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COORDINATION COMPOUNDS

DEAN F. MARTIN

University of Illinois

BARBARA B. MARTIN

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1

THE WORLD OF COORDINATION COMPOUNDS

1-1 AN INTRODUCTION TO A NEW AND AN OLD WORLD

The world of coordination compounds is a familiar, an unfamiliar, a new and an old world. Though this statement is seemingly paradoxical, it is nonetheless true. Coordination compounds are so ubiquitous that we cannot avoid encountering them; they are familiar to us, yet they remain unfamiliar because we ignore them or take them for granted. These compounds represent a world that is old in terms of its uses, new in terms of our understanding of it. The world of coordination compounds is a strange one, often resembling something out of a science-fiction novel.

Imagine a world of inhabitants so highly gregarious that they are unable to exist as individuals, so highly regimented that they exist in select groups of two, four, and six individuals surrounding a leader in highly symmetrical arrangements. Imagine a world of drab individuals and colorful crowds. In joining the crowd, the individuals lose their identities, are influenced by, and in turn influence, the leader. Some groups of inhabitants are without a leader, but their standards are strict and their requirements quix-

otic; often they reject a leader solely on the basis of size or shape. The groups because of their association have special powers. They can capture a sunbeam, hold, and use it. They serve as blacksmiths and can forge vast chains. They can influence the course of other combinations and are useful for this power.

This analogy, while seemingly fantastic, does have a basis in fact. The leader is a metal ion and the individuals are molecules or ions which are arranged about the metal ion. Intensely colored dyes and pigments often result from the combination of relatively, colorless metal ions and molecules. It is often found that certain molecules will arrange themselves about only those metal ions that meet highly specific requirements of size or charge. Such molecules are of great interest in analytical chemistry because of their great specificity. By virtue of their nature, coordination compounds have special properties. Chlorophylls, which are found in green plants, are able to use solar energy to convert carbon dioxide and water to starch and oxygen. Hemoglobin in blood is able to store, transfer, and later release oxygen. Other coordination compounds play important roles in biological processes, prevent the deterioration of rubber and other products, and serve to control the course of chemical reactions.

While coordination compounds are of great practical interest, they are also of theoretical interest. They represent a fundamental pattern of chemical combination which is common to all the materials mentioned previously and which is consistent with modern theory.

As a first step in understanding coordination compounds, we need to define some terms. In the broadest sense, a *coordination entity* may be defined* as a molecule or ion in which there is a metal atom or ion to which are closely attached other atoms (A) or

* This definition is based upon one suggested by the Commission on the Nomenclature of Inorganic Chemistry, International Union of Pure and Applied Chemistry.¹ (Superior numbers indicate References at the end of the chapter.)

groups (B). The metal atom is called the *central atom*, or *center of coordination*. The atoms directly attached to the central atom are called *coordinating atoms*, or *donor atoms*. Atoms (A) and groups (B) are referred to as *ligands*.

Thus, there are several features of a coordination entity. One is the metal ion (or occasionally atom), and, of course, the nature of the metal, its size, and the magnitude of its charge are important. A second feature is the ligand, which may be an atom, an ion (anion or, less commonly, a cation, e.g., H_2NNH_3^+), or a molecule. The third feature is the *coordination number*, i.e., the number of atoms attached to the central metal. Of course the geometry of the arrangement of the ligands is particularly important (see Chap. 3). Finally, the metal and the ligands surrounding it comprise the *coordination sphere*, which is conventionally represented by the bracket-enclosed symbols.

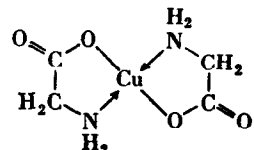
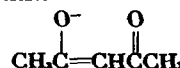
Many of the properties of coordination compounds are due to the ligand: the nature and the number of donor atoms and the charge on the ligand. The common donor atoms are nitrogen, oxygen, and sulfur. The ligand may contain one donor atom and be *unidentate*,* or the ligand may have two donor atoms and be *bidentate*. When the ligand contains two or more donor atoms, it is *multidentate* and is said to be a *chelate*.† The metal derivative is properly called a *metal-chelate compound*. When we look at Table 1-1, we see that the most obvious feature of the metal-chelate structure is the formation of a ring, usually of five or six members. Finally, the charge on the ligand is important because it determines many properties of the compound. If the sum of the negative charges of the ligands is equal to the charge on the metal

* One point of attachment; literally the group has "one tooth" (from *uni* plus *dens*).

