Coordination Chemistry Reviews, 9 (1972–1973) 339–363

ALFRED WERNER'S RESEARCH ON POLYNUCLEAR COORDINATION COMPOUNDS

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(Received April 3rd, 1972)

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A. INTRODUCTION

A review article devoted primarily to the research efforts of one man is unusual. But when the field is coordination chemistry, and the man in question is Alfred Werner, its founder[1], the limitation in the scope of such an article is more apparent than real. Werner played such a central and monopolistic role in coordination chemistry that his name is virtually synonymous with the field. Even today, more than a half-century after his death, coordination compounds, particularly metal–ammines, are known as Werner complexes, and the coordination theory, the theoretical and practical basis for the field, is colloquially called Werner's theory.

Consequently, although this article on polynuclear complexes, mostly those of cobalt, is limited primarily to Werner's achievements, it should nevertheless provide a wide coverage of the most important and fundamental problems in this area and be of use to practicing chemists as well as to historians of science. Also, in the words of Sykes and Weil[2], "It is fitting once again to give credit to the work of Werner and his students, which continues to dominate the background of the field despite the corrections and elaborations which have now been made."

The viewpoint in this review is largely "historical", in the sense that no pretense is made as to coverage of the contemporary literature. Although in some cases Werner's results have been related to later developments, this article is in no way intended to compete with excellent recent reviews, whose number underscores the increasing interest in the field. Many of these are concerned largely with polynuclear complexes containing $-O_2-$ bridges, a research area of considerable current activity[2-10], while others deal with different bridging groups[11,12]. Summaries of the literature can be found in *Gmelin's Handbuch*[13] and Pascal's *Traité*[14], and preparative procedures[15-17] and English translations of significant papers by Werner[18,34] and others[19] are also available. Inasmuch as Werner's procedures often leave much to be desired regarding reproducibility and yield, the devising of modern syntheses should be encouraged.

B. POLYNUCLEAR COMPLEXES

Polynuclear cobalt–ammines, i.e. those containing more than one central atom and more than one coordination sphere in the complex, were first prepared in 1852 by the French chemist Edmond Fremy[20]. They were subsequently investigated by Gibbs[21], Vortmann and Blasberg[22-25], Jørgensen[26-29], Maquenne[30], and Mascetti[31]. Yet it was not until the beginning of this century that their constitutional formulae were unequivocally established as a result of the extensive and systematic studies of Werner and his students. Werner not only succeeded in showing that a number of the longest-known "compounds" of this class such as Fremy's "oxycobaltammines"[20] and Vortmann's[22-25] "anhydrooxycobaltammines", "melano chloride" and "fusco sulfate" were actually mixtures, but under the guiding star of his coordination theory he also went on to prepare series after series of complexes undreamed of by his predecessors. During the sixteen-year period between his first[32] (1898) and last[33] (1914) publications devoted to these complexes, his views developed and matured. He himself recognized a number of his earlier assigned constitutional formulae[32] as incorrect, and consequently he revised these to formulae more in keeping with the properties and reactions of the compounds in question[34].

It would be a mistake to regard polynuclear complexes as merely a peripheral chapter in the history of the coordination theory. In keeping with their central role, Werner devoted no less than fifteen articles exclusively to them, including one of his longest publications, a comprehensive review of 144 pages[34], a classic of its kind summarizing the work of twenty-four *Doktoranden* and *Assistenten*, replete with both practical and theoretical considerations of previously prepared compounds as well as of thirty-nine new series of complexes. On the practical side, many polynuclear complexes are intermediates in the formation of mononuclear complexes, and a proper knowledge of their properties and reactions is of immense value in the development of synthetic methods. On the theoretical side, the formation of mononuclear complexes by the cleavage of polynuclear complexes was frequently used by Werner as a means of establishing the structure of these compounds; the most crucial and familiar of such structural proofs was the formation of violeo salts from octaammine-di-μ-hydroxo-dicobalt(III) salts (di-μ-hydroxobis [tetraamminecobalt(III)] salts)[35]. Another theoretically important application of polynuclear complexes has been their resolution, particularly that of the completely inorganic tris[tetraammine-di-μ-hydroxocobalt(III)]-cobalt(III) salts, which provided a final, cogent proof[33] for the octahedral configuration of cobalt(III). Investigations of polynuclear complexes have also served to throw much light on the nature of primary and secondary valence[36–39].

Werner began work on this intriguing but complicated class of compounds relatively early in his career. In his article[40] on the nomenclature of cobalt–ammines (1897), he referred to "substantially more complex series of compounds, which contain several cobalt atoms" *("wesentlich komplexere, mehrere Kobaltatome enthaltende Verbindungsreihen"),* but he postponed their discussion to a future study and made no proposals for their classification or nomenclature.

In a letter of January 14, 1897, Werner wrote to a colleague in an unusually elated outburst of enthusiasm (ref. 1, p. 36):

"We have definitely clarified the constitution of the polynuclear metal–ammines. I am firmly convinced that I will be able to clarify all the cobalt–ammines by the end of this year". A premature and unjustified prediction in view of the fact that he had really only begun work on the polynuclear metal–ammines and had only published about half a dozen articles on coordination chemistry. This quotation is an example of Werner's consistent underestimation, during his early career, of the magnitude of the task remaining before him. From the time in question to his premature death at the age of fifty-two, more than 140 additional articles were to flow from his prolific pen.

The introduction to Werner's first paper (58 pp.) on polynuclear complexes[32] – number eleven in the series *Beitrag zur Konstitution anorganischer Verbindungen* – establishes his experimental concern with these compounds as dating from late 1894:

"Although the investigation, the results of which we shall concern ourselves with in the following, has not been concluded, I nevertheless feel obliged to report the results obtained so far, since the experimental material has become quite voluminous, but especially since the facts to be reported are in many respects of fundamental importance for the field to be considered and therefore they may also be of interest to wider circles.

"As is well known, Jørgensen has discovered complex chromium–ammine compounds: the rhodo, erythro, and rhodoso compounds*; until now, similar cobalt compounds have not been known or have not been investigated in detail, although the number of superficially observed compounds not corresponding to ordinary cobalt–ammine salts seems to be a relatively large one. The investigations which are reported here thus involve a field which has

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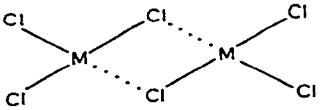
* See next page for footnote.

not yet been cultivated, and they turned out to be even more difficult than was expected, since among these complex compounds new phenomena, differing substantially from those observed among simple cobalt–ammine compounds, appear. This is the reason why the investigation which was begun three years ago has only now succeeded to the extent that definite facts supporting a view for the constitution of the compounds to be discussed have been attained."

The class of polynuclear compounds quite properly encompasses a dazzling variety of substances, including, for example, the following:

(1) Polymeric metal halides such as Al_2Cl_6 or Fe_2Cl_6, formulated by Werner as[**]



(2) The complicated derivatives of chromium, iron, and similar metals with organic ligands, many of which contain more than one kind of metal atom[‡].

(3) A large number of minerals, of which the following formulations by Werner are typical.

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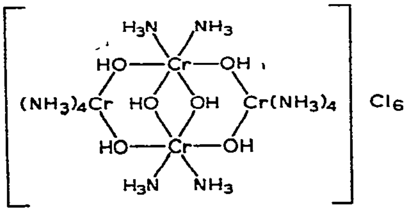
[*] In terms of Werner's coordination theory, these three series were formulated as $[(NH_3)_5CrOHCr(NH_3)_5]X_5$ (ref. 27), $[(NH_3)_5CrOHCr(NH_3)_4H_2O]X_5$ (ref. 41) and $[Cr\{(OH)_2Cr(NH_3)_4\}_3]X_6$ (ref. 43), respectively. The rhodoso salts, $[Cr_4(OH)_6(NH_3)_{12}]X_6$, were thus believed to be constitutionally similar to tris[tetraammine-di-μ-hydroxo-cobalt(III)]cobalt(III) salts that Werner resolved[33] in 1914. However, a recent crystallographic study[43] has shown that the chloride of this series is actually di-μ-hydroxo-tetrakis-μ-hydroxo-bis(tetraamminechromium(III))-bis(diamminechromium(III) chloride, i.e.



