol precipitates diammino-dihydrazino-platinous chloride in colourless prismatic

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[1] Tschugaeff and Tschernjaev, *Compt. rend.*, 1915, 161, 637; *Trans. Chem. Soc.*, 1918, 113, 884.

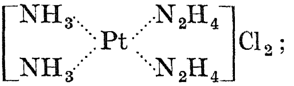
[2] Tschugaeff and Tschernjaeff, *Trans. Chem. Soc.*, 1918, 113, 884.

[3] Werner, *Neuere Anschauungen auf dem Gebiete der anorganische Chemie* (3rd edition), 5, 197.

[4] Tschugaeff and Tschernjaeff, *Compt. rend.*, 1915, 161, 792.

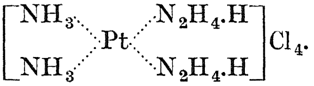
crystals. The compound may be kept for some time, but gradually darkens in colour due to liberation of platinum. Other salts of the series are prepared from the chloride by double decomposition. If hydrochloric acid be added to an aqueous solution of the chloride, a much less soluble crystalline compound is deposited which has composition $[Pt(NH_3)_2(N_2H_4)_2]Cl_2.2HCl$.

From the behaviour of the chloride, Tschugaeff and Grigorieff[1] assume that its constitution is represented by the formula



$$\left[\begin{array}{ccc} NH_3 & & N_2H_4 \\ & Pt & \\ NH_3 & & N_2H_4 \end{array}\right]Cl_2;$$

whilst the dihydrochloride is given the structure,



$$\left[\begin{array}{ccc} NH_3 & & N_2H_4.H \\ & Pt & \\ NH_3 & & N_2H_4.H \end{array}\right]Cl_4.$$

2. *Acido-triammino-platinous Salts*, $[Pt(NH_3)_3R]R$.

The series was discovered by Cleve, hence the chloride, $[Pt(NH_3)_3Cl]Cl$, is known as *Cleve's salt.* This is the best known member of the series, and the one which has been most thoroughly investigated.

Chloro-triammino-platinous Chloride, $[Pt(NH_3)_3Cl]Cl$, may be obtained by the addition of ammonia to dichloro-diammino-platinum, $[Pt(NH_3)_2Cl_2]$, or by the elimination of ammonia from tetrammino-platinous chloride by the action of hydrochloric acid thus :

$$[Pt(NH_3)_2Cl_2]+NH_3 \longrightarrow [Pt(NH_3)_3Cl]Cl;$$
$$[Pt(NH_3)_4]Cl_2+HCl \longrightarrow [Pt(NH_3)_3Cl]Cl+NH_4Cl.$$

Both methods, however, give very poor yields, as the addition or elimination of ammonia cannot be regulated, and therefore cannot be stopped at the required stage.

The salt is most conveniently prepared by the addition of ammonia to dichloro-diammino-platinum, using the salts of cyanic acid, which evolve ammonia when hydrolysed.

Cis-dichloro-diammino-platinum is boiled with potassium cyanate till solution is complete. The resulting liquid is then mixed with hydrochloric acid, heated to boiling and cooled, when unchanged dichloro-salt crystallises and is filtered off. An excess of potassium chloroplatinite is added to the filtrate, yielding a precipitate of tetrammino-platinous chloroplatinite and chloro-triammino-platinous chloroplatinite. The mixture of salts is treated with hot water and hydrochloric acid, when the chloro-triammino-platinous chloroplatinite passes into solution, leaving the green salt undissolved. It crystallises from hot water in flesh-coloured, square-shaped plates.

The *chloride* is obtained from the chloroplatinite by dissolving it in hot water slightly acidified with hydrochloric acid and treating the solution with tetrammino-platinous chloride, when the following reaction takes place :—

$$[Pt(NH_3)_3Cl]_2PtCl_4+[Pt(NH_3)_4]Cl_2 \longrightarrow 2[Pt(NH_3)_3Cl]Cl+[Pt(NH_3)_4]PtCl_4.$$

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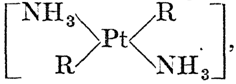
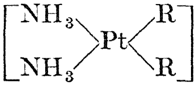
[1] Tschugaeff and Grigorieff, *Ber.*, 1914, 47, 244.

The cooled solution is freed from tetrammino-platinous chloroplatinite by filtration, and the salt crystallised by evaporation *in vacuo*.[1]

Chloro-triammino-platinous Sulphate, $[Pt(NH_3)_3Cl]SO_4$, is obtained by treating the chloroplatinite with silver sulphate. It crystallises in colourless needles which are sparingly soluble in cold water but soluble in boiling water.

3. *Diacido-diammino-platinum Salts,* $[Pt(NH_3)_2R_2]$.

There are two classes of these compounds, the symmetrical or *trans*-series, originally known as platos-ammines, with configuration , and the asymmetrical or *cis*-series, originally known as plato-semi-diammines, with configuration .

Symmetrical or Trans-diacido-diammino-platinum Compounds.

