

# 20

## Coordination Chemistry

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- Key Concepts**
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  - 20-2** Nomenclature for coordination compounds. Monodentate ligands and bidentate ligands. Chelating agents and chelates. Structural isomers and geometrical isomers. Optical isomers or enantiomers. Asymmetric or chiral centers.
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*The first attempt at generalization seldom  
succeeds; speculation anticipates experience,  
for the results of observation accumulate  
but slowly.*

**J. J. Berzelius (1830)**

**M**any compounds of platinum, cobalt, and other transition metals have strange empirical formulas and are often brightly colored. These are called **coordination compounds**. Their major distinguishing feature is the presence of two, four, five, six, and sometimes more chemical groups positioned geometrically around the metal ion. These groups can be neutral molecules, cations, or anions. Each coordinating group can be a separate entity, or all the groups can be connected in one long, flexible molecule that wraps itself around the metal. Coordinating groups significantly change the chemical behavior of a metal. The colors of the compounds provide clues about their electronic energy levels.

For instance, every plant depends on the green magnesium coordination complex known as chlorophyll. The combination of magnesium and its coordinating groups in chlorophyll has electronic properties that the free metal or ion does not have, and can absorb visible light and use the energy for chemical synthesis. Every oxygen-breathing organism requires **cytochromes**, coordination compounds of iron that are essential to the breakdown and combustion of foods and the storage of the energy released by the breakdown. Most larger organisms need hemoglobin, another iron complex in which the coordinating groups enable the iron to bind oxygen molecules without being oxidized. Large areas of biochemistry are really applied transition-metal chemistry. In this chapter we shall look at the structures and properties of some coordination compounds.

## 20-1 PROPERTIES OF TRANSITION-METAL COMPLEXES

The transition metals are often encountered in highly colored compounds with complex formulas. Although  $\text{PtCl}_4$  exists as a simple compound, there are other compounds in which  $\text{PtCl}_4$  is combined with two to six  $\text{NH}_3$  molecules or with  $\text{KCl}$  (Table 20-1). Why should such apparently independent, neutral compounds associate with other molecules, and why should they do so in varying proportions? Measurements of electrical conductivity of solutions, and the precipitation of  $\text{Cl}^-$  ions by  $\text{Ag}^+$ , indicate how many ions are present in aqueous solution. This and other evidence lead us to propose the ionic structures listed at the right of the table. These substances that contain ammonia are coordination compounds, in which the  $\text{NH}_3$  molecules are arranged around a central  $\text{Pt}^{4+}$  ion. The  $\text{Pt(IV)}$  complexes are octahedrally coordinated. In contrast, complexes of  $\text{Pt(II)}$  are in a square planar coordination, with a coordination number of 4. Complexes of metals with a coordination number of 4 may also be tetrahedral.

### Color

Color is a distinctive property of coordination compounds of transition metals. The octahedral complexes of cobalt exist in a wide spectrum of colors, which depend on the groups coordinated to it (Table 20-2). Such coordinated groups are called **ligands**. In solution, color arises from the association of solvent molecules with the metal as ligands, and not from the metal cation itself. In concentrated sulfuric acid (a potent dehydrating

**Table 20-1**

**Platinum Complexes, Numbers of Ions Produced, and Complex Structures**

Complex	Molar conductivity ( $\text{ohm}^{-1}$ )	Number of $\text{Cl}^-$ ions precipitated by $\text{Ag}^+$	Total number of ions	Ions produced
$\text{PtCl}_4 \cdot 6\text{NH}_3$	523	4	5	$\text{Pt}(\text{NH}_3)_6^{4+}$ ; $4\text{Cl}^-$
$\text{PtCl}_4 \cdot 5\text{NH}_3$	404	3	4	$\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}$ ; $3\text{Cl}^-$
$\text{PtCl}_4 \cdot 4\text{NH}_3$	229	2	3	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}$ ; $2\text{Cl}^-$
$\text{PtCl}_4 \cdot 3\text{NH}_3$	97	1	2	$\text{Pt}(\text{NH}_3)_3\text{Cl}_3^+$ ; $\text{Cl}^-$
$\text{PtCl}_4 \cdot 2\text{NH}_3$	0	0	0	$\text{Pt}(\text{NH}_3)_2\text{Cl}_4^0$
$\text{PtCl}_4 \cdot \text{NH}_3 \cdot \text{KCl}$	109	0	2	$\text{K}^+$ ; $\text{Pt}(\text{NH}_3)\text{Cl}_5^-$
$\text{PtCl}_4 \cdot 2\text{KCl}$	256	0	3	$2\text{K}^+$ ; $\text{PtCl}_6^{2-}$