† The adjective "chelate" was suggested by G. T. Morgan and H. D. K. Drew [*J. Chem. Soc.*, 117, 1456 (1920)] because of a fancied resemblance to the claw of a crab. The adjective was once limited to bidentate ligands, but is now universally applied to any multidentate ligand.

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Table 1-1 EXAMPLES OF TERMS USEFUL IN UNDERSTANDING COORDINATION CHEMISTRY

<i>Types of Coordination Compounds</i>			
<i>Complex ion</i>	<i>vs.</i>	<i>Metal-chelate compound*</i>	
$\left[\begin{array}{c} \text{NH}_3 \\ \downarrow \\ \text{H}_3\text{N} \rightarrow \text{Cu} \leftarrow \text{NH}_3 \\ \uparrow \\ \text{NH}_3 \end{array} \right]^{++}$			
Tetraamminecopper(II) ion		Bis(glycinato)copper(II)	
<i>Types of Ligands</i>			
<i>Unidentate</i>	<i>vs.</i>	<i>Chelate</i>	
$\text{NH}_3, \text{H}_2\text{O}, \text{CN}^-, \text{Cl}^-$	Bidentate		
	Terdentate	$\text{HN}(\text{CH}_2\text{COO}^-)_2$	
	Quadridentate	$\text{N}(\text{CH}_2\text{COO}^-)_4$	
<i>Typical Ligands</i>			
Nitrogen donors: NH_3	Amines: RNH_2	(primary)	
	R_2NH	(secondary)	
	R_3N	(tertiary)	
Oxygen donors: $\text{OH}^-, \text{H}_2\text{O}, \text{RCOO}^-, \text{ROH}, \text{R}_2\text{CO}, \text{RCHO}$			
Donors related to nitrogen and oxygen:	R_3As	R_3P	R_2S
	arsines	phosphines	thioethers
Halide ions: $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$			
π-bonding ligands†:	CN^-	NCS^-	CO

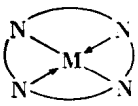

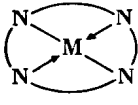
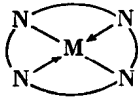
* Arrow indicates coordinate covalent bond.

† See page 70.

ion, the compound is a nonelectrolyte; otherwise it is an electrolyte.

The advantage, and the disadvantage, of the preceding definition of a coordination compound is that it is all-encompassing and includes any metal ion in water because the ion is surrounded by water molecules. It also includes many types of compounds

Table 1-2 FAMILIAR SUBSTANCES THAT ARE ACTUALLY COORDINATION COMPOUNDS

<i>Example</i>	<i>Representation</i>
Human blood (heme)	 $M = \text{Fe}^{\text{II}}$
Vitamin B ₁₂	 $M = \text{Co}^{\text{III}}$
Invertebrate animal blood (hemocyanin)	 $M = \text{Cu}^{\text{I}}$
Chlorophyll	 $M = \text{Mg}^{\text{II}}$
Silicates	CaSiO_4 or $\text{Ca}[\text{SiO}_4]$
Hydrates	$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$
Hydroxides	$\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ or $[\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]$
Ammoniates	$\text{CuSO}_4 \cdot 4\text{NH}_3$ or $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
Double salts	$\text{Fe}(\text{CN})_2 \cdot 4\text{NaCN}$ or $\text{Na}_4[\text{Fe}(\text{CN})_6]$

* The structures that are represented are related to the metal phthalocyanines (Fig. 1-3). All have the same essential feature, that is, they are metal derivatives of a quadridentate ligand having four donor nitrogen atoms that are joined in a ring.

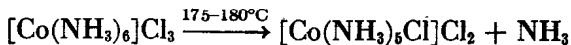
such as hydrates, ammoniates, double salts, and double oxides, that are most conveniently regarded as examples of coordination compounds. Finally, it includes, of course, such diverse representatives of the animal, vegetable, and mineral kingdoms as blood, chlorophyll, and silicates, respectively (see Table 1-2). On the other hand, the definition says nothing about stability. For example, $\text{NaCl} \cdot 2\text{NH}_3$ exists only in contact with liquid ammonia or at low temperatures. In contrast, $\text{K}_3\text{Fe}(\text{CN})_6$ is so stable that it does not give the usual reaction for ferric or cyanide ion, because too few of these ions are present.