These substances are obtained by heating the corresponding tetrammino-platinous salts. They dissolve in aqueous ammonia with re-formation of the tetrammino-salts, and they can take up two atoms of chlorine yielding the corresponding platinic compound thus :

$$[Pt^{II}(NH_3)_2R_2]+Cl_2 \longrightarrow [Pt^{IV}(NH_3)_2R_2Cl_2].$$

The compound most easily obtained is dichloro-diammino-platinum, and this forms the starting-point in the preparation of other members of the series. The conductivity of the substances in solution is practically zero, which agrees with the formula $[Pt(NH_3)_2R_2]$, where the acid radicles form part of the complex.

s-Dichloro-diammino-platinum, $[Pt(NH_3)_2Cl_2]$, is obtained by heating tetrammino-platinous chloride in the dry state till ammonium chloride begins to volatilise. As ammonia is lost the colour of the compound changes from white to yellow. The residue is treated with water to remove the more soluble unchanged salt, and the crude product is then purified by treating it with aqueous silver nitrate, thus forming the nitrate and the chloro-compound precipitated from solution by the addition of hydrochloric acid. It is a yellow crystalline powder made up of microscopic rhombohedra, and is sparingly soluble in cold, and more soluble in hot, water. Silver nitrate reacts with it immediately, with precipitation of all the chloride as silver chloride and formation of the nitrato-compound, $[Pt(NH_3)_2(NO_3)_2]$.[2]

Dibromo-diammino-platinum, $[Pt(NH_3)_2Br_2]$, is precipitated from a solution of the nitrate by potassium bromide. It is a yellow crystalline powder which is sparingly soluble in both hot and cold water.

Di-iodo-diammino-platinum, $[Pt(NH_3)_2I_2]$, is produced by loss of ammonia on boiling a solution of tetrammino-platinous iodide. It is precipitated as a bright yellow powder which is sparingly soluble in water.[3]

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[1] Tschugaeff, *Trans. Chem. Soc.*, 1915, 107, 1247; Klason, *J. prakt. Chem.*, 1903, 67, 1; Peyronne, *Annalen*, 1847, 61, 178.

[2] Peyronne, *Annalen*, 1844, 12, 193; 1846, 16, 422.

[3] Reiset, *Compt. rend.*, 1840, 10, 870; 11, 711.

The *sulphato*-derivative, $[Pt(NH_3)_2SO_4].H_2O$, is formed by treating the chloro- or iodo-derivative with silver sulphate. It is yellowish white in colour and soluble in hot water.

The *chloro-sulphito*-derivative, $[Pt(NH_3)_2Cl.SO_3H]$, is produced by the action of sulphur dioxide on a boiling solution of the chloro-compound. It is readily soluble in water.

The *hydroxo*-compound of the series, *dihydroxo-diammino-platinum*, $[Pt(NH_3)_2(OH)_2]$, is formed by treating the sulphato-derivative with baryta water. A solution is obtained which is strongly alkaline, liberates ammonia from ammonium salts, absorbs carbon dioxide, and precipitates metallic salts. From the solution the hydroxide may be easily crystallised.[1]

Asymmetrical or Cis-diacido-diammino-platinous Compounds.

The chloride again forms the starting material for the preparation of the other members of the series.

Cis-dichloro-diammino-platinum, $[Pt(NH_3)_2Cl_2]$, was first prepared by Peyronne.[2] It is easily formed by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, when a greenish-yellow voluminous precipitate separates. This is boiled with water and filtered hot, when, on cooling the filtrate, the substance crystallises in yellow microscopic needles. It is sparingly soluble in water, and is more pure yellow than the isomeric *trans*-compound. Both *cis*- and *trans*-dichloro-diammino-platinum are obtained on heating tetrammino-platinous chloride with hydrochloric acid.

Cis-dinitrato-diammino-platinum, $[Pt(NH_3)_2(NO_3)_2]$, is produced by acting on the dichloro-compound with silver nitrate. It is a yellow powder.

The *dibromo*-compound, $[Pt(NH_3)_2Br_2]$, is formed by the action of potassium bromide on the nitrate. It crystallises in golden-yellow needles.

The *iodo*-derivative, $[Pt(NH_3)_2I_2]$, separates as a microcrystalline yellow powder on mixing aqueous potassium iodide and the nitrato-compound. It is only slightly soluble in water.

Both series of compounds easily add on halogen, passing into the corresponding platinic derivatives. The configuration of the compounds is established by their behaviour on the addition of pyridine, as already explained under the tetrammino-platinous salts (see p. 228).

4. *Triacido-ammino-platinous Salts,* $[Pt(NH_3)R_3]M$.

This series of compounds may be produced by the elimination of ammonia from the previous series by means of hydrochloric acid. It is probable that the acid, $[Pt(NH_3)R_3]H$, is formed, but this has not been isolated, and only the potassium, ammonium, and silver salts are known.

Potassium Trichloro-ammino-platinite, $[Pt(NH_3)Cl_3]K.H_2O$, is obtained by the interaction of potassium chloroplatinite and tetra-ammino-platinous chloride.[3] It crystallises in orange-yellow ortho-rhombic prisms, is easily soluble in water and insoluble in alcohol.

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[1] Odling, *Chem. News*, 1870, 21, 269.

[2] Peyronne, *Ann. Chim. Phys.*, 1844, 12, 193; 1846, 16, 462.

[3] Cossa, *Ber.*, 1890, 23, 2503.

Hydrochloric acid slowly transforms it into potassium chloroplatinite, and ammonia into dichloro-diammino-platinum, chloro-triammino-platinous chloride, and tetrammino-platinous chloride. Chlorine oxidises it, forming the corresponding salt of the platinic series.

Silver Trichloro-ammino-platinite, $[Pt(NH_3)Cl_3]Ag$, is precipitated as a yellow powder which is insoluble in water.