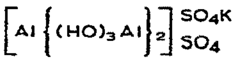
The corresponding ethylenediamine complex has been shown to have a similar structure[44]. Polynuclear chromium complexes were later extensively investigated by Pfeiffer, Dubský, Weinland, and others, but, with the two exceptions mentioned near the end of the present review article (Sect. H), not at all by Werner.

[**] In this article, I have followed Werner's custom of using solid lines to denote primary or principal valency (Werner's *Hauptvalenz*) and dotted lines to denote secondary or auxiliary valency (Werner's *Nebenvalenz*). Werner, however, felt that the two types of valencies no longer differed in the final complex, and he did not always distinguish between the two kinds of valency bond. According to Schwarzenbach[45], Werner never seemed to have been quite satisfied with the valency dichotomy that he had proposed.

[‡] See next page for footnote.

$[Cu\{(HO)_2Cu\}_3]X_3$

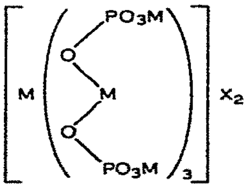
Atacamite



$\left[Al\{(HO)_3Al\}_2\right]\begin{matrix}SO_4K\\SO_4\end{matrix}$

Alumite

and



Apatite

(4) The isopoly and heteropoly acids and their salts[*] (e.g. $K_2Cr_2O_7$ and $R_7[P(Mo_2O_7)_6]$, respectively)[48a]. In this review we shall limit ourselves almost exclusively to what is probably the most thoroughly investigated class of polynuclear complexes – the polynuclear cobalt–ammines.

Polynuclear complexes result from the formation of bridges by atoms, ions or molecules which are coordinatively unsaturated, i.e. which, after forming one bond, still contain at least one unshared pair of electrons and are thus able to form an additional bond. The most widely studied of such bridging groups, all of which were investigated by Werner, include O^{2-}, O_2^-, O_2^{2-}, OH^-, NH_2^-, NH^{2-}, SO_4^{2-}, $HCOO^-$ and CH_3COO^-. Other bridging groups include[2,17] HO_2^-, SeO_4^{2-}, NO_2^-, $C_2O_4^{2-}$, $N_2O_2^{2-}$, HPO_4^{2-}, Cl^- and Br^-. Recently, cobalt complexes involving ambidentate bridging groups, e.g. $[(NH_3)_5CoCNCo(CN)_5]\cdot H_2O$, have been prepared[46].

The difference between a singly coordinatively bonded group and a bridge group may be illustrated most strikingly by reference to the –OH group. In the first case (*hydroxo*), the oxygen atom is coordinatively unsaturated and can combine with a hydrogen ion to form

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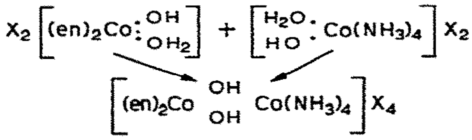
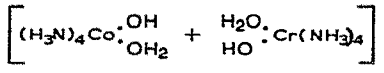
‡ Although Werner apparently never prepared such compounds, he clearly foresaw their existence and most likely tried to prepare them, as the following excerpt from his notebook of 1909 shows: "We should try to join together the following two radicals:



[Although it is not specified, these are obviously cis isomers.] If this succeeds, then the following would also be possible:



$\left[(H_3N)_4Co\begin{matrix}OH\\OH_2\end{matrix} + \begin{matrix}H_2O\\HO\end{matrix}Cr(NH_3)_4\right]$

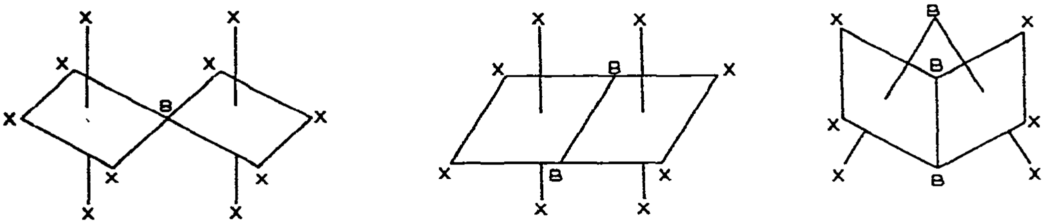
A cobalt–chromium compound!!"

[*] Much of the pioneering work on the structures of these compounds was carried out by Werner's friend Arturo Miolati (1869–1956)[47], who employed physicochemical measurements very similar to those used to elucidate the constitution of metal–ammines. Miolati's structural proposals were developed further by Hippolyte Copaux (1872–1934), Arthur Rosenheim (1865–1942) and Paul Pfeiffer (1875–1951). Werner's views of heteropoly compounds are found in his magnum opus, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*[48].

an aquo group. In the second case (*μ-hydroxo* or *ol*)*, the oxygen atom has already fulfilled its maximum coordination number of three (the positions are occupied by the hydrogen and the two central metal atoms) and thus cannot combine with a hydrogen ion. Consequently, in aqueous solution, complexes containing an ol group exhibit a neutral reaction, whereas complexes with hydroxo groups show a distinctly basic one[54]. Similar differences exist between the singly bonded and the doubly bonded (bridge) species for the other groups listed above.

Werner apparently did not realize that his polynuclear complexes constituted a transition between coordination compounds and the infinite structure of the crystal lattice[45,55]. Inasmuch as he knew that certain groups, especially hydroxide, could coordinate with two metal atoms simultaneously to form bridges, it is possible that he might have considered the possibility of infinite structures with metal atoms bonded in this manner. In the case of ol bridges, this infinite olation process would result in the lattice structure of crystalline metal hydroxides, e.g. hydrargyllite, as established by X-ray crystallography. However, Werner apparently did not reach such conclusions, and it remained for Pfeiffer[56] and Niggli[57] to point out that crystal structures were in beautiful agreement with the coordination theory.

Bridges may be formed singly (by joining the corners of two octahedra), doubly (by joining the edges of two octahedra) or triply (by joining the faces of two octahedra) — an obvious parallel to the formation of the single, double and triple bonds formed by carbon (Fig. 1). It should be obvious from Fig. 1 that the number of bridges connecting two metal ions cannot exceed three. It is also evident that for binuclear complexes containing one, two or three bridges, each of the cobalt atoms can still be bonded to five, four or three groups (X), respectively. If these positions are occupied by ammonia molecules, decaam-



Single bridge (corner) Double bridge (edge) Triple bridge (face)

Fig. 1. Bridging in polynuclear complexes.

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* In 1907, Werner[49] introduced the term *ol* to distinguish the $-OH$ bridge from the $-OH$ group coordinatively bonded to only one metal atom in the usual manner. Although the term *ol* has not been recognized by the Inorganic Chemistry Section of the International Union of Pure and Applied Chemistry[50], which recommends the designation μ-hydroxo instead, the term is a useful one and will be used interchangeably with μ-hydroxo in this article. The use of the letter μ to designate bridged groups, incidently, was introduced by Werner in 1907 in connection with the $-NH_2$ group[51]. Olation, the formation of ol compounds from hydroxo compounds, was considered by Werner, especially in connection with his theory of acids, bases and hydrolysis[52,53].