1-2 FACTORS THAT INFLUENCE THE FORMATION OF COORDINATION COMPOUNDS

Now that we know what coordination compounds are, the next question that comes to mind is "Why do they form?" This is a question that has yet to be answered satisfactorily, because it is not an easy matter to understand the behavior of coordination entities. There are many simple rules and generalizations, but few work successfully in all cases. We can at least consider some of the factors involved. These include environmental factors such as temperature and pressure, and more important factors such as the nature of the metal ion and the nature of the ligand. The importance of each of these factors can be summarized as follows.

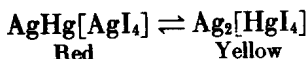
Environmental Factors: Temperature and Pressure

The effect of heat can be twofold. Volatile ligands may be lost at higher temperatures. This is exemplified by the loss of water by hydrates and by the loss of ammonia by $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ on heating, though this complex ion is inert* in strongly acid solution:



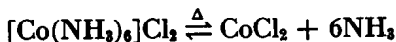
* Rigorously, it is necessary to make a distinction between "stability-instability" and "inertness-lability." Stability and instability are equilibrium

A second effect of temperature is the transformation of certain coordination compounds from one form to another. For example, Ag_2HgI_4 is reversibly transformed at 45°C from a red to a yellow form:



At this temperature, a shifting of ions occurs and two different structures are involved: one in which mercury is the central metal, and one in which the iodide ions surround a silver(I) ion.

The effect of pressure is ordinarily one of concentration. Since the formation of coordination compounds involves chemical equilibria, it is apparent that altering the pressure of volatile ligands is merely an application of the Le Chatelier principle. For example, solid $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ loses ammonia upon heating but can be reformed by treatment of anhydrous cobalt(II) chloride with ammonia vapor.³



The Metal

Several characteristics of the metal should be considered. These include intrinsic size and charge, electronic arrangement, and the size of the metal relative to that of the ligand. Some generalizations that have been observed follow.

Size and Charge. For a given ligand, the strength of the metal-ligand bond should depend upon the size of the ion and the magnitude of the ionic charge, and should be the greatest for small ions of high charge. These requirements are met by transition-metal ions, but not exclusively so. Beryllium(II) ion, which has a high charge-to-radius ratio, forms stable coordination compounds, especially when oxygen donor atoms are present. How-

ever, thermodynamic properties, whereas lability is a kinetic property. A labile complex is one that is very reactive and undergoes complete reaction within one minute at room temperature; an inert or robust complex is one that reacts at a rate too slow to measure or at a measurable rate.

ever, alkali metal ions also form metal-chelate compounds, though the stability of such compounds is not great.

In many ways, this simple picture is useful and satisfying, but it is also too simple because it is apparent that other factors are involved. For example, cadmium and calcium ions have the same charge-to-radius ratio, but the compounds of the former ion are far more stable. The ability of cobalt(II) and zinc(II) ions to form coordination compounds is not even approximately equal though both have a charge-to-radius ratio of 2.4. Other factors are involved, as will become evident later.

Electronic Configuration and Effective Atomic Number. The tendency of an atom to attain the electronic configuration of the nearest inert gas is well known. This end is achieved by transfer of one to three electrons (electrovalent bond) or by sharing (covalent bond). The latter is also observed for coordination compounds. An atom or ion may accept a share in a sufficient number of electrons, supplied by donor atoms, to have the electronic configuration or the *effective atomic number* (E.A.N.) of the next inert gas. The E.A.N. is equal to the number of electrons in the metal ion plus the number of electrons gained by coordination. For example, Co^{3+} in the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ has 24 electrons and effectively gains 12 electrons (two each from the six ammonia molecules). Thus, the E.A.N. of Co in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is 36, the atomic number of the next inert gas, krypton.

The E.A.N. concept has been useful for rationalizing observed coordination numbers. The concept has been particularly successful with metal carbonyls.³ Instability is suggested when the E.A.N. is one or two units greater or less than the atomic number of the next inert gas. Thus, the E.A.N. of cobalt in $[\text{Co}(\text{CN})_6]^{4-}$ is 37 and this complex ion is readily oxidized to $[\text{Co}(\text{CN})_6]^{3-}$ for which the E.A.N. is 36. A flaw in the concept is indicated by the observation that $[\text{Fe}(\text{CN})_6]^{4-}$ (E.A.N. of Fe = 36) is slowly oxidized by air to $[\text{Fe}(\text{CN})_6]^{3-}$ (E.A.N. of Fe = 35). There are a number of other exceptions to the E.A.N. generalization.³

Size of the Metal, Size of the Ligand, the Radius Ratio.