Ammonium Trichloro-ammino-platinite, $[Pt(NH_3)Cl_3]NH_4.H_2O$, is obtained in the same way as the potassium salt, using ammonium chloroplatinite instead of the potassium salt. It crystallises in orange-red prisms. It easily loses hydrochloric acid, being transformed into dichloro-diammino-platinum.[1]

In the ammino-platinous compounds there is, as in the other ammino-metallic compounds, a complete transition series from tetrammino-platinous salt to tetra-acido-platinous salt; for example, tetrammino-platinous chloride, $[Pt(NH_3)_4]Cl_2$, chloro-triammino-platinous chloride, $[Pt(NH_3)_3Cl]Cl$, dichloro-diammino-platinum, $[Pt(NH_3)_2Cl_2]$, trichloro-ammino-platinous salt, $[Pt(NH_3)Cl_3]K$, and potassium chloroplatinite, $[PtCl_6]K_2$, where all the ammonia is replaced by chlorine. Comparing the molecular conductivities, the first-mentioned compound has conductivity at 1000 litres dilution of 260, the next 115·8; in the third compound the conductivity drops almost to zero, the fourth has conductivity of 106·8, and the last salt has conductivity of 267.[2]

B. Ammino-derivatives of Platinic Salts.

These compounds may be derived from the platinous series by the addition of two monovalent acido-groups or two atoms of halogen.

1. *Hexammino-platinic Salts*, $[Pt(NH_3)_6]R_4$.

The first compound of the series was prepared by Drechsel, hence is referred to as "Drechsel's base." He found that platinum dissolves in a solution of ammonium carbonate if suitably influenced by an alternating current, giving a crystalline compound which is the carbonate, $[Pt(NH_3)_6](CO_3)_2$, of the series.

Hexammino-platinic Carbonate, $[Pt(NH_3)_6](CO_3)_2$, is a colourless powder which is almost insoluble in water but soluble in acids with evolution of carbon dioxide and formation of the corresponding salt.[3]

Hexammino-platinic Chloride, $[Pt(NH_3)_6]Cl_4$, is produced by the addition of hydrochloric acid to a solution of the carbonate in sodium carbonate. From the liquid colourless needles are gradually deposited. It is soluble in warm water and may be crystallised from aqueous solution.

Hexammino-platinic Sulphate, $[Pt(NH_3)_6](SO_4)_2.H_2O$, is precipitated as a white amorphous powder on decomposing the chloride with sulphuric acid or a soluble sulphate. It is almost insoluble in water.

Hexammino-platinic Hydroxide, $[Pt(NH_3)_6](OH)_4$, may be obtained by treating a boiling aqueous solution of the chloride with

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[1] Jörgensen, *Zeitsch. anorg. Chem.*, 1900, **24**, 153.

[2] Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506; Werner and Hertz, *ibid.*, 1901, **33**, 331.

[3] Drechsel, *J. prakt. Chem.*, 1879, **20**, 378.

silver oxide. It crystallises in hexagonal plates which are sparingly soluble in water, give a strongly alkaline solution, and decompose ammonium salts and absorb carbon dioxide from the atmosphere.

The *nitrate*, $[Pt(NH_3)_6](NO_3)_4$, is easily soluble in water, crystallises in small colourless needles, and may be produced by treating the carbonate with nitric acid.[1]

2. *Acido-pentammino-platinic Salts*, $[Pt(NH_3)_5R]R_3$.

These are represented by the chloro-pentammino-platinic salts. This series is difficult to prepare, but the chloro-derivatives may be obtained by the action of liquid ammonia on ammonium chloroplatinate, $[PtCl_6](NH_4)_2$, in absence of water in a sealed tube at ordinary temperature.

Chloro - pentammino - platinic Chloride, $[Pt(NH_3)_5Cl]Cl_3$, is produced along with hexammino-platinic chloride by the action of liquid ammonia on ammonium chloroplatinate in a closed tube, keeping the materials dry. The mixture of the two platinic derivatives is separated by crystallisation, as the chloro-pentammino-derivative is more soluble in water than the hexammino-derivative.

Chloro-pentammino-platinic Nitrate, $[Pt(NH_3)_5Cl](NO_3)_3$, is formed by treating the chloride with concentrated nitric acid. It is less soluble than the chloride, and silver nitrate does not remove chlorine from it even on boiling.

The *carbonate*, $[Pt(NH_3)_5Cl]_2(CO_3)_3$, and the *sulphate*, $[Pt(NH_3)_5Cl]_2(SO_4)_3$, are almost insoluble in water but easily soluble in sodium hydroxide.

The trivalency of the complex ion, $[Pt(NH_3)_5Cl]^{\cdots}$, is confirmed by conductivity measurements, the chloride having conductivity 404 at 1000 litres dilution, and by the power of the salts to coagulate colloidal solutions of arsenic trisulphide.

All the salts may be reduced by means of zinc and dilute hydrochloric acid, yielding the corresponding tetrammino-platinous salts.[2]

A series of compounds has been prepared containing a hydroxo-group in place of an acidic group in the pentammino-platinic compounds. These have general formula $[Pt(NH_3)_5OH]R_3$.

Hydroxo - pentammino - platinic Carbonate, $[Pt(NH_3)_5OH]_2(CO_3)_3$, is easily prepared by passing a current of ozone through a mixture of dichloro-diammino-platinum, ammonium carbonate, and excess of ammonia. It is precipitated as formed, being insoluble in water. The carbonate is decomposed by acetic acid, yielding the acetate, $[Pt(NH_3)_5OH](C_2H_3O_2)_3$, and from this other salts of the series may be formed by the action of mineral acids.

The *chloride*, $[Pt(NH_3)_5OH]Cl_3.H_2O$, crystallises in rhombic plates. The *nitrate*, $[Pt(NH_3)_5OH](NO_3)_3$, crystallises in needles. Both salts are soluble in water. The carbonate and the sulphate, like those of the hexammino- and the chloro-pentammino-series, are practically insoluble in water but soluble in sodium hydroxide. The chloride is easily reduced by zinc and hydrochloric acid, forming tetrammino-platinous chloride.[3]

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[1] Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, **12**, 54; 1894, **14**, 506.