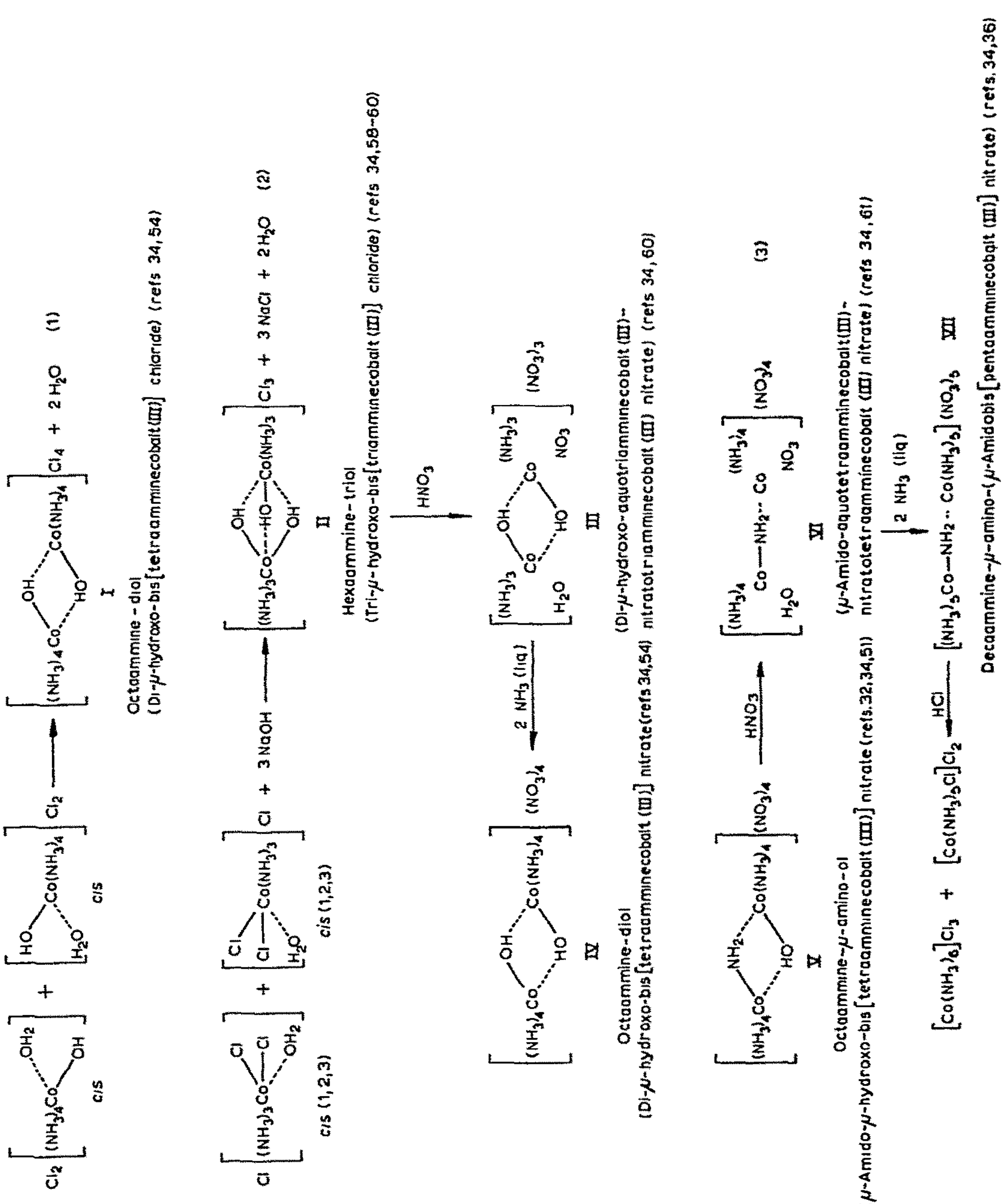
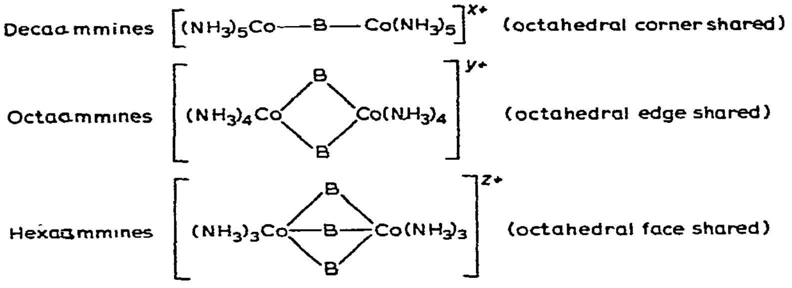


Fig. 2. Syntheses and interrelationships of polynuclear cobalt complexes.



mines, octaammines or hexaammines result, as shown by the above formulae, in which B designates a bridging group.

Relationships between, and typical synthetic methods for, these compounds, as exemplified in Werner's work, are shown in Fig. 2, in which Werner's nomenclature is used, with modern nomenclature in parentheses. Just as in organic chemistry, the structures of polynuclear compounds were established by their formation from, or their "degradation" (cleavage) into, mononuclear "fragments" of known structure. Conversely, the structures of mononuclear complexes have sometimes been determined by their formation from polynuclear complexes of known structure.

Of course, just as is the case among mononuclear complexes, varying numbers of ammonia molecules can be replaced by other neutral molecules or anions (see compounds III and VI in Fig. 2). Also, since two different cobalt atoms are involved, unsymmetrical substitution of the ammonia molecules may give rise to types of isomerism not possible among mononuclear complexes. Furthermore, for complexes containing more than one bridge, the bridging groups B need not be the same. Finally, although binuclear complexes are by far the most common or polynuclear complexes, compounds containing three or four cobalt atoms are possible. All these factors contribute toward making the chemistry of even the polynuclear cobalt–ammines alone extremely complex. Consequently, in the following review of Werner's work, we shall limit ourselves to the simplest of these compounds in order to prevent the treatment from becoming too unwieldy.

C. SINGLE-BRIDGED DINUCLEAR COMPLEXES

As mentioned in the Introduction, much recent research on polynuclear complexes has centered around complexes with $—O_2—$ bridges. Single-bridged peroxo complexes are important intermediates in the preparation of other dicobalt complexes and are useful as models of oxygen carriers in biological systems. In his first paper devoted exclusively to these compounds (1898), Werner already recognized the difficulty in defining the oxygen-containing bond in them (ref. 62, p. 251):

"In conclusion, it may be pointed out that the bonding of the oxygen in the compounds discussed here is so peculiarly labile that one will be scarcely able to give a satisfactory answer to the question as to whether valence bonding or molecular addition is present in them, in so far as the question in this form has any validity at all." Although it was early recognized, even before Werner's time, that oxygen-bridged polynuclear complexes were of two main types, it is only recently that a satisfactory and unequivocal explanation for the bonding in these compounds has been given. According to X-ray[63–66], EPR[67] and infrared[68] studies, the two types of compounds are now best considered as containing peroxide ($-O_2^{2-}-$) and superoxide* ($-O_2^{-}-$) bridges.

(i) μ-Peroxo complexes

The general method for the preparation of many cobalt(III)–ammines involves the atmospheric oxidation of ammoniacal solutions of cobalt(II) salts. Inasmuch as peroxo-bridged complexes are formed as intermediates in these synthetically important processes, it is not surprising that they are among the earliest known and best investigated of binuclear complexes. The brownish, unstable, diamagnetic so-called *Oxykobaltiake* of Fremy[20], Vortmann and Blasberg[22–25], and Jφrgensen[28,29], which are the first of the oxidation products that are formed, were shown by Werner and Mylius[62] to be decaammine-μ-peroxo-dicobalt(III) salts (modern, μ-peroxobis(pentaamminecobalt(III) salts) or in a formal sense the addition products of one mole of oxygen to two moles of a pentaamminecobalt(II) salt.

$$2\,Co(NO_3)_2 + 10\,NH_3 + O_2 \rightarrow [(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5](NO_3)_4 \qquad (1)$$

This brown binuclear complex is stable in solution only in about 7 *M* ammonia. It decomposes into mononuclear cobalt(III) complexes slowly, but especially at higher temperatures, e.g.

$$[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+} \xrightarrow{H+} 2\,[Co(NH_3)_5H_2O]^{3+} \qquad (2)$$

In highly acidic solutions it decomposes to simple cobalt(II) salts with evolution of oxygen[8,62]:

$$[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+} + 10\,H^+ \longrightarrow 2\,Co^{2+} + 10\,NH_4^+ + O_2\uparrow \qquad (3)$$

The oxygenation reaction shown in eqn. (1) is reversible[69,70] and can be reversed by increasing the ammonia concentration or by reducing the partial pressure of oxygen, e.g. by passing nitrogen through the solution[69]. Because of the biological importance of such oxygen-carrying systems, the diamagnetic μ-peroxo-bis(pentaammine)cobalt(III) salts[69,70] and μ-peroxo binuclear cobalt(III) compounds with ligands other than ammonia[71,72] have been extensively investigated and reproducible syntheses devised[17]. In most particulars, Werner's

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* The use of the term *superoxyd* by Werner and others in the older literature to indicate that which we now call *peroxide* (O_2^{2-}) should not be confused with the current designation *superoxide* (O_2^{-}), as used in Sect. C(ii) of this review.

conclusions about these complexes, especially in regard to the peroxo (O_2^{2-}) linkage, have been confirmed[2,8,73].