We should expect to find that the relative sizes of the ligand and metal ion are important in determining the number of ligands that can be accommodated around the metal ion. If the ligand is exceptionally large or if the metal ion is exceptionally small, fewer ligands can be arranged about the metal than would be possible with optimum sizes (Fig. 1-1). In other words, there are several limiting radius ratios (radius of central atom to radius of ligand) which determine the coordination number of the metal ion. These are summarized in Table 1-3. Generally, the agreement between

Table 1-3 RADIUS RATIO AND COORDINATION NUMBER

Formula	Radius ratio = $\frac{\text{radius M}}{\text{radius A}}$	Coordination number	Arrangement*
MA ₂	0-0.15	2	Collinear
MA ₃	0.15-0.22	3	Triangular plane
MA ₄	0.41-0.59	4	Planar
MA ₄	0.22-0.41	4	Tetrahedral
MA ₆	0.41-0.59	6	Octahedral

* Cf. page 46.

observed and predicted coordination number is very good for oxygen coordination.

The Ligand

In theory, a ligand is any ion or molecule which has some atom capable of electron donation, usually of a so-called lone pair of electrons. In practice, the number of donor atoms is quite limited, and the coordination tendencies of ligands vary from nil to great. In discussing the donor atoms we need to keep in mind several factors, including the nature of the donor atom, the group of which

it is a part (i.e., unidentate vs. multidentate), and the steric requirements of the metal vs. those of the ligand.

The Donor Atom. A number of typical ligands are listed in Table 1-1. A comparatively few elements serve as donor atoms; many do not because of unfavorable size or electronic effects. Many elements which might function as donor atoms have not

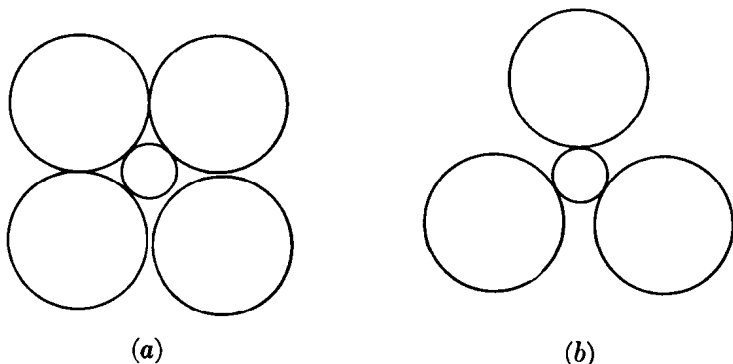


FIGURE 1-1 The radius ratio concept showing an unfavorable situation (a) (large ligand, small ion) in which the maximum coordination number is not attained because of ligand-ligand interaction. The favorable situation (b) (large ligand, small ion) results when ligand-ligand interaction is reduced because of fewer ligands.

been fully investigated. Some, such as sulfur, arsenic, and selenium, form compounds which are sufficiently obnoxious, toxic, or difficult to prepare to discourage most chemists.

The relationship between the donor and acceptor atoms has been summarized elsewhere,² but it may be noted that a number of metals show definite preference for a given donor atom. Also, some metals show definite preference for certain members of a set of related ligands. For example, the fluoride complexes of

aluminum(III) are the most stable and the best characterized of the aluminum-halogen complexes, but the halide complexes of the related thallium(III) ion are limited to those of chlorine, bromine, and iodine.²

The unsaturated ligands listed in Table 1-1 are especially interesting. Some of the compounds involving double-bonded ligands, e.g., Zeise's salt, $K[PtCl_3C_2H_4]$, have been known since the beginning of the nineteenth century. However, the nature of the bonding has become clarified only within recent years.

Unidentate vs. Multidentate. The formation of rings by chelate or multidentate ligands when combined with a metal ion results in greatly enhanced stability. Although it is not practicable to list here all of the chelates that are known, many types have been listed by Diehl.⁴ We can think of chelates as being made up of unidentate ligands. For example, methylamine, CH_3NH_2 , is just about one-half of the chelate ethylenediamine, $H_2NCH_2CH_2NH_2$. Also, the anion of an amino acid, $RCH(NH_2)COO^-$, is a stronger coordinating agent than its "components," a primary amine, RNH_2 , and the anion of carboxylic acid, $RCOO^-$. The picture of chelating agents as being composed of unidentate ligands is not always correct. For example, acetone, $(CH_3)_2C=O:$, does not form stable complex ions, nor does the chelate

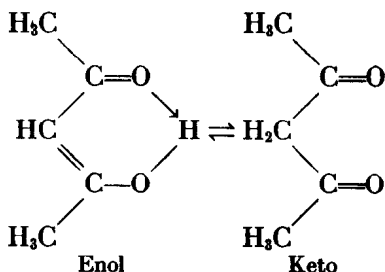


but an alternative combination, acetylacetonate ion,

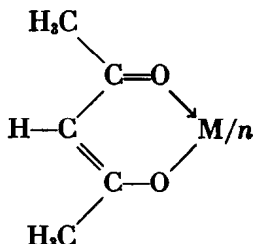


does form stable metal derivatives.