Table 20-2

**Octahedral Complexes of Co(III), Their Colors, and Estimates of Electronic Transition Energy**

Complex <sup>a</sup>	Color	Spectral color absorbed	Approximate wavelength (nm)	Approximate transition energy (wave number, cm <sup>-1</sup> )
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	Yellow	Indigo	430	23,200
Co(NH <sub>3</sub> ) <sub>5</sub> NCS <sup>2+</sup>	Orange	Blue	470	21,200
Co(NH <sub>3</sub> ) <sub>5</sub> H <sub>2</sub> O <sup>3+</sup>	Red	Blue-green	500	20,000
<i>cis</i> -Co(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>3+</sup>	Red	Blue-green	500	20,000
Co(NH <sub>3</sub> ) <sub>5</sub> OH <sup>2+</sup>	Pink	Blue-green	500	20,000
Co(NH <sub>3</sub> ) <sub>5</sub> CO <sub>3</sub> <sup>+</sup>	Pink	Blue-green	500	20,000
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	Purple	Green	530	18,900
Co(EDTA) <sup>-</sup>	Violet	Yellow	560	17,800
<i>cis</i> -Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	Violet	Yellow	560	17,800
<i>trans</i> -Co(en) <sub>2</sub> Br(NCS) <sup>+</sup>	Blue	Orange	610	16,400
<i>trans</i> -Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	Green	Red	680	14,700
<i>trans</i> -Co(en) <sub>2</sub> Br <sub>2</sub> <sup>+</sup>	Green	Red	>680	14,700

<sup>a</sup>(en) is an abbreviation for ethylenediamine, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>.

agent) Cu<sup>2+</sup> is colorless; in water it is aquamarine, and in liquid ammonia it is a deep ultramarine. Complexes of metals in high oxidation states have brilliant colors if they absorb energy in the visible spectrum: CrO<sub>4</sub><sup>2-</sup> is bright yellow and MnO<sub>4</sub><sup>-</sup> is an intense purple.

Whenever a certain energy of visible electromagnetic radiation,  $E$ , is absorbed by a compound during the excitation of an electron to a higher quantum state, the wavelength ( $\lambda$ ) of light absorbed can be calculated from the expression

$$E = h\nu = hc\bar{\nu} = hc/\lambda$$

where  $h$  is Planck's constant,  $\nu$  is frequency,  $\bar{\nu}$  is wave number, and  $c$  is the speed of light. If the energy is given in wave numbers, as frequently is done, then the wavelength is simply the reciprocal:  $\lambda = 1/\bar{\nu}$ . The color that we see in the compound is the *complementary* color to the color absorbed; it is the color that remains in the spectrum after the particular spectral color has been removed. These colors are listed in Table 20-3. If the energy absorbed is so small that it corresponds to wavelengths in the infrared, or so large that it occurs in the ultraviolet (which is usually the case in compounds of representative elements), then the compound will be colorless or white. With transition-metal compounds, interesting things happen during ab-