(ii) μ-Superoxo complexes

If the oxidation process shown in eqn. (1) is allowed to proceed to completion, acidopentaamminecobalt(III) salts are eventually formed, but if the decaammine-μ-peroxo-dicobalt(III) salts are warmed with dilute nitric acid, it is possible to isolate paramagnetic deep green *Anhydrooxykobaltiake* of empirical formula[16,17] $Co_2(NH_3)_{10}O_2X_5$. Analytically, such salts are similar to the previously described *Oxykobaltiake* in that they possess the same cation $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{x+}$, but in the *Oxykobaltiake* the charge on the cation is $x = 4+$, whereas in the *Anhydrooxykobaltiake*, $x = 5+$. The differences in properties and constitution between the two series, however, are profound. The green paramagnetic pentapositive cation can also be formed from the brown diamagnetic tetrapositive cation by a reversible redox reaction[74].

Vortmann[24], who was the first to prepare these compounds, regarded them as *Oxykobaltiake* containing one additional anion for each two cobalt atoms. Werner and Mylius[62] considered them in a formal sense as addition products of one mole of oxygen to one mole of a pentaamminecobalt(II) salt and one of a pentaamminecobalt(III) salt. He later regarded them[34] as containing one atom of tripositive and one of tetrapositive cobalt—$[N(NH_3)_5Co^{III}{-}O{-}O{-}Co^{IV}(NH_3)_5]X_5$. We know today that they contain two cobalt(III) ions joined by a superoxo (O_2^-) bridge.

The *Anhydrooxykobaltiake* can be differentiated from the *Oxykobaltiake* by their reaction with aqueous sulfur dioxide and hydrochloric acid. Whereas both series of compounds yield a cobalt(II) salt and oxygen, the *Anhydrooxykobaltiake* also yield chloropentaamminecobalt(III) chloride. Titration with reducing agents constitutes another distinguishing test, which has also been offered as evidence of an average oxidation state greater than three for the *Anhydrooxykobaltiake*. For example, four equivalents of sodium arsenite are sufficient to reduce completely one mole of *Oxykobaltiake* to cobalt(II) (one equivalent for each cobalt atom and two for the peroxo group), whereas for *Anhydrooxykobaltiake* five equivalents are required[75]. Furthermore, the former brownish compounds are diamagnetic (as expected for cobalt(III)), while the latter green compounds are paramagnetic with effective magnetic moments of ca. 1.7 Bohr magnetons (as expected for the one unpaired electron originally believed to be present in cobalt(IV) but now known to be present in the superoxo group)[76]. More recently, paramagnetic resonance studies[77,78] have shown that the single unpaired electron interacts equally with both cobalt nuclei and has an equal probability of being on either atom; however, it is predominantly (80%) found on the $-O_2-$ bridge. Thus the formal oxidation number of each of the cobalt atoms is three.

In a private communication of June 21, 1946 to Prof. John C. Bailar, Jr., Dr. E.O. Brimm[79] suggested that, inasmuch as all the complexes which, according to Werner, contain "tetrapositive cobalt" also contain $-O_2-$ bridges*, the magnetic evidence cited on behalf of the

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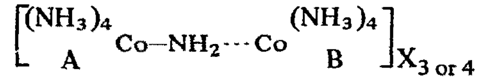
* See next page for footnote.

Co^{IV} state proposed by Werner could be explained equally well by assuming these compounds to contain the superoxide group (O_2^-) and tripositive cobalt. It was not until twenty years later that this view was confirmed experimentally[5,63–65,77,79a,80,81]. Today, the older designations *paramagnetic peroxo* (as contrasted to *diamagnetic peroxo*)[82] as well as Werner's *peroxocobalt(III, IV)*[78] terminology, implying non-equivalent cobalt atoms, have finally been discarded in favor of the designation *superoxo* complexes[2,17].

(iii) μ-Amido complexes

Decaammines containing an amido group (amino group, in Werner's nomenclature) in place of a peroxo group are well known and can be prepared from octaammine-μ-amino-ol dicobalt(III) salts (μ-amido-μ-hydroxo-bis[tetraamminecobalt(III)] salts) as shown in reaction scheme (3) of Fig. 2 (see ref. 34, p. 43 and ref. 61, pp. 3915–3921). According to Sykes and Weil[2], both the existence of the salt shown in reaction scheme (3) and the formulation of its cation need to be confirmed. Because of their similarity to the so-called rhodochromium salts of Jørgensen[27] in color and crystal form as well as manner of preparation, Werner et al.[34] considered the bluish-red decaammine salts as analogous to the rhodochromium salts but containing a bridging amido group $[(NH_3)_5Co{-}NH_2\cdots Co(NH_3)_5]X_5$ in place of the ol group $[(NH_3)_5Cr{-}OH\cdots Cr(NH_3)_5]X_5$. The bridged amino group, of course, does not exhibit the basic reaction characteristic of a singly bonded $-NH_2$ group. Werner proved the structure of these compounds by their cleavage with hydrochloric acid into mononuclear hexaamminecobalt(III) and chloropentaamminecobalt(III) salts (see the last step in reaction scheme (3) of Fig. 2). The structure of the μ-amidobis[pentaamminecobalt(III)] ion in the pentanitrate salt has been determined by X-ray diffraction[83,84], and the infrared spectrum of the ion has been reported[85,86].

Formally related to the above compounds are the substituted octaammines of formula



$$\left[\begin{matrix}(NH_3)_4 & & (NH_3)_4\\ & Co{-}NH_2\cdots Co & \\ A & & B\end{matrix}\right]X_{3\text{ or }4}$$

described in Werner's immense compendium[34] ($A = H_2O$, $B = NO_3$ (p. 12); $A = Cl$, $B = NO_3$ (pp. 13, 49); $A = H_2O$, $B = Cl$ (pp. 45–48); $A = CNS$, $B = Cl$ (p. 48), and $A = H_2O$, $B = Br$

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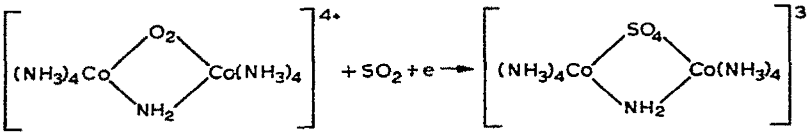
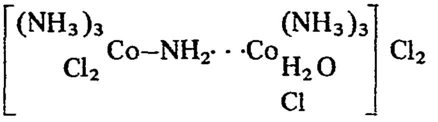
[*] For example, Werner found that if the "peroxo" group in binuclear complexes is replaced by other groups, the "Co^{IV}" is simultaneously "reduced" to the trivalent state[34].



On the other hand, if the first ion were warmed with concentrated sulfuric acid, three equivalents of oxygen per mole of the ion were liberated, a fact that Werner interpreted by assuming that Co^{III}, Co^{IV} and O_2^{2-} were present.

(pp. 12, 50, 51)). Werner proved the symmetrical distribution of the eight ammonia molecules and the $-NH_2$ bridge in these compounds by cleaving them with hot concentrated hydrochloric acid into mononuclear pentaamminecobalt(III) and tetraamminecobalt(III) salts.