Acetylacetone is an interesting compound which exists in two forms, called the enol and the keto:



The enol form can lose a proton, react with a metal ion, and thus form a metal-chelate compound, which we represent as



The physical properties of these compounds are often those of organic materials rather than metal salts, as indicated by the

Table 1-4 PHYSICAL PROPERTIES OF TRIS(2,4-PENTANEDIONO)CHROMIUM(III)*,†

	Temp., °C	Other properties
Melting point	216	Red-violet, crystalline
Boiling point	ca. 340	Very soluble in benzene
Partial sublimation as low as	100	Insoluble in water

* W. C. Fernelius and J. E. Blanch, *Inorganic Syntheses*, 5, 130 (1957).

† W. C. Fernelius and B. E. Bryant, *Inorganic Syntheses*, 5, 105-113 (1957).

properties of chromium acetylacetonate ($M = Cr; n = 3$) listed in Table 1-4. The stability of this compound is illustrated by the fact that it can be distilled at such a high temperature.

Steric Requirements of the Ligand. Very often the steric requirements of the ligand are not compatible with the normal

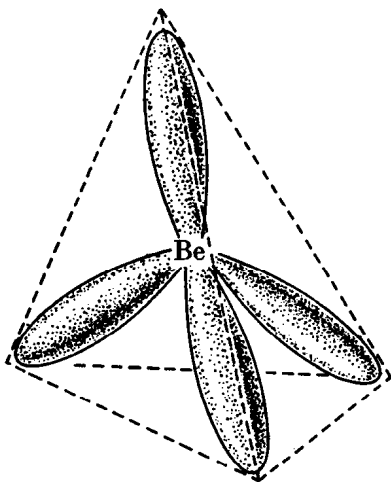


FIGURE 1-2 Beryllium in preferred tetrahedral configuration.

configuration of the metal. A coordination compound may be formed, but not willingly, as it were. The situation is known as a *forced configuration*, and it represents a Procrustean bed of chemistry.

The outstanding examples of this are the metal derivatives of phthalocyanine, which is a planar, quadridentate ligand. The bonds between the metal and this ligand should lie in a plane, but metals such as beryllium which normally have bonds directed at the corners of a tetrahedron (Fig. 1-2) do form complexes with phthalocyanine (Fig. 1-3).

The preceding example might suggest that the spatial arrange-

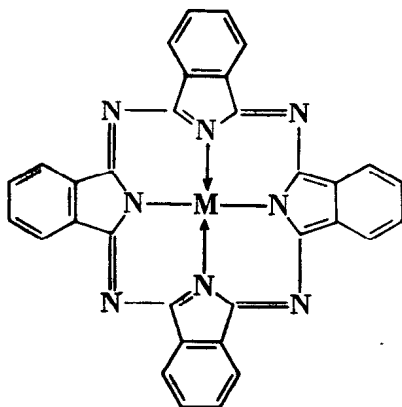


FIGURE 1-3 Metal phthalocyanine complex.

ment of the metal bonds simply changes to conform to the ligand requirements, but this is not accurate. A sounder view is that the bonds are distorted from the normal, optimum situation as a result of stress. If the strain imposed by the requirements of the ligand is too severe, either distortion will occur or a forced configuration will not exist. Platinum(II) and palladium(II) complexes are normally planar. The platinum(II) and palladium(II) derivatives of β, β', β'' -triaminotriethylamine (abbreviated "tren"), $N(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, should have a tetrahedral arrangement of bonds (Fig. 1-4), if all four nitrogen atoms are attached to the same metal atom. It is now generally concluded that in these compounds forced configuration does not exist. Rather, one coordination position is occupied by a water molecule or an atom belonging to another ligand.*

* An alternate arrangement has been observed for $[\text{Ni}(\text{tren})](\text{NCS})_2$. The ligand occupies four positions of a regular octahedron with two anions in the remaining positions. [D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 346 (1958).]