**Table 20-3****Colors of Compounds, Spectral Colors, Wavelengths, and Energies**

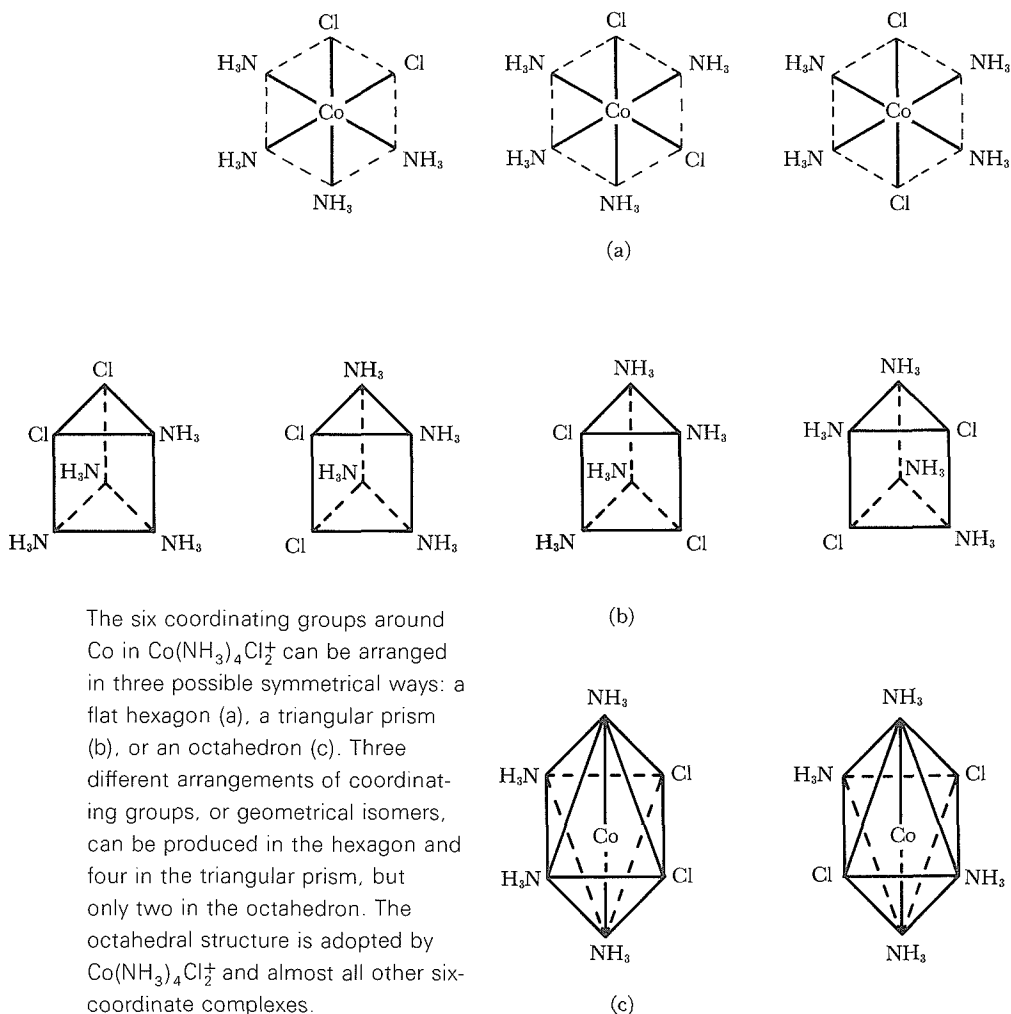
<b>Color of compound</b>	<b>Spectral color absorbed</b>	<b>Approximate wavelength (nm)</b>	<b>Energy difference between electronic levels (wave number, <math>\text{cm}^{-1}</math>)</b>
Colorless	Ultraviolet	< 400	> 25,000
Lemon yellow	Violet	410	24,400
Yellow	Indigo	430	23,200
Orange	Blue	480	20,800
Red	Blue-green	500	20,000
Purple	Green	530	18,900
Violet	Lemon yellow	560	17,900
Indigo	Yellow	580	17,300
Blue	Orange	610	16,400
Blue-green	Red	680	14,700
Green	Purple-red	720	13,900
Colorless	Infrared	> 720	< 13,900

sorption in the visible spectrum region of energy. Often you can learn something about trends in chemical behavior by “eyeball spectroscopy.”

The colors of transition-metal complexes explain the trick of writing with invisible ink made from  $\text{CoCl}_2$ . If you write with a pale-pink solution of  $\text{CoCl}_2$ , the writing is virtually undetectable on paper. If the paper is heated gently over a candle flame, the message appears in a bright blue. Upon cooling, the writing slowly fades. The pink color is that of the octahedral hydrated cobalt ion:  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ . Heating drives away the water and leaves a blue chloride complex with tetrahedral geometry. This compound is **hygroscopic**; that is, it absorbs water from the atmosphere and fades to the pale-pink hydrate again.

