Elementary Coordination Chemistry

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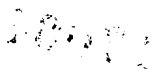

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CHAPTER

1

Introduction

SCOPE

One of the most surprising aspects of coordination compounds is the very unobtrusive manner in which they occur in numerous systems of chemical and biological importance. The name "complex compounds" suggests esoteric knowledge of a rather impractical sort to most ears, yet these materials are the key to the very breath of every human being. They are also an integral part of the complicated system of reactions by which plants remove carbon dioxide from the atmosphere for use in their growth processes. It is in their multifarious uses that we find our interests most directly affected.

An understanding of the chemical principles underlying the behavior of these compounds requires all of the theoretical chemistry that we can muster. In describing these systems we shall find it necessary to use many disciplines foreign to the field of inorganic chemistry proper. In many respects the field of coordination chemistry constitutes an area roughly analogous to that of organic chemistry, but with more of its fundamental problems unsolved. Inorganic stereochemistry, much of which is concerned with coordination compounds, is a field of considerably greater diversity than organic stereochemistry as central atoms with as many as eight or ten atoms bonded to them are encountered. All in all, we shall find the field to be one which is characterized by a bewildering, and at times chaotic, variety. This variety we hope ultimately to fit together into a coherent and meaningful pattern; only parts of this pattern are apparent at the present time.

Under the heading of "coordination compound" or "complex compound" (which terms are frequently but not always used interchangeably) will be includ-

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ed all those combinations of two or more atoms, ions or molecules which arise as the result of the formation of a bond by the sharing of a pair of electrons *originally associated with only one of the components* and which further possess some identifiable physical or chemical characteristics of a distinct species. Thus these will be systems where one of the constituents is a Lewis acid and the other(s) will act as Lewis bases. The Lewis bases will commonly be referred to as *ligands*. We will also consider a number of substances which do not fit neatly into this category. For the most part we will center our attention on those combinations of a central metallic cation (Lewis acid) with one or more molecules of a Lewis base or different Lewis bases in which the resultant species has physical and chemical properties quite different from those of its constituents. Within this rather hazy framework will be found species with a rather wide range of stabilities. Some possess such a transitory existence that they are barely detectable by the most subtle and sensitive methods of probing matter. Others are found which are among the most stable molecules known, capable of being sublimed at 800° C![1]

One might reasonably ask why this group of compounds should be singled out for special study. There are several kinds of answers to such a question but some of a rather practical nature are:

1. These compounds are formed by so many elements that any comprehensive chemical study must include them and any comprehensive chemical theory must explain their existence and behavior.

2. Their applications are more numerous than might be expected and new applications are being discovered each year.

3. Many chemical phenomena are exhibited to a superlative degree by these compounds (e.g., molecular rotation of polarized light and catalysis of oxygen transfer).

4. They are of vital importance in biological systems. Living matter utilizes both very stable complexes and rather unstable ones as catalysts for chemical processes.

DEVELOPMENTS PRIOR TO THE WORK OF ALFRED WERNER. It is very difficult to determine the date of the preparation of the first coordination compound. There are two reasons for this. First, some coordination compounds are found in nature and second, some practical processes known from antiquity make use of complexes, though usually poorly defined ones (a few dyes are an exception). The chemistry of complexes may be said to have originated in 1704 with the discovery of Prussian blue by Diesbach, a color maker. He told the details of his discovery to the chemist Dippel who investigated the preparation and published his results.[2] This material was prepared by heating equal parts

[1] Copper phthalocyanine: E. A. Lawton, *J. Phys. Chem.* **62**, 384 (1958).

[2] See R. Abegg, editor, *Handbuch der Anorganischen Chemie*, IV, 3, 2, Teil B, 465–469, S. Hirzel, Leipzig (1935).

of cream of tartar and saltpeter with oxblood (or animal flesh). The product was then dissolved in water, treated with green vitriol and alum, and finally hydrochloric acid to obtain the desired blue pigment. This material, called Prussian blue, has a structure which has only recently been elucidated. It is more conveniently prepared by the addition of ferric salts to solutions of soluble ferrocyanides.

After this, one may cite the investigation of the products of oxidation of ammoniacal cobalt solutions by Tassaert.[3] In the years that followed, a large amount of effort was expended on studies of the complexes of chromium, cobalt, nickel, iron, and the platinum metals. Much of this older work is reviewed in the standard works on inorganic chemistry such as the major writings of Gmelin, Dammer, and Abegg, and the texts of Pascal, Mellor, and Friend. It is generally considered that the first reliable work on the composition of the cobalt(III) ammines was begun by F. A. Genth at Marburg about 1847.[4] Following this a number of workers began a systematic study of the compositions and reactions of complexes. Names such as Cleve, Woolcott Gibbs, Blomstrand, Marignac, and Fremy are today almost forgotten; yet their work and the work of their lesser known contemporaries served as a foundation for all later theories and experiments in this field.