A series of amido-bridged substituted hexaammines was the subject of Werner's first paper on polynuclear complexes[32]. For a number of years, it had been known that a difficultly soluble black salt (*schwarzes Salz*), later named *Melanochlorid* by Vortmann[22–24], could be precipitated by adding concentrated hydrochloric acid to a partially oxidized ammoniacal solution of a cobalt(II) salt[87]. According to Werner, this was not a pure substance but rather a mixture consisting mainly of a chloride of formula

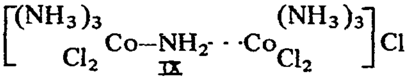


$$\left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ Cl_2 & Co{-}NH_2\cdot\cdot\cdot Co & H_2O \\ & & Cl \end{matrix}\right] Cl_2$$

(ref. 32, pp. 119, 159, 162; ref. 34, pp. 88, 89)

VIII

or

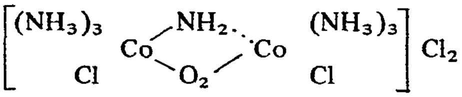


$$\left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ Cl_2 & Co{-}NH_2\cdot\cdot\cdot Co & Cl_2 \end{matrix}\right] Cl$$

IX

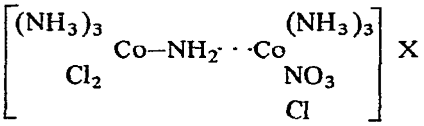
(ref. 32, p. 162)

together with a small amount of the doubly bridged binuclear compound



$$\left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ & Co\begin{matrix} NH_2 \\ O_2 \end{matrix}Co & \\ Cl & & Cl \end{matrix}\right] Cl_2$$

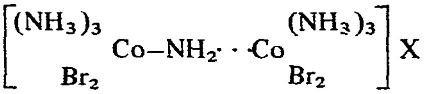
Werner also succeeded in preparing the compound



$$\left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ & Co{-}NH_2\cdot\cdot\cdot Co & \\ Cl_2 & & NO_3 \\ & & Cl \end{matrix}\right] X$$

(ref. 34, p. 97)

related to VIII and



$$\left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ & Co{-}NH_2\cdot\cdot\cdot Co & \\ Br_2 & & Br_2 \end{matrix}\right] X$$

(ref. 34, pp. 26, 97, 98, 110)

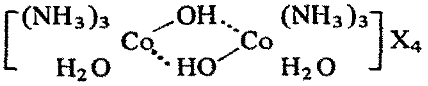
related to compound IX.

Until recently, the source of all amido-bridged complexes was Vortmann's sulfate[24]. Even with Werner's improved syntheses[49,51,54,59,88] this preparation is time-consuming and gives poor yields, and better methods are now available for the μ-amido-μ-sulfato and μ-amido-μ-superoxo components of Vortmann's sulfate (ref. 2, pp. 56 et seq.).

D. DOUBLE-BRIDGED DINUCLEAR COMPLEXES

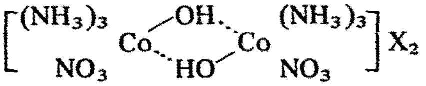
(i) Identical bridged complexes

With the exception of hydroxo-bridged species, polynuclear complexes having more than one bridging group of the same kind are relatively rare[17]. The preparation and reactions of dinuclear compounds containing two –OH bridges (ref. 2, pp. 76 et seq.) have already been given (reaction schemes (1) and (2) of Fig. 2). Many polynuclear complexes were not at first recognized as such. For example, the formula for the chloride of compound I in Fig. 2, originally prepared by Gentele[89] in 1856, was for many years written as $Co(OH)Cl_2 \cdot 4NH_3$ until Werner[54] in 1907 proposed that this formula be doubled. In addition to the diol compounds I, III and IV in Fig. 2, Werner et al.[34,60] prepared the substituted hexaammine diols



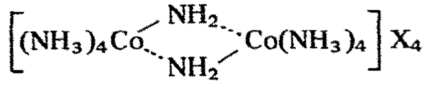
$$\left[\begin{array}{c}(NH_3)_3\\ H_2O\end{array} Co \begin{array}{c}OH\\ HO\end{array} Co \begin{array}{c}(NH_3)_3\\ H_2O\end{array}\right]X_4$$

and



$$\left[\begin{array}{c}(NH_3)_3\\ NO_3\end{array} Co \begin{array}{c}OH\\ HO\end{array} Co \begin{array}{c}(NH_3)_3\\ NO_3\end{array}\right]X_2$$

As an example of a dinuclear complex with two amido bridges we can cite Werner's

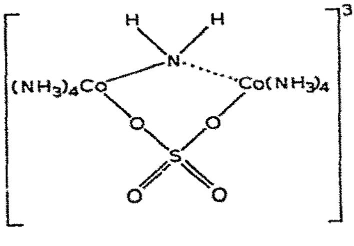


$$\left[(NH_3)_4Co \begin{array}{c}NH_2\\ NH_2\end{array} Co(NH_3)_4\right]X_4$$

(ref. 2, p. 64; ref. 13; ref. 34, pp. 23, 87)

(ii) Non-identical bridged complexes

Dinuclear complexes containing two different kinds of bridges are much more numerous than those with identical bridges and can be mentioned only very briefly here. For a number of such compounds, Werner's first proposed structures proved to be incorrect, and he subsequently modified them, as shown in Fig. 3. Infrared studies of the compounds X in Fig. 3 have confirmed Werner's conclusion that the $-NO_2-$ group does indeed form a bridge and that this bridging is through the nitrogen atom and one of the two oxygen atoms[91–93]. X-ray[93a] and infrared studies[85,94,95] of compounds XII in Fig. 3 have also confirmed Werner's conclusion that the $-SO_4-$ group forms a bridge and that the cation probably contains a six-membered non-planar ring, viz.



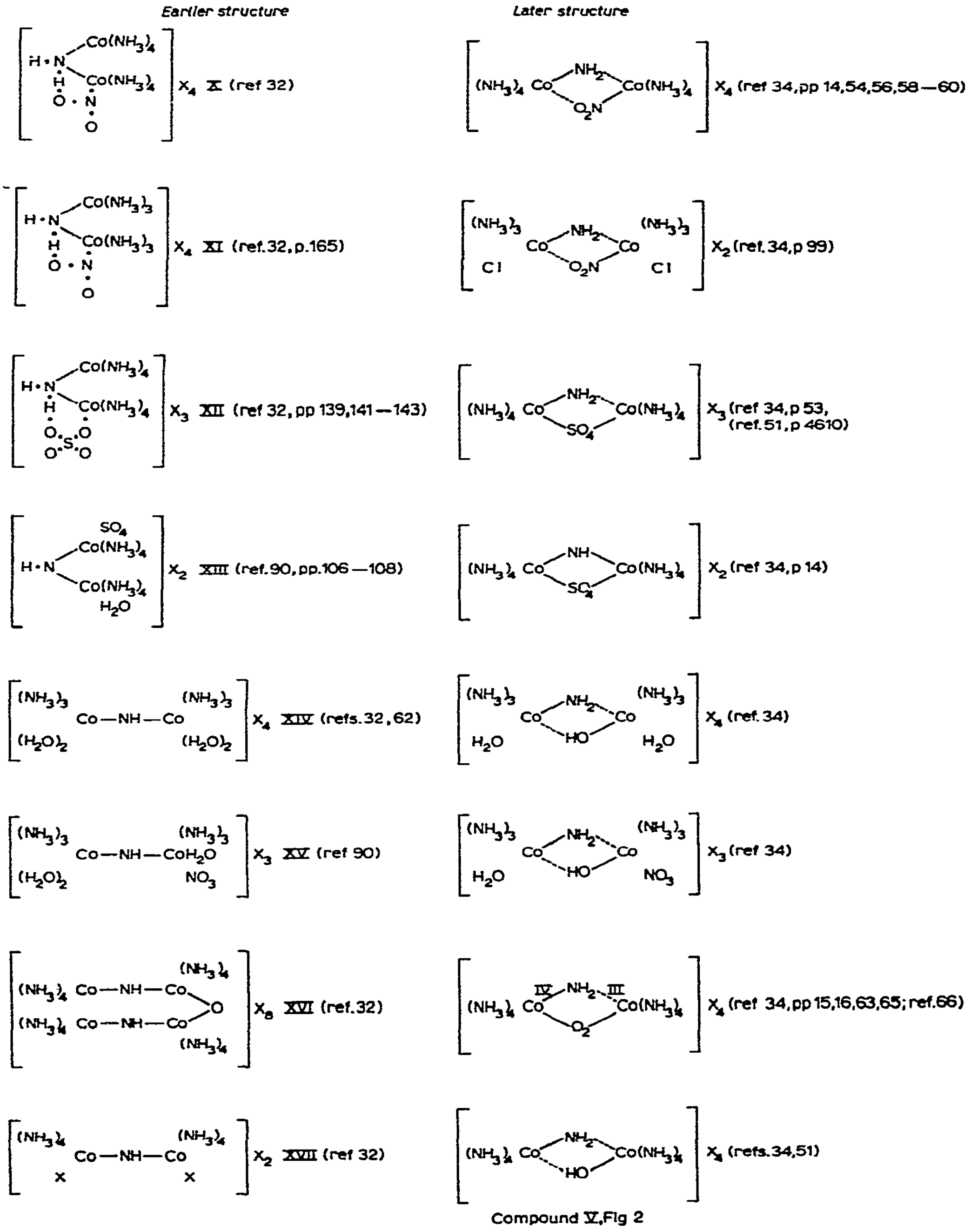
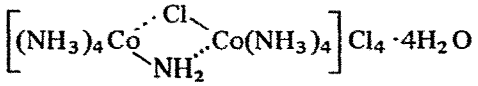