[2] Tschugaeff and Vladimiroff, *Compt. rend.*, 1915, **160**, 840.

[3] Tschugaeff and Chlopin, *ibid.*, 1915, **161**, 699.

3. *Diacido-tetrammino-platinic Salts*, $[Pt(NH_3)_4R_2]R_2$.

This series of compounds is formed by the action of halogen or nitric acid on tetrammino-platinous salts, or by the addition of ammonia to tetracido-diammino-platinum compounds.

Two acidic radicles are within the complex and two are outside the complex and therefore ionised in solution.

Dichloro-tetrammino-platinic Chloride, $[Pt(NH_3)_4Cl_2]Cl_2$, is prepared by passing chlorine gas through a solution of tetrammino-platinous chloride till the liquid begins to turn red. From the cold dilute solution the salt crystallises with one molecule of water of crystallisation, whilst from more concentrated solutions the anhydrous salt is deposited. It may also be obtained by the action of ammonia on tetrachloro-diammino-platinum. It crystallises in pale yellow microscopic octahedra, is sparingly soluble in water, and only half of the chlorine is precipitated as silver chloride when the aqueous solution is treated with a cold solution of silver nitrate. Sulphuric acid eliminates only two molecules of chlorine.[1]

Dichloro-tetrammino-platinic Bromide, $[Pt(NH_3)_4Cl_2]Br_2$, is produced by treating the nitrate of the series with ammonium bromide, when the salt is precipitated as a yellow crystalline powder. Silver nitrate replaces two atoms of bromine by two nitrate radicles.

Dichloro - tetrammino - platinic Sulphate, $[Pt(NH_3)_4Cl_2]SO_4$, separates as a white crystalline powder when sulphuric acid is added to a warm aqueous solution of the nitrate. If the solution be kept cool a hydrated salt separates in small needles. The salt is sparingly soluble in water, and silver nitrate does not remove chlorine from a cold aqueous solution.

Dichloro-tetrammino-platinic Nitrate, $[Pt(NH_3)_4Cl_2](NO_3)_2$, is obtained by treating tetrammino-platinous chloroplatinite with small quantities of nitric acid. It crystallises in slightly yellow prisms.

The *chloroplatinite*, $[Pt(NH_3)_4Cl_2]PtCl_4$, may be prepared by the action of chloroplatinic acid on tetrammino-platinous chloride, or by the action of chlorine on Magnus' green salt suspended in boiling water. It is a red crystalline substance which is only slightly soluble in water. Silver nitrate transforms the salt into a mixture of silver chloroplatinite and dichloro-tetrammino-platinic nitrate.

The *chloroplatinate*, $[Pt(NH_3)_4Cl_2]PtCl_6$, is obtained by mixing solutions of sodium chloroplatinate and dichloro-tetrammino-platinic nitrate, or by the prolonged action of chlorine on either the green salt of Magnus or the preceding salt suspended in water. It crystallises in brilliant yellow prisms which are soluble in hot water. Hydrochloric and nitric acids precipitate the chloride and the nitrate respectively.[2]

Dibromo-tetrammino-platinic Chloride, $[Pt(NH_3)_4Br_2]Cl_2$, is isomeric with dichloro-tetrammino-platinic bromide. It is formed by double decomposition between ammonium chloride and dibromo-tetrammino-platinic nitrate, when the salt separates as a yellow crystalline powder. Silver nitrate precipitates all the chloride and one atom of bromine in the molecule.

Dibromo-tetrammino-platinic Bromide, $[Pt(NH_3)_4Br_2]Br_2$, is precipitated as a sparingly soluble orange-coloured powder on the

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[1] Grimm, *Annalen*, 1856, 99, 67; Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, 12, 54.

[2] Cossa, *Ber.*, 1890, 23, 2503.

addition of ammonium bromide to the nitrate. Silver nitrate acts upon the warm solution with precipitation of three atoms of bromide.

The *sulphate*, $[Pt(NH_3)_4Br_2]SO_4$, separates as a lemon-yellow microcrystalline powder on adding bromine to a solution of tetrammino-platinous sulphate. It is sparingly soluble in water.

The *nitrate*, $[Pt(NH_3)_4Br_2](NO_3)_2$, is produced by the action of bromine on tetrammino-platinous nitrate. It crystallises in flat yellow prisms which are soluble in water, and silver nitrate precipitates in boiling solution one atom of bromine, replacing it by a hydroxo-group.

The mixed salt, **chloro-bromo-tetrammino-platinic chloride,** $[Pt(NH_3)_4ClBr]Cl_2$, separates as a yellow powder which is almost insoluble in water on the addition of hydrochloric acid to bromo-hydroxo-tetrammino-platinic nitrate, $[Pt(NH_3)_4Br(OH)](NO_3)_2$.

Di-iodo-tetrammino-platinic Iodide, $[Pt(NH_3)_4I_2]I_2$, is formed by adding excess of potassium iodide to a solution of dichloro- or di-iodo-tetrammino-platinic nitrate. It gradually loses iodine when mixed with a solution of silver nitrate. Ammonia transforms it into a yellow crystalline powder, which appears to be a derivative of a diplatinic salt.[1]

Di-iodo-tetrammino-platinic Sulphate, $[Pt(NH_3)_4I_2]SO_4$, is a brownish crystalline powder obtained by the action of iodine on tetrammino-platinous sulphate.