By 1870 a great deal of information on these complexes had been gathered and it is from this date that the work of Sophus Mads Jorgensen[5] assumes importance. Jorgensen, a professor at Copenhagen, methodized much of this field by the preparation and careful characterization of a great number of complex compounds. In this way he was able to establish the existence of several instances of isomerism, even though his explanation of the nature of the isomerism was erroneous.

As a result of the increase in activity, a great mass of experimental information of high accuracy had accumulated by 1890. However, there was no really satisfactory theoretical framework into which the information could be fitted nor was there any indication that a general system could be developed from the structural ideas then current in the field. By and large, the purely empirical viewpoint prevailed among the chief investigators of these compounds. This was soon to suffer a drastic change during the years in which the impact of Alfred Werner's ideas and experimental prowess dominated this field of study.

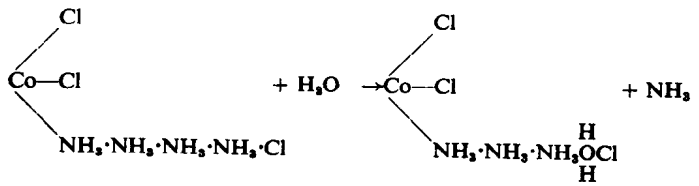
THE WORK OF ALFRED WERNER. At the beginning of Alfred Werner's work in this field, Jorgensen was its acknowledged master. Werner himself did not hesitate to concede his indebtedness to Jorgensen's careful experimental results. In 1890 the enormous mass of experimental data which had accumu-

[3] Tassaert, *Annales de Chimie*, (1) **28**, 106–107 (1799).

[4] Published as a preliminary notice in 1851. The work was completed by Genth in collaboration with Woolcott Gibbs and is reprinted in the *American Journal of Science*, (2) **23**, 234, 319 (1857); **24**, 86 (1857).

[5] G. B. Kaufman, *J. Chem. Educ.* **36**, 521 (1959); *Chymia* **6**, 180 (1960).

lated appeared to be completely chaotic to most chemists. The principal theory available for its interpretation was that of Blomstrand. This theory, which was accepted and extended by Jorgensen, considered that long chains of NH_3 groups were present in the ammines (ammonia complexes). Typical structural formulae may be seen in those presented by Jorgensen[6] for what are now named dichlorotetramminecobalt(III) chloride and the product of its reaction with water, dichloroaquotriamminecobalt(III) chloride:



The chief objection to this theory was the fact that an able exponent of it could *explain* the occurrence of certain kinds of isomerism in complexes but could not successfully *predict* such behavior.

This whole field was then changed practically overnight by the genius of Alfred Werner. The anecdotes that relate how this occurred are of some interest. Werner had been concerned with a number of aspects of valence theory and had presented some of these in outline in his article "Beitrage zur Theorie der Affinitat."[7] As his interest turned away from the problems of organic stereochemistry and toward those of inorganic stereochemistry he began to develop the germ of structural theory for coordination compounds. N. Bjerrum[8] has related the following account of the manner in which this theory assumed its final form. At this time (1892) Werner was an assistant professor and a professorship was soon to be open at Zurich when Hantzsch was called to Leipzig. Werner (whose account was repeated by Bjerrum) was told by Hantzsch that he could be promoted to succeed Hantzsch if his ideas on complexes became more widely known. Hantzsch was convinced of their great importance and told Werner to write a paper in which this was made evident, especially those parts of it dealing with sixfold coordinate compounds. Werner then went into a room with a box of cigars, paper, and pen and did not leave the room until the box of cigars was gone and the paper was written. The paper was published the following year.[9] A somewhat different version is given by both Pfeiffer[10] and Berl.[11] According to both, Werner had been thinking about this problem for some time and, one morning at two he awoke with its entire

[6] S. M. Jorgensen, *Zeit. anorg. Chem.* **11**, 448 (1885); **14**, 417 (1897).

[7] A. Werner, *Vierteljahresschrift der Zuricher Naturforschungs Gesellschaft* **36**, 1 (1891).