### Isomers and Geometry

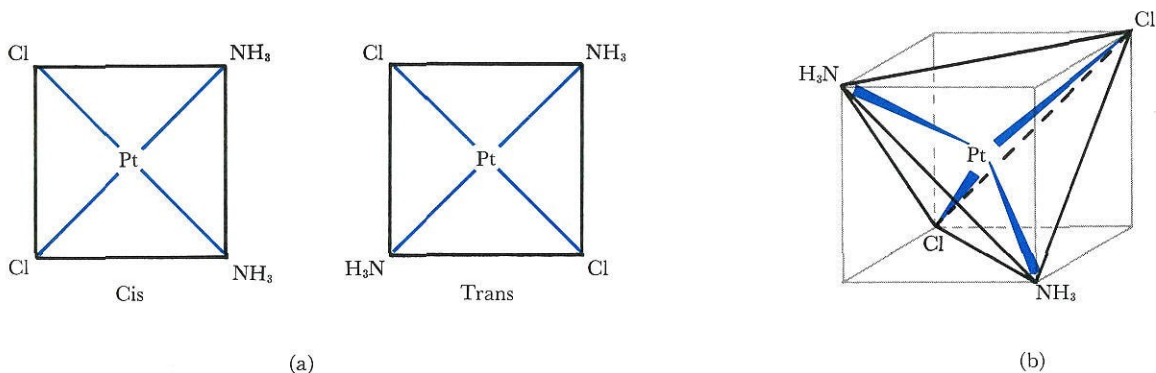
The compound whose empirical formula is  $\text{CoCl}_3 \cdot 4\text{NH}_3$  can be either green or violet. This fact provided transition-metal chemists with convincing evidence that the coordination in this compound is octahedral. Both the green and the violet  $\text{CoCl}_3 \cdot 4\text{NH}_3$  dissociate to produce only one  $\text{Cl}^-$  ion per molecule, so the cation must be  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$ , with a coordination number of 6. How are the six ligands arranged? We can suggest three possibilities: a flat six-membered ring, a trigonal prism, or an octa-

**Figure 20-1**

The six coordinating groups around Co in  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$  can be arranged in three possible symmetrical ways: a flat hexagon (a), a triangular prism (b), or an octahedron (c). Three different arrangements of coordinating groups, or geometrical isomers, can be produced in the hexagon and four in the triangular prism, but only two in the octahedron. The octahedral structure is adopted by  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$  and almost all other six-coordinate complexes.

hedron. In each of these three structures there is more than one way of placing the two  $\text{Cl}^-$  ions among the six coordination positions. Such structures, which differ only in the arrangement of the same ligands around the central metal, are called **geometrical isomers**. As Figure 20-1 shows, the existence of only two geometrical isomers of  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$  is convincing evidence for the octahedral structure. Octahedral coordination, with a coordination number of 6, is by far the most common structure for such transition-metal compounds.

Fourfold coordination also is found. Is this coordination tetrahedral or square? Again, data on the number of variant forms of a compound with the same empirical formula provide the answer. The compound with the

**Figure 20-2**

If the neutral molecule  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  has square planar coordination, two isomers are possible (a). But if the coordination is tetrahedral, only one can exist (b). Two isomers have been found, so the tetrahedral structure is eliminated. Why is this proof more convincing than that of Figure 20-1?

formula  $\text{PtCl}_2 \cdot 2\text{NH}_3$ , or  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , occurs in two forms that presumably are geometrical isomers. Both isomers are a creamy white, but they differ in solubility and chemical properties. As illustrated in Figure 20-2, there cannot be isomers for the tetrahedral structure, whereas the square planar structure has two. Therefore, the compound  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  must be square planar. (As an example of a comparable tetrahedral structure,  $\text{CH}_2\text{Cl}_2$  has only one form and not two.)

Square planar geometry is characteristic of  $\text{Pd}(\text{II})$ ,  $\text{Pt}(\text{II})$ , and  $\text{Au}(\text{III})$ , all of whose cations have eight  $d$  electrons, or a  $d^8$  structure (Table 20-4). Tetrahedral coordination is encountered most often in transition-metal compounds in which the coordinating group is  $\text{O}^{2-}$ , as in  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$ . Now coordination structures can be examined directly by x-ray crystallography, and the conclusions about geometrical isomers from other experiments have been confirmed.