The *nitrate*, $[Pt(NH_3)_4I_2](NO_3)_2$, is produced in the same manner by the direct addition of iodine to tetrammino-platinous nitrate. It is soluble in hot water, and silver nitrate in boiling solution transforms the compound into nitrato-hydroxo-platinic nitrate.

Dinitrato - tetrammino - platinic Chloride, $[Pt(NH_3)_4(NO_3)_2]Cl_2.H_2O$, is prepared by treating a boiling solution of hydroxo-nitrato-tetrammino-platinic nitrate, $[Pt(NH_3)_4(OH)(NO_3)](NO_3)_2$, with hydrochloric acid. It separates as a white crystalline powder which may be recrystallised from water in large rhombic crystals. It is soluble in cold water, and loses water of hydration on heating to 100° C. Chlorine is completely precipitated by silver nitrate; it therefore differs in this respect from the nitrate of dichloro-tetrammino-platinic series, with which it is isomeric.

Chloro - nitrato - tetrammino - platinic Sulphate, $[Pt(NH_3)_4Cl(NO_3)]SO_4.H_2O$, is obtained by dissolving chloro-nitrato-tetrammino-platinic nitrate in concentrated sulphuric acid and diluting with water. It crystallises in small prisms.

Chloro - nitrato - tetrammino - platinic Nitrate, $[Pt(NH_3)_4Cl(NO_3)](NO_3)_2$, is formed by mixing a boiling saturated solution of chloro-hydroxo-tetrammino-platinic nitrate with concentrated nitric acid. It crystallises in orthorhombic prisms, and is decomposed by water with re-formation of the hydroxo-compound.[2]

Hydroxo - chloro - tetrammino - platinic Nitrate, $[Pt(NH_3)_4(OH)Cl](NO_3)_2$, was first obtained by Raewsky [3] by the action of excess of nitric acid on the green salt of Magnus; hence it is referred to as the nitrate of Raewsky.

It is conveniently prepared by treating dichloro-tetrammino-platinic nitrate with silver nitrate. It crystallises in small white

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[1] Jörgensen, *J. prakt. Chem.*, 1877, 15, 427.

[2] Gros, *Ann. Chim. Phys.*, 1838, 69, 204; Raewsky, *ibid.*, 1848, 22, 278; Hadow, *J. prakt. Chem.*, 1867, 100, 30.

[3] Raewsky, *Compt. rend.*, 1847, 23, 353.

needles which are very sparingly soluble in cold water. Silver nitrate only acts on the solution after boiling for several hours. Hydrochloric acid attacks the salt, with formation of dichloro-tetrammino-platinic chloride. The other salts of the series are prepared from the nitrate by double decomposition.

Hydroxo-chloro-tetrammino-platinic Chloride, $[Pt(NH_3)_4(OH)Cl]Cl_2$, is precipitated in crystalline form by the addition of ammonium chloride to a solution of the nitrate.

The *carbonate*, $[Pt(NH_3)_4(OH)Cl]CO_3$, and the *bromide*, $[Pt(NH_3)_4(OH)Cl]Br_2$, are white crystalline powders.

Hydroxo-bromo-tetrammino-platinic Nitrate, $[Pt(NH_3)_4(OH)Br](NO_3)_2$, is prepared by treating a boiling solution of dibromo-tetrammino-platinic nitrate with silver nitrate. It is a pale yellow, sparingly soluble powder.

The *bromide*, $[Pt(NH_3)_4(OH)Br]Br_2$, is a pale yellow crystalline powder.

The *chloride*, $[Pt(NH_3)_4(OH)Br]Cl_2$, is a colourless crystalline powder. These and other salts of the series are obtained from the nitrate.

Hydroxo-nitrato-tetrammino-platinic Nitrate, $[Pt(NH_3)_4(OH)(NO_3)](NO_3)_2$, is obtained by acting on tetrammino-platinous nitrate with concentrated nitric acid. The mixture is heated till oxides of nitrogen are no longer evolved, and the residue crystallised from boiling water. It may also be produced by prolonged boiling of di-iodo-tetrammino-platinic nitrate with a solution of silver nitrate. It crystallises in short colourless prisms which are sparingly soluble in cold water and in dilute nitric acid, and decompose on heating.

A series of *dihydroxo-tetrammino-platinic salts*, $[Pt(NH_3)_4(OH)_2]R_2$, has been investigated by Carlgreen and Cleve.[1] They are produced by oxidising tetrammino-platinous salt with hydrogen peroxide.

Dihydroxo-tetrammino-platinic Chloride, $[Pt(NH_3)_4(OH)_2]Cl_2$, is prepared by the action of hydrogen peroxide on tetrammino-platinous chloride, or by decomposing the sulphate of the series with barium chloride. It crystallises in colourless monoclinic plates.

Dihydroxo-tetrammino-platinic Bromide, $[Pt(NH_3)_4(OH)_2]Br_2$, is obtained by treating the sulphate with barium bromide. It crystallises in short colourless prisms.

The *iodide*, $[Pt(NH_3)_4(OH)_2]I_2$, is produced by the action of barium iodide on the sulphate, and crystallises in small hexagonal prisms.

The *nitrite*, $[Pt(NH_3)_4(OH)_2](NO_2)_2$, is obtained from the chloride by the action of silver nitrite. It crystallises in needles which explode when heated.

The *nitrate*, $[Pt(NH_3)_4(OH)_2](NO_3)_2$, is formed by decomposition of the sulphate with barium nitrate, or from tetrammino-platinous nitrate by treating it with hydrogen peroxide. It crystallises in small flat rhombic plates and decomposes explosively on heating.