[8] N. Bjerrum, *Proceedings of the Symposium on Coordination Compounds*, Danish Chemical Society, Copenhagen (1954), pp. 14–15.

[9] A. Werner, *Zeit. anorg. Chem.* **3**, 267–330 (1893).

[10] P. Pfeiffer, *J. Chem. Educ.* **5**, 1090–1098 (1928); *Ber.* **53A**, 9–11 (1920).

[11] E. Berl, *J. Chem. Educ.* **19**, 153 (1942).

solution in his mind. He then got up and wrote until five to complete his theory. As a result he was promoted to a full professorship in 1893.[12] Regardless of the exact manner in which the ideas assumed their final form, subsequent events in this field have substantiated the validity of the theory which was developed and Werner himself spent the next twenty years of his life working toward this end.

In outline, Werner showed that a systematic structural chemistry of coordination compounds could be built up from the following assumptions: first, that the valencies of a metal atom may fall into primary and secondary types and second, that a constant number of directly attached atoms or groups must be arranged in a definite, fixed geometrical pattern about a central metal atom.

Werner proposed that a metallic ion, such as Co^{+3}, has two kinds of valencies which we may call principal (ionic) and auxiliary (coordinate) valencies. In the immediate neighborhood of the central ion there will be a number (usually but not invariably a fixed number) of groups which are bonded directly to the central atom and retained with greater or lesser tenacity by it. In addition to these coordinated groups (in the "inner sphere") there are present ions of charge opposite to that of the complex ion which are required to form an electrically neutral solid. Since anions as well as neutral molecules are commonly found in the coordination sphere the actual number and charge type of these other lattice ions (in the "outer sphere") will be determined by the requirement of electrical neutrality. When such a species is dissolved in water, the groups (anions or neutral molecules) in the inner or coordination sphere will tend to remain bonded to the central atom while the remaining species required to build up the neutral lattice (spoken of as the species in the outer sphere) will behave as independent particles in solution (e.g., they will conduct an electrical current, affect the colligative properties, etc.). Furthermore, the arrangement of the coordinated groups about the central ion is restricted to a relatively small number of rather highly symmetrical patterns. Thus, six groups will be arranged octahedrally about the central ion in complex species such as $Co(NH_3)_6^{+3}$, $Ir(NH_3)_6^{+3}$, $Cr(NCS)_6^{-3}$, $PtCl_6^{-4}$, $Rh(CN)_6^{-3}$, FeF_6^{-3}, and literally thousands of other complexes of the same coordination type.

When a coordinating molecule such as ethylenediamine ($H_2NCH_2CH_2NH_2$ abbreviated as "en") is present in an ion such as $Co(en)_3^{+3}$ the coordinated nitrogen atoms are again arranged at the apices of an octahedron. Such molecules, which contain two or more coordinating groups, are now called *chelating agents* or *chelons*. They usually, but not invariably, give rise to complexes with the same stereochemical disposition of ligand atoms as is found for complexes of the same central ion with simpler ligands such as NH_3 or CN^-. When four groups are found coordinated to a given central atom, two of the many possible arrangements are found to be used almost exclusively. These are the square planar arrangement of ligands such as is found in the com-

[12] According to Pfeiffer he succeeded Viktor Merz. Hantzsch left Zurich in 1893 to go to Wurzburg as Emil Fischer's successor.

plexes of Pd(II), Cu(II), Pt(II), and many other transition metal ions and the tetrahedral arrangement, examples of which may be seen in the complexes of Zn(II), Be(II), B(III), and many other nontransition metal ions as well as a few transition metal ions. These types are illustrated in Figure 1.

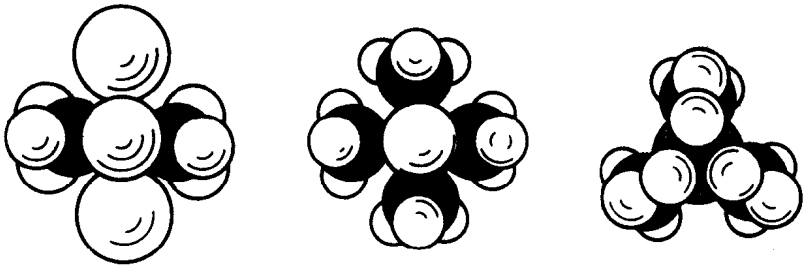


Fig. 1 Structures of *trans*-dichlorodiammineplatinum(II), the tetramminecopper(II) ion, and the tetramminezinc(II) ion.