## Magnetic Properties

Some transition-metal complexes are diamagnetic, which indicates no unpaired electrons. Many others are paramagnetic and have one or more unpaired electrons. For example,  $\text{Co}(\text{NH}_3)_6^{3+}$  is diamagnetic, whereas  $\text{CoF}_6^{3-}$  is paramagnetic and has four unpaired electrons per ion. The ionic charge is not the governing factor, since  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ , which has four unpaired electrons, is paramagnetic, yet  $\text{Fe}(\text{CN})_6^{4-}$  is diamagnetic. The magnetic properties of several other octahedral complexes are illustrated in Figure 20-3. One of our goals will be to explain this magnetic behavior in terms of electronic arrangement.

**Table 20-4****Valence Electronic Configurations of Transition Metals<sup>a</sup>**

Configuration	$d^1s^2$	$d^2s^2$	$d^3s^2$	$d^4s^2$	$d^5s^2$	$d^6s^2$	$d^7s^2$	$d^8s^2$	$d^9s^2$	$d^{10}s^2$
Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Valence electrons										
Neutral atom	3	4	5	6	7	8	9	10	11	12
$M^{2+}$ ion	1	2	3	4	5	6	7	8	9	10
( <i>d</i> electrons)										
$M^{3+}$ ion	0	1	2	3	4	5	6	7	8	9
( <i>d</i> electrons)										

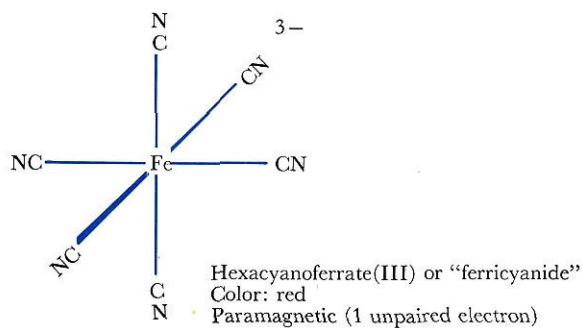
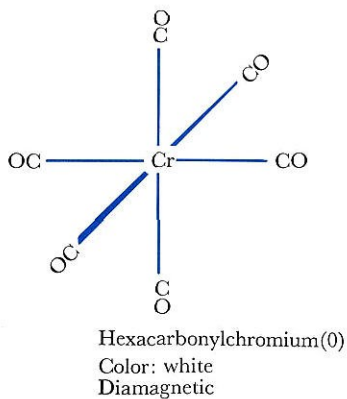
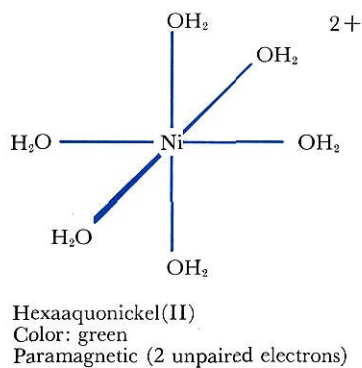
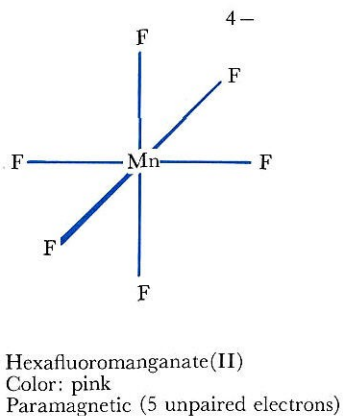
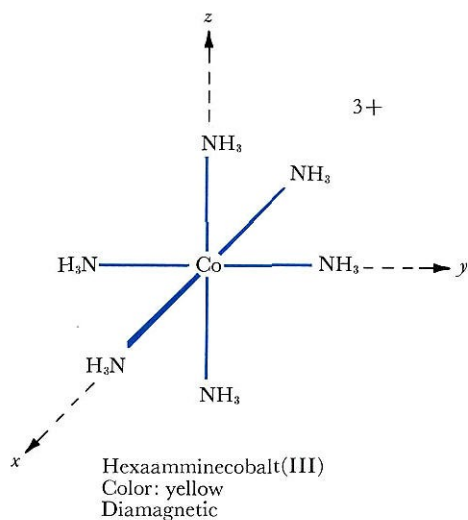
<sup>a</sup>All configurations are given as  $d^n s^2$ , since what interests us here is the number of electrons in the ion and not the electronic configuration of the neutral atom.