The *sulphate*, $[Pt(NH_3)_4(OH)_2]SO_4$, is produced by oxidising tetrammino-platinous sulphate with hydrogen peroxide, or by the action of baryta on hydroxo-sulphato-tetrammino-platinic sulphate. The first method of preparation yields a hydrated form containing four molecules of water, which crystallises in long needles and is sparingly soluble in boiling water. The second method of preparation yields the anhydrous form, which crystallises in easily soluble prisms. It is

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[1] Carlgreen and Cleve, *Zeitsch. anorg. Chem.*, 1892, I, 65.

not possible to convert the anhydrous salt into the hydrated salt even on repeated crystallisation.[1]

The dihydroxo-salts show little tendency to form aquo-salts. Thus the chloride if mixed with hydrochloric acid yields hydroxo-aquo-tetrammino-platinic chloride, but the substance is so unstable that atmospheric moisture converts it quickly into the dihydroxo-chloride and hydrochloric acid.[1]

The hydroxide of the series, $[Pt(NH_3)_4(OH)_2](OH)_2$, is not known.

4. *Triacido-triammino-platinic Salts,* $[Pt(NH_3)_3R_3]R$.

These salts are obtained from the acido-triammino-platinous salts by oxidation.

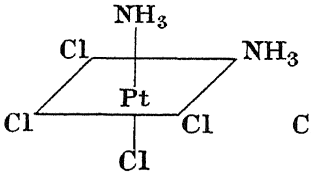
Trichloro-triammino-platinic Chloride, $[Pt(NH_3)_3Cl_3]Cl$, is obtained by boiling nitrato-triammino-platinous nitrate with aqua-regia. It separates in shining leaflets of a yellow colour and is soluble in water.

Dibromo-nitrato-triammino-platinic Nitrate, $[Pt(NH_3)_3Br_2(NO_3)]NO_3$, separates as a golden-yellow crystalline powder, and is prepared by addition of bromine to bromo-triammino-platinous nitrate.

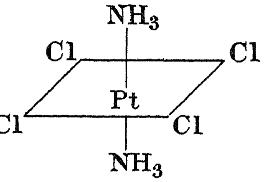
Dihydroxo-nitrato-triammino-platinic Nitrate, $[Pt(NH_3)_3(OH)_2(NO_3)]NO_3$, is formed by boiling a solution of the preceding compound with excess of silver nitrate. All the bromine is precipitated as silver bromide, and on evaporation of the filtrate colourless microscopic needles of the dihydroxo-compound separate. It is easily soluble in water. The triammino-series has not been very fully investigated, and the compounds described have been mostly prepared by Cleve.[2]

5. *Tetracido-diammino-platinic Compounds,* $[Pt(NH_3)_2R_4]$.

This series are non-electrolytes, all the acidic groups being within the complex.[3] Two isomeric series are known, one derived from *cis*-diacido-diammino-platinum, and one from *trans*-diacido-diammino platinum. These are distinguished as platini-semi-diammino-compounds and platinammino-compounds respectively. A direct determination of the constitution of the two series has not yet been carried out, but from the structure of the two corresponding platinous compounds, from which the platinic derivatives may be obtained by addition of halogen, it is reasonable to ascribe to the compound from *cis*-diacido-diammino-platinum the structure I., and to that derived from *trans*-diacido-diammino-platinum the structure II. thus :



I.
Cis-.



II.
Trans.

Compounds having configuration I. are orange in colour ; those with configuration II. are yellow.

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[1] Werner, *Ber.*, 1907, 40, 4093.

[2] Cleve, *Öfvers. K. Vet.-Akad. Forh.*, 1871, 28, 175, 187.

[3] Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, 12, 54 ; 1894, 14, 506.

(a) *Tetracido-cis-diammino-platinum Compounds.*

Tetrachloro-diammino-platinum, $[Pt(NH_3)_2Cl_4]$, is produced by treating *cis*-dichloro-diammino-platinum with chlorine or by boiling it with aqua-regia. It may also be produced by the action of a concentrated aqueous solution of ammonium chloride on silver chloroplatinate. It crystallises in small orange-yellow plates which are soluble in water, and on treatment with sulphurous acid are reduced to the platinous compound.

Tetrabromo-diammino-platinum, $[Pt(NH_3)_2Br_4]$, is prepared in the same manner by the action of bromine on dibromo-diammino-platinum suspended in water. It crystallises from warm water in microscopic orange-red plates which are sparingly soluble in water, but notwithstanding give an intense yellow solution.

Tetra-iodo-diammino-platinum, $[Pt(NH_3)_2I_4]$, is formed by adding an alcoholic solution of iodine to di-iodo-diammino-platinum. The substance separates in brilliant reddish-purple crystals.

Dinitrito-dibromo-diammino-platinum, $[Pt(NH_3)_2Br_2(NO_2)_2]$, is formed by the action of bromine on dinitrito-diammino-platinum. It crystallises in long orange-red needles which are sparingly soluble in water.

(b) *Tetracido-trans-diammino-platinum Compounds.*

Tetrachloro-trans-diammino-platinum, $[Pt(NH_3)_2Cl_4]$, is prepared by treating *trans*-dichloro-diammino-platinum suspended in boiling water with chlorine or aqua-regia, or a mixture of hydrochloric acid and potassium permanganate, till the liquid becomes yellow. On crystallisation from boiling water the substance is obtained in lemon-yellow octahedra. It dissolves in warm aqueous ammonia, yielding trichloro-triammino-platinic chloride, and is not attacked by nitric acid or sulphuric acid. Ammonia is liberated from the compound on warming with sodium hydroxide, and silver nitrate only precipitates chlorine from it on prolonged boiling.[1]

Dichloro-dinitrito-diammino-platinum, $[Pt(NH_3)_2Cl_2(NO_2)_2]$, is obtained as a soluble crystalline substance on warming a concentrated solution of dinitrato-nitrito-triammino-platinic nitrite, $[Pt(NH_3)_3(NO_3)_2(NO_2)](NO_2)$, with excess of hydrochloric acid.