The opposition to Werner's theory was initially very extensive; it was accepted by Jorgensen only years later. The consequences of these ideas were far-reaching and implied that certain definite types of behavior would be observed in compounds of previously unknown types. Practically all of the stereochemical implications of Werner's ideas have been proven in detail. His treatment of isomerism in coordination compounds is still the basis for this subject, though our present knowledge of the intimate details of structure naturally extends beyond the meager information available to him.

From the publication of this theory in 1893 until the continued onslaughts of arteriosclerosis caused his mind to be deranged (i.e., for over twenty years), Werner worked out its numerous consequences in a series of brilliant experimental studies. Among the consequences, by far the most impressive are those dealing with the optical isomerism of coordination compounds. As a result of the octahedral structure of complexes such as $Cr(en)_3^{+3}$, $[Co(en)_2(NO_2)_2]^+$, and $[Co(en)_2(NH_3)(Cl)]^{+2}$, they are not superposable upon their mirror images. When a compound is superposable upon its mirror image every atom can be brought into the same relative position in both structures. When such superposability of a compound and its mirror image is not possible the result is enantiomorphs or optical isomers of the sort familiar from organic chemistry, e.g., *d*- and *l*-tartaric acid. Werner's resolution of $[Co(en)_2(NH_3)(Cl)]^{+2}$ via its +-bromcamphor-π-sulfonate in 1911 was the first such successful attempt (the experimental work was done by V. King). It was followed by numerous other resolutions and a full realization that here indeed was a powerful argument for the essential validity of Werner's theoretical postulates.

Many other aspects of Werner's work will be considered later; they are an

inextricable and important part of every phase of coordination chemistry. In all, Werner published over two hundred papers and supervised over one hundred and fifty doctoral theses. Many of these contain important experimental evidence bearing on the extension of the coordination theory to an unbelievably wide range of topics. It is odd that no full scale biography of this man exists, though there are a few sketches of his life and work.[13]

DEVELOPMENTS SINCE THE INITIAL WORK OF ALFRED WERNER. Following the publication of Werner's theory the study of coordination compounds took a new and more resolute direction. It attracted numerous adherents throughout the world. A number of alternative theories appeared, but none of them has stood the test of time. The work of later investigators has refined our knowledge of the structure of complexes without destroying the grand design due to Werner.

Werner was fortunate in having a number of able contemporaries who accepted his structural ideas and used them as a guide in the detailed development of various parts of this field. These include P. Pfeiffer, L. A. Tschugaev, and H. Ley, who developed the field of inner complex salts and chelates. In 1905 Tschugaev discovered the reaction of nickel(II) and dimethylglyoxime so commonly used in analytical work and Ley gave the correct interpretation of the reaction of copper(II) and glycine in this same year (this was independently proposed by G. Bruni). The work of G. Bodlander, N. Bjerrum, and others on the stability constants of complexes began shortly after 1893 and gained new momentum from the work of J. Bjerrum, I. Leden, and G. Schwarzenbach in the late 1930's and early 1940's. The stereochemical aspects of coordination theory were extended especially by F. M. Jaeger and F. G. Mann during the 1920's and early 1930's, while the systematic exploitation of the coordination chemistry of the platinum metals was carried out by a large group of Russian chemists of whom the most prominent are I. I. Tscherniaev and A. A. Grinberg. Early work on the catalytic properties of complexes may be seen in the work of Y. Shibata and K. Shibata while the related problems involving biochemically interesting coordination compounds were attacked by F. Haurowitz, O. Warburg, F. J. W. Roughton, and others. Studies of the stabilization of unusual oxidation states were carried out by P. Ray while numerous applications of coordination compounds in analytical chemistry and the theoretical principles underlying their mode of action were examined by F. Feigl, W. Prodinger, J. Yoe, and many others. The preparative aspects of the field were not neglected either, as may be seen in the example of the work of Delepine (especially on iridium complexes) and Dubsky (polynuclear complexes).

[13] Pfeiffer, loc. cit.; Berl, loc. cit.; G. T. Morgan, *J. Chem. Soc.* **117**, 1639 (1920); P. Pfeiffer, *Angew. Chem.* **33**, 37 (1920); J. Lifschitz, *Zeit. Elektrochem.* **26**, 514 (1920); P. Karrer, *Helv. Chim. Acta* **3**, 196 (1920); idem, C. Matschoss *Manner der Technik* (1925), p. 290; idem, *Schweizerische Chemikerzeitung*, p. 73 (1920); W. Klemm, *Zeit. anorg. Chem.* **248**, 314 (1941).

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