**Lability and Inertness**

A coordination complex that rapidly exchanges its ligands for others is **labile**; a complex that releases its ligands slowly is **inert**. Inertness is not the same as stability in the thermodynamic sense. A complex can be unstable, which means that it is not the most favored state according to the principles of thermodynamics discussed in Chapter 16. Given enough time, the complex will change to some other state. Yet if the transition to the most favored state is extremely slow, the unstable complex is inert. As an example of an inert yet unstable system,  $H_2$  and  $O_2$  can be kept as a mixture for years without an appreciable spontaneous formation of water. However, if a small amount of platinum black (finely divided Pt) is supplied as a catalyst, or if a flame is brought near, the reaction to make the more stable  $H_2O$  is sudden, complete, and violent. A mixture of  $H_2$  and  $O_2$  by itself is unstable, yet inert.

Returning to coordination compounds, we note that  $Cu(NH_3)_4SO_4$  can be dissolved in water and the  $Cu(NH_3)_4^{2+}$  can be allowed to react with dilute acid to produce  $NH_4^+$  and  $Cu(H_2O)_6^{2+}$  as fast as the solutions are mixed. In contrast,  $Co(NH_3)_6Cl_3$  can be heated in concentrated sulfuric acid to drive off HCl gas and make  $[Co(NH_3)_6^{3+}]_2(SO_4^{2-})_3$  without breaking the bonds between Co and  $NH_3$ . The copper complex is labile; the cobalt complex is inert. Tripositive ions with three or six *d* electrons form especially inert complexes; these complexes are also remarkably stable in the thermodynamic sense.



**Figure 20-3**

Several octahedral complexes, with systematic names, colors, and magnetic properties.

## Oxidation Number and Structure

Coordination number 6 appears to be optimal for ions with oxidation numbers +2 and +3; these include many transition-metal compounds. An oxidation number of +1 is too low to attract six electron-donor groups to build a complex ion. Most complexes of +1 ions have smaller coordination numbers, such as 2 for  $\text{Ag}^+$  and  $\text{Cu}^+$  in  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{CuCl}_2^-$ . Stable complexes of rather high coordination number do occur with +1 ions and neutral atoms. But in most of these instances, such as  $\text{Mn}(\text{CN})_6^{5-}$  and  $\text{Mo}(\text{CO})_6$ , these ligands have special  $\pi$ -bonding features that transcend simple electron donation.

Complexes of central ions having oxidation numbers greater than +3 are rare. They usually exist only with  $\text{O}^{2-}$  and  $\text{F}^-$ . We expect stronger bonding as the oxidation number of the central ion increases. However, if the oxidation number becomes too high, the central ion attracts ligand electrons so strongly that they are pulled completely away from the ligand. Then the complex is not stable, and the metal is reduced to a lower oxidation state. For this reason,  $\text{Fe}^{3+}$  forms no complex with  $\text{I}^-$ ; instead, it oxidizes  $\text{I}^-$  to  $\text{I}_2$ . Since O and F are so electronegative, and since  $\text{O}^{2-}$  and  $\text{F}^-$  when bound to a central metal are so difficult to oxidize, they can exist in complexes in which the central ion has an oxidation state higher than the usual +2 or +3.

## Influence of the Number of $d$ Electrons

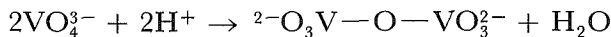
Much of coordination chemistry can be understood in terms of the number of  $d$  electrons on the central metal ion. As we have already mentioned, the +2 and +3 oxidation states are most common. Table 20-4 gives the number of net  $d$  electrons for neutral atoms and for +2 and +3 cations; we shall use this table frequently. In addition to this preference for +2 and +3 states, ions with the  $d$ -shell configurations  $d^0$ ,  $d^5$ , and  $d^{10}$  are particularly favored.