Fig. 3. Structures of some of Werner's non-identical double-bridged cobalt complexes.

Just as Werner showed *Melanochlorid* to be a mixture, so did he show that Vortmann's insoluble red *Fuskosulfat*, one of the earliest known polynuclear "compounds"[20,22–25,28], actually consisted of a mixture of the sulfates of series XVI and XVII in Fig. 3. As mentioned earlier, Werner's postulate of cobalt(IV) has not withstood the test of time. X-ray diffraction studies of the nitrate salt of the green paramagnetic series XVI in Fig. 3 have shown the presence of a superoxo bridge[66]. The cation is thus μ-amido-μ-superoxo-bis[tetraamminecobalt(III)]. A reproducible synthesis for the nitrate has recently been published[17].

Werner et al. originally prepared[32] the chloride of the red diamagnetic series XVII in Fig. 3 in 1898, at which time it was noted that the chlorine content of the compound was too high (ref. 32, p. 151). In 1907, Werner reported an alternative preparation for the tetrahydrated chloride, which gave much better analytical results for chlorine (28.34% found; 28.30% calculated)[51]. In their long paper of 1910, Werner et al. again commented that the chloride content of this compound was too high, viz. 34.3% instead of the 28% required by theory (ref. 34, p. 44). Probable reasons for the discrepancies have been recently suggested by Barro et al.[96]. They believe that the compound described by Werner et al. in 1898 (ref. 32) and 1910 (ref. 34) was identical with the compound that they prepared and showed by X-ray diffraction to be μ-chloro-μ-amido-bis[tetraamminecobalt(III)] chloride tetrahydrate, the first dicobalt species shown to contain a chloro bridge.

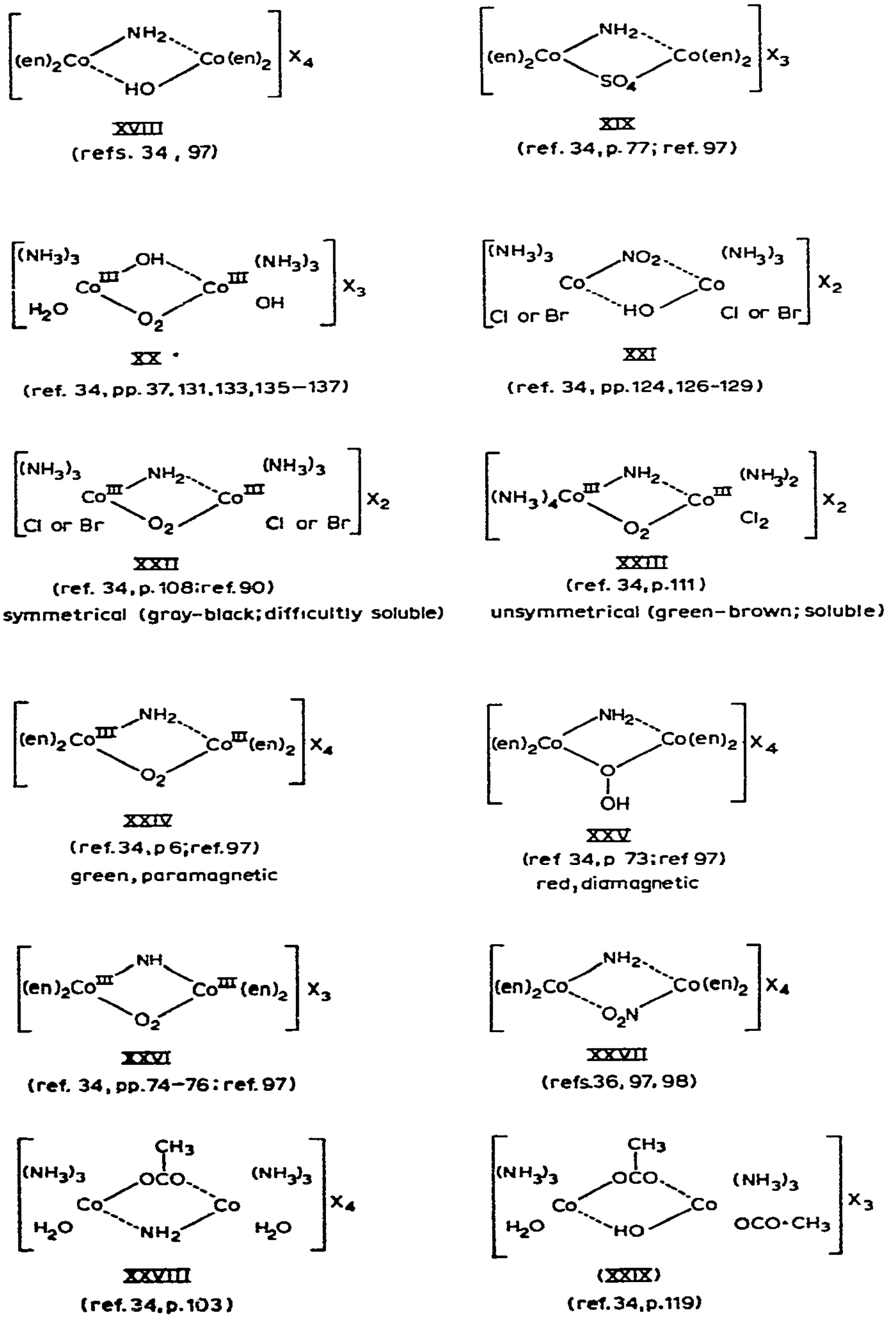


$$\left[(NH_3)_4Co\begin{matrix}Cl\\ \\ NH_2\end{matrix}Co(NH_3)_4\right]Cl_4\cdot 4H_2O$$

The compound obtained by Werner[51] in 1907, then, was the true chloride of the series XVII in Fig. 3. This compound and the chloro-bridged compound are closely related, and the former can be readily prepared from the latter by standing in aqueous solution. Syntheses for both compounds have recently been published[17].

Some idea of the variety of doubly bridged dinuclear complexes prepared by Werner may be conveyed by the following series of complexes, shown in Fig. 4. Among polynuclear complexes, isomeric relationships can become quite complicated, and methods for calculating the number of isomers in these cases have been devised[99,100]. Optical isomerism occurs among a number of these compounds, and Werner succeeded in resolving compounds of series XVIII, XIX and XXIV–XXVII into enantiomers[97]. The cation of series XXVII has the distinction of being the first polynuclear complex to be resolved. For a detailed account of Werner's work on optically active coordination compounds see another paper by the present author[101]. Of the series of compounds shown in Fig. 4, series XXII and XXIII are isomeric with each other as are series XXIV and XXV.