Trichloro-nitrito-diammino-platinum, $[Pt(NH_3)_2Cl_3(NO_2)]$, crystallises in small yellow leaflets which are sparingly soluble in cold water.

Tetrabromo-diammino-platinum, $[Pt(NH_3)_2Br_4]$, is formed by adding bromine to *trans*-dibromo-diammino-platinum suspended in water. It separates in small plates of yellow colour and is sparingly soluble in water.

Dibromo-dinitrito-diammino-platinum, $[Pt(NH_3)_2Br_2(NO_2)_2]$, separates as a yellow crystalline powder when *trans*-dinitrito-diammino-platinum is mixed with bromine. It is sparingly soluble in water.

Tetra-iodo-diammino-platinum, $[Pt(NH_3)_2I_4]$, is obtained as an amorphous black powder when an alcoholic solution of iodine is mixed with *trans*-di-iodo-diammino-platinum.

6. *Pentacido-ammino-platinates,* $[Pt(NH_3)R_5]M$.

The series is represented by the potassium salt and the tetrammino-platinous salt.

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[1] Gerhardt, *Compt. rend.*, 1850, 31, 241.

Potassium Pentachloro-ammino-platinate, $[Pt(NH_3)Cl_5]K.H_2O$, is produced by treating potassium trichloro-ammino-platinite, $[Pt(NH_3)Cl_3]K$, with chlorine. It separates in yellowish triclinic crystals.

Tetrammino-platinous Pentachloro-ammino-platinate, $[Pt(NH_3)Cl_5]_2Pt(NH_3)_4$, crystallises in orange-red needles which are sparingly soluble in water. The compound is unstable and decomposes at ordinary temperature. It is produced by mixing solutions of tetrammino-platinic chloride and potassium pentachloro-ammino-platinate.[1]

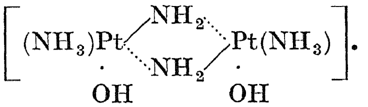
The analogous pyridine compound, $[Pt\,pyCl_5]K$, **potassium penta-chloro-pyridino-platinate,** has been prepared.[2] It crystallises in silky yellow needles. Bromine acts upon the salt, with formation of the corresponding pentabromo-derivatives.

A large number of complex platinum salts is known containing organic bases in place of ammonia. These are easily formed, and have the same general characteristics as the ammines themselves.

Some ammino-platinum compounds have been described containing two platinum atoms in the molecule. These should belong to the same class of derivatives as the polynuclear cobalt-ammines and chromi-ammines, but so far they have not been fully investigated.

C. Diplato-ammino-salts.

When dichloro-diammino-platinum is boiled with sodium hydroxide no ammonia is liberated, and it is transformed into a greyish-white insoluble powder of composition $Pt_2(NH_3)_2(NH_2)_2(OH)_2$. The composition and behaviour of the substance points to the following constitution :—

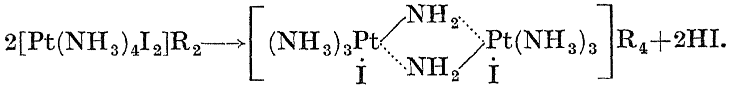


$$\left[(NH_3)\underset{\substack{\cdot\\ OH}}{Pt}\begin{matrix}NH_2\\ NH_2\end{matrix}\underset{\substack{\cdot\\ OH}}{Pt}(NH_3)\right].$$

Hydrochloric, nitric, and sulphuric acids transform the powder into black amorphous compounds containing acidic residues in place of the hydroxo-groups.[3]

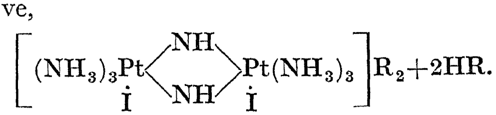
D. Diplati-ammino-salts.

Cleve describes a series of compounds obtained by removal of hydrogen iodide from di-iodo-tetrammino-platinic salts thus :



$$2[Pt(NH_3)_4I_2]R_2 \longrightarrow \left[(NH_3)_3\underset{\substack{\cdot\\ I}}{Pt}\begin{matrix}NH_2\\ NH_2\end{matrix}\underset{\substack{\cdot\\ I}}{Pt}(NH_3)_3\right]R_4+2HI.$$

They are bright yellow crystalline salts, and on treatment with ammonia lose two molecules of the corresponding acid, being transformed into the imino-derivative,



$$\left[(NH_3)_3\underset{\substack{\cdot\\ I}}{Pt}\begin{matrix}NH\\ NH\end{matrix}\underset{\substack{\cdot\\ I}}{Pt}(NH_3)_3\right]R_2+2HR.$$

These bodies are also yellow crystalline substances.

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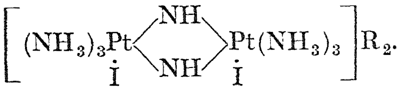
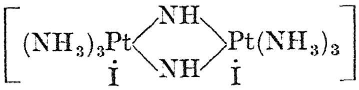
[1] Cossa, *Gazzetta*, 1890, 20, 725; 1895, 25, 505; *Ber.*, 1890, 23, 2503.