Of the series shown in Fig. 4, Werner considered series XX, XXII–XXIV and XXVI to contain peroxo bridges and one atom of tetrapositive cobalt. These series are now known to involve superoxo bridges, and both cobalt atoms are tripositive. The O–O distance in the tetra-hydrated nitrate salt of Werner's green paramagnetic series XXIV was found by X-ray diffraction[63] to be 1.36 Å. (Alkali metal superoxides have an O–O distance of 1.28 Å, while in most peroxides the distance is about 1.48 Å.) Further evidence of a superoxo



XVIII (refs. 34, 97)

XIX (ref. 34, p. 77; ref. 97)

XX * (ref. 34, pp. 37, 131, 133, 135–137)

XXI (ref. 34, pp. 124, 126–129)

XXII (ref. 34, p. 108; ref. 90) symmetrical (gray-black; difficultly soluble)

XXIII (ref. 34, p. 111) unsymmetrical (green-brown; soluble)

XXIV (ref. 34, p 6; ref. 97) green, paramagnetic

XXV (ref 34, p 73; ref 97) red, diamagnetic

XXVI (ref. 34, pp. 74–76: ref. 97)

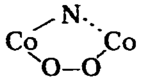
XXVII (refs. 36, 97, 98)

XXVIII (ref. 34, p. 103)

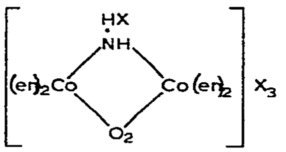
(XXIX) (ref. 34, p. 119)

Fig. 4. Additional non-identical double-bridged dicobalt complexes prepared by Werner.

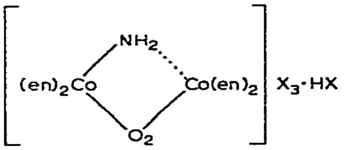
bridge was the fact that the five-membered ring



is almost planar. A synthesis for the nitrate has recently been published[17]. Thewalt and Marsh also showed that the dihydrated nitrate salt of Werner's red diamagnetic series XXV contained a hydroperoxo bridge with a pyramidal arrangement of bonds around the bridging oxygen atom[63]. Werner formulated this series as



but later the formula

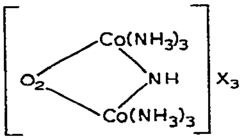


was suggested.

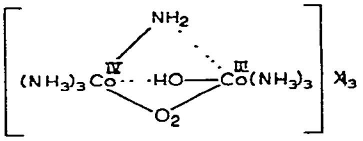
E. TRIPLE-BRIDGED DINUCLEAR COMPLEXES

Among compounds of this type we have already encountered the tri-μ-hydroxo-bis(triamminecobalt(III)) series (compound II in Fig. 2), which are isomeric with the tris[tetraammine-di-μ-hydroxo-cobalt(III)]cobalt(III) salts. The latter series, which were the first carbon-free coordination compounds to be resolved, have twice the molecular weight of the former series. Other compounds prepared by Werner are shown in Fig. 5.

X-ray diffraction studies[102] of the bromide and iodide salts of the tri-μ-hydroxo-bis[triamminecobalt(III)] ion (series XXX in Fig. 5) have confirmed the presence of the three bridges postulated by Werner. Since Werner's time, little work has been done on the triple-bridged di-μ-hydroxo compounds of the type shown as series XXXII and XXXIII in Fig. 5. X-ray diffraction studies of compounds of series XXXIII have shown that the acetato bridge is bonded symmetrically to the cobalt atoms by the oxygen atoms[103]. Series XXXV in Fig. 5, prepared from crude *Melanochlorid*, should contain a superoxo bridge. It was originally formulated by Werner et al. (ref. 90, p. 109) as

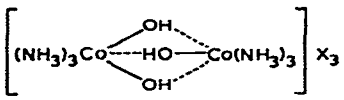


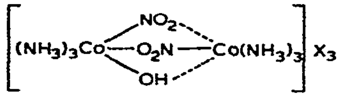
and later[34] as

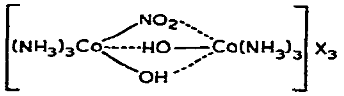


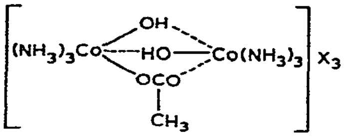
F. TRINUCLEAR COMPLEXES

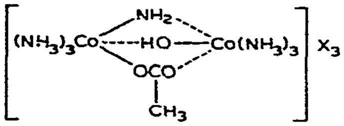
As examples of this type which were prepared by Werner, we can cite the following compounds, containing four, five and six ol bridges, respectively.


XXX (ref. 34, p. 34; refs. 58–60)


XXXI (ref. 34, p 130)


XXXII (ref. 34, pp. 121–123)


XXXIII (ref. 34, pp. 115, 117, 118)


XXXIV (ref. 34, pp. 101, 102)

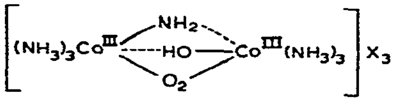
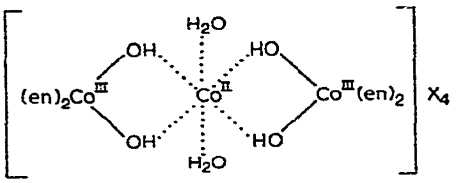
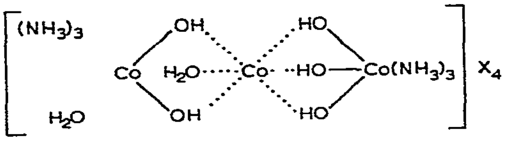

XXXV (ref. 90, p 109; ref. 34, pp 28, 31, 104, 107, 108, 110)

Fig. 5. Some triple-bridged dicobalt complexes prepared by Werner.

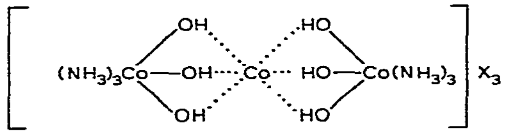


(ref. 88, pp. 4429–4433; ref. 34, p. 41)



(ref. 34, p. 143)

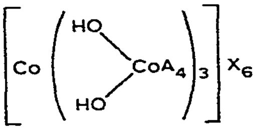
and



(ref. 34, pp. 141–143)

G. TETRANUCLEAR COMPLEXES

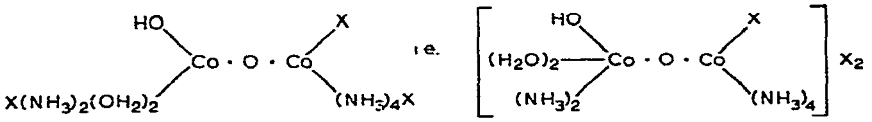
Compounds of this type were the first in which Werner definitely recognized the presence of an –OH bridge. Only two series are known. These correspond to the formula



$$\left[Co\left(\begin{matrix}HO\\HO\end{matrix}CoA_4\right)_3\right]X_6$$

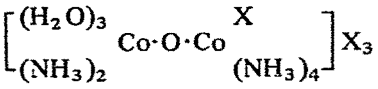
in which[49] $A = NH_3$ or $\frac{1}{2}$ en. The ammonia compounds were the first completely inorganic coordination compounds to be resolved[33]. It is one of those ironies of history that the resolution of this series of compounds, first prepared by Sophus Mads Jørgensen[104], Werner's principal scientific adversary[105,106], marked the final vindication of Werner's coordination theory. Although the structure of these compounds has not been determined by X-ray diffraction studies, the structure of the corresponding ethylenediamine cation has been so determined[107]. Both because of their intrinsic importance and also in order to illustrate his method of proof of structure, we shall now examine in some detail Werner's reasons for assigning these compounds the above constitutional formula.