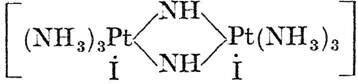
[2] Werner, *Zeitsch. anorg. Chem.*, 1896, 12, 46.

[3] Cleve, *Öfvers. K. Vet.-Akad. Forh.*, 1870, 27, 777; 1871, 28, 175.

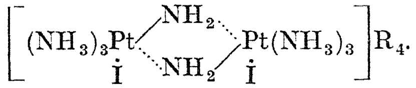
Di-iodo-hexammino-μ-imino-diplatinic Salts,

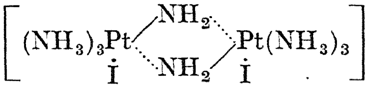


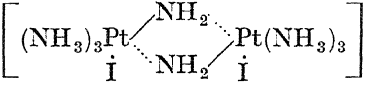
The *iodide*,  I_2, is produced by treating di-iodo-tetrammino-platinic iodide with ammonia. It crystallises in yellow microscopic plates.

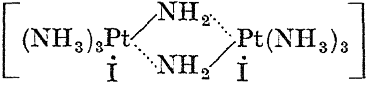
The *nitrate*,  $(NO_3)_2$, is obtained by treating a boiling solution of di-iodo-tetrammino-platinic nitrate with excess of ammonia. A crystalline precipitate is formed consisting of yellow octahedral crystals. On treatment with hydrochloric acid it yields iodo-chloro-tetrammino-platinic chloride, and with nitric acid iodo-nitrato-tetrammino-platinic nitrate.[1]

Di-iodo-hexammino-μ-amino-diplatinic Salts,

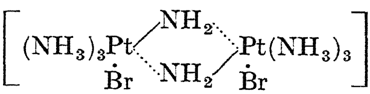


The *iodide*,  I_4, is precipitated on the addition of potassium iodide to the nitrate of the series, or from the imino-derivative by treatment with ammonia.

The *sulphate*,  $(SO_4)_2$, is an amorphous yellow powder which is insoluble in water and is precipitated from the nitrate of the series on the addition of sulphuric acid.

The *nitrate*,  $(NO_3)_4$, is produced by treating the imino-compound with nitric acid. It crystallises from a warm solution in orange prisms which are almost insoluble in cold water. Ammonia reacts with the substance, regenerating the imino-derivative.

Dibromo-hexammino-μ-amino-diplatinic Nitrate,

 $(NO_3)_4.2H_2O$,

is prepared from the corresponding imino-derivative, produced by the action of ammonia on dibromo-tetrammino-platinic nitrate, by treating it with nitric acid. It crystallises in glistening yellow plates which are easily soluble in warm water. Silver nitrate does not precipitate bromine, and ammonia regenerates the imino-derivative.

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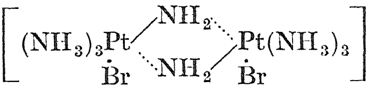
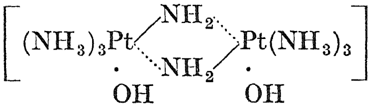
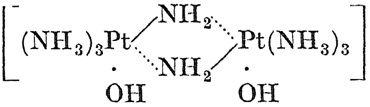
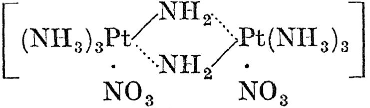
[1] Jörgensen, *J. prakt. Chem.*, 1886, 33, 489.

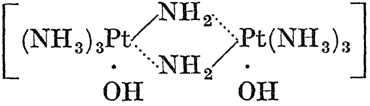
The *sulphate*,  $\left[(NH_3)_3\underset{\substack{\cdot\\ Br}}{Pt}\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\underset{\substack{\cdot\\ Br}}{Pt}(NH_3)_3\right](SO_4)_2.2H_2O$, separates as a yellowish-white powder on the addition of sulphuric acid to the nitrate.

The *chloride* separates in microscopic yellow needles on the addition of hydrochloric acid to the nitrate.

A series of **dihydroxo-derivatives** is also known. These may be represented by the formula  $\left[(NH_3)_3\underset{\substack{\cdot\\ OH}}{Pt}\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\underset{\substack{\cdot\\ OH}}{Pt}(NH_3)_3\right]R_4$.

The *nitrate*,  $\left[(NH_3)_3\underset{\substack{\cdot\\ OH}}{Pt}\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\underset{\substack{\cdot\\ OH}}{Pt}(NH_3)_3\right](NO_3)_4.2H_2O$, may be prepared by boiling di-iodo-hexammino-μ-amino-diplatinic nitrate with a solution of silver nitrate. It is sparingly soluble in cold water.

On boiling the compound with nitric acid it is transformed into the *dinitrato-compound*,  $\left[(NH_3)_3\underset{\substack{\cdot\\ NO_3}}{Pt}\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\underset{\substack{\cdot\\ NO_3}}{Pt}(NH_3)_3\right](NO_3)_4.2H_2O$.

The *chloride*,  $\left[(NH_3)_3\underset{\substack{\cdot\\ OH}}{Pt}\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\underset{\substack{\cdot\\ OH}}{Pt}(NH_3)_3\right]Cl_4$, is obtained from the nitrate by precipitation with hydrochloric acid. It crystallises in sparingly soluble white needles.[1, 2]

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[1] Cleve, *Öfvers. K. Vet.-Akad. Forh.*, 1870, 27, 777; 1871, 28, 175.

[2] Moissan, *Traité de Chimie Minérale*, 5, 849 (Masson, Paris, 1906).

NAME INDEX.

SUBJECT INDEX.

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