These brown, lustrous crystals[103] were first prepared by Jørgensen[42,105], who named the series anhydrobasic tetraamminediaquodiammine cobalt salts and proposed for them the constitutional formula



$$\begin{matrix}HO\\X(NH_3)_2(OH_2)_2\end{matrix}Co\cdot O\cdot Co\begin{matrix}X\\(NH_3)_4X\end{matrix} \quad \text{i.e.} \quad \left[\begin{matrix}HO\\(H_2O)_2\text{—}\\(NH_3)_2\end{matrix}Co\cdot O\cdot Co\begin{matrix}X\\(NH_3)_4\end{matrix}\right]X_2$$

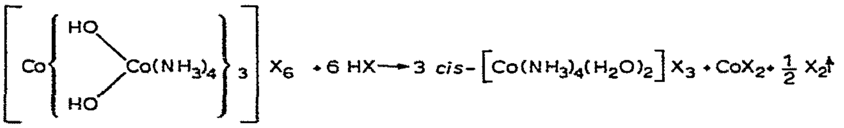
with a molecular weight one half that for Werner's formula. Werner et al.[49] rejected Jørgensen's formula for a number of reasons: (1) The hydroxide group could not be bonded to the cobalt atom in the usual manner, for then it would react with dilute mineral acids to yield the compound



$$\left[\begin{matrix}(H_2O)_3 & & X\\ & Co\cdot O\cdot Co & \\ (NH_3)_2 & & (NH_3)_4\end{matrix}\right]X_3$$

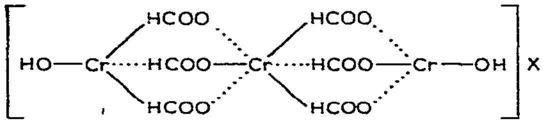
which was contrary to the observed facts. (2) An anion X could not be bonded directly to a cobalt atom because treatment of the salts with soluble sulfates yielded precipitates of X-free insoluble sulfates.(3) According to Jørgensen's formula, cleavage of the salts with mineral acids should yield a cobalt–tetraammine and a cobalt–diammine in equimolar amounts. Yet despite the known stability of cobalt–diammines, no trace of such compounds was found on treatment with mineral acids. (4)Quantitative determination of decomposition products did not lead to results in agreement with Jørgensen's formula. For example, cleavage of the sulfate with hydrochloric acid should yield 89.6% of *cis*-diaquotetraamminecobalt(III) chloride according to Werner's formulation but only 68.1% according to Jørgensen's structure. Since *cis*-$[Co(NH_3)_4(H_2O)_2]Cl_3$ is fairly soluble, the experimentally determined value of 81.1% seems much more in accord with Werner's formula than with Jørgensen's.

Not only did treatment of these salts with cold concentrated hydrochloric acid produce the amount of diaquotetraammine salt required by Werner's formula, but also the amount of chlorine liberated (one half mole, i.e. one atom per four cobalt atoms) showed that one of the four cobalt atoms in these salts is reduced to the divalent state during this process. Since, according to all Werner's previous experience, the only type of cobalt(III) radical that is reduced to a cobalt(II) radical is one in which the cobalt is not bonded to ammonia or an amine, he assumed that in the compound in question one of the four cobalt atoms is not bonded to ammonia, and he therefore apportioned the twelve ammonia molecules equally among the remaining three cobalt atoms. The following equation is in agreement with all the facts.

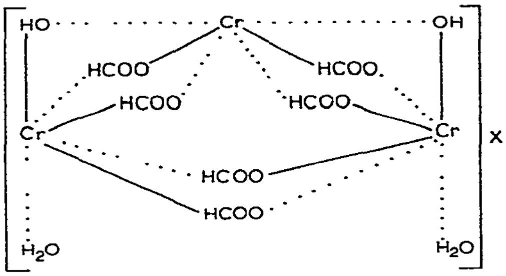


H. POLYNUCLEAR COMPLEXES OF CHROMIUM

Werner generally confined his work on polynuclear complexes to those of cobalt. Yet he did, on a few occasions[109–111], investigate those of chromium although without ascertaining their structures. Together with Jovanovits[109], he prepared a series of green acetato complexes which he formulated as $[Cr_3NH(OCOCH_3)_6(H_2O)_4]X$ (where $X = NO_3 \cdot 2H_2O$, I, $AuCl_4$, or $\frac{1}{2}PtCl_6$). They considered a closely related compound $[Cr_3NH(OCOCH_3)_6(H_2O)_3SCN]$ to be a non-electrolyte. In another paper[110,111], in addition to preparing a number of mononuclear hexaaquochromium(III) salts, Werner et al. prepared a series of extremely stable compounds $[Cr_3(OH)_2R_2]X$, where R = formate or acetate. Such organic complexes of chromium, although extremely complicated, have been thoroughly studied because of their application in the tanning industry. For the trinuclear formate complexes, Balányi (ref. 112, p. 169) has proposed the formula

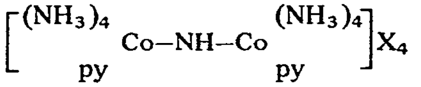


in which only one chromium atom has a coordination number of six, while the remaining two each have a coordination number of four. This structure should correspond to a symmetrical combination of two tetrahedra with an octahedron, i.e. a rhombohedron[113]. Perhaps Werner would have preferred the constitution suggested by his former student and assistant Edmund Stiasny[114], who agreed with Werner's view that the the two –OH groups are bound as ol bridges.



I. POLYNUCLEAR COMPLEXES OF UNKNOWN CONSTITUTION

Although Werner's systematic and extensive research on polynuclear cobalt–ammines explained the constitution of virtually all of these compounds, it is not true that the structures of all these complexes have been clarified. For example, in 1905 Werner and Feenstra[115] prepared a yellow chloride and a yellow-brown bromide of empirical formula $Co_2(NH_3)_8(py)_2NHX_4$, which they regarded as octaamminedipyridine-μ-iminodicobalt(III) compounds. i.e.

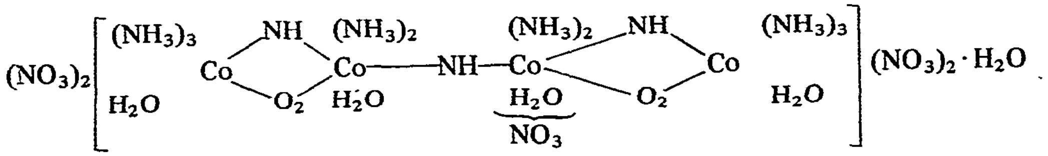


$$\left[\begin{matrix}(NH_3)_4 & & (NH_3)_4\\ & Co{-}NH{-}Co & \\ py & & py\end{matrix}\right]X_4$$

In a later (1908) article (ref. 61, pp. 3913, 3914), Werner stated that their constitution was quite different from that which had been originally proposed. He planned to discuss the question later but neglected to return to it.

As another case, one might cite the so-called dioxotriimidododecamminetetracobalt(III) salts, $[Co_4\{(O_2)_2(NH)_3\}(NH_3)_{10}]X$, where $X = (NO_3)_5\cdot 5H_2O$, $Cl_8\cdot 2H_2O$, or $Br_8\cdot H_2O$ (ref. 90, pp. 112, 113).

Werner et al. (ref. 90, p. 105) assigned to the nitrate the constitutional formula



Since these compounds are not mentioned in Werner's comprehensive summary of polynuclear compounds[34], in which all complexes described previously as containing a single μ-imino bridge are assigned different structures, the above constitutional formula is highly unlikely. Nevertheless, despite such minor discrepancies, it is obvious that the foundations, both experimental and theoretical, of our present-day knowledge of polynuclear cobalt complexes were laid largely by one man—Alfred Werner.

ACKNOWLEDGMENTS

The author is indebted to Dr. William P. Schaefer for assistance in the preparation of this paper. He also wishes to acknowledge the assistance of the John Simon Guggenheim Memorial Foundation for a Guggenheim Fellowship, the California State University, Fresno for a sabbatical leave, and the California State University, Fresno, Research Committee.

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