■ *Noble-gas shell,  $d^0$ .* The noble-gas configuration with no  $d$  electrons is especially stable. The ion  $\text{Sc}^{3+}$  has this configuration, as does Ti(IV) in  $\text{TiF}_6^{2-}$ . It is increasingly difficult for ions to attain the  $d^0$  structure from left to right across the periodic table. The reason is that the resulting charge on the central metal ion increases. Stabilization is then possible only by coordination to oxide ions. Therefore, we find  $\text{VO}_4^{3-}$  instead of  $\text{V}^{5+}$ ,  $\text{CrO}_4^{2-}$  instead of  $\text{Cr}^{6+}$ , and  $\text{MnO}_4^-$  instead of  $\text{Mn}^{7+}$ .

This series of oxide complexes provides a good example of the application of eyeball spectroscopy. Photons of the appropriate energy can excite electrons from the ligand oxygen atoms to the empty  $d$  orbitals of the metal. This process is called **charge transfer** and is a common origin for color in transition-metal complexes. The higher the oxidation state of the metal, the easier it is for electrons to transfer, and the lower is the energy

of the photons required to bring about the transfer. The required energy in  $\text{VO}_4^{3-}$  occurs with photons in the ultraviolet region. Therefore, the  $\text{VO}_4^{3-}$  ion is colorless. In  $\text{CrO}_4^{2-}$ , the absorption of photons is in the violet region, at approximately  $24,000\text{ cm}^{-1}$ ; thus the chromate ion in solution appears yellow from the frequencies of light that are *not* absorbed (Table 20-3). (In accordance with standard spectroscopic practice, we express energy in wave numbers,  $\text{cm}^{-1}$ . See Section 8-2.) The  $\text{Mn}^{7+}$  ion has the highest oxidation state of all, and absorbs green light (around  $19,000\text{ cm}^{-1}$ ) for the charge-transfer excitation. Therefore,  $\text{MnO}_4^-$  appears purple. The colors in these charge-transfer complexes are usually quite intense, which indicates strong absorption. Increasing the size of the central ion makes charge transfer more difficult and moves the absorption into the ultraviolet; thus  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ , and  $\text{ReO}_4^-$  are colorless.

The greater attraction of a large positive charge on the central ion for the negative charge on the ligands is reflected in the decreasing tendency of ligands in the coordination ion to bind to other cations. In the series  $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ , and  $\text{MnO}_4^-$ , the vanadate ion is a fairly strong base and will bind  $\text{H}^+$  or other cations. The chromate ion is a reasonably strong base also. But the permanganate ion is a weak base; the compound  $\text{HMnO}_4$  is completely ionized in water. The acid  $\text{HMnO}_4$  is one of the strongest known (Table 11-2). Reactions of the type



occur easily with the vanadate ion, which forms polyvanadates with many  $-\text{O}-$  bridges, and with the chromate ion, which forms dichromate,  $\text{Cr}_2\text{O}_7^{2-}$ , in acid. In contrast,  $\text{MnO}_2\text{O}_7$  can be made only in concentrated sulfuric acid, which acts as a powerful dehydrating agent. Once formed, it is so unstable that it is a dangerous explosive.

■ *Filled and half-filled shells.* The filled  $d^{10}$  structure in  $\text{Zn}^{2+}$  and  $\text{Ag}^+$ , and the half-filled  $d^5$  structure in  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ , make these ions particularly stable, even though the complexes that  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Zn}^{2+}$  form are relatively weak and contribute little to stabilizing the metal. This behavior is another example of the stability of filled and half-filled shells that we have seen so often.

■ *Ions with  $d^3$ ,  $d^6$ , or  $d^8$  structures.* The prominence of the oxidation number +3 for  $\text{Cr}(d^3)$  and for  $\text{Co}(d^6)$ , plus the remarkable inertness of their complexes in chemical reactions—recall  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  in hot sulfuric acid—cannot be explained on the basis of the ideas presented so far. Nor can we account for the special tendency of  $d^8$  ions to adopt square planar rather than octahedral or tetrahedral coordination. To explain these structures and the existence of complexes of metals with oxidation number zero, we must examine how  $d$  orbitals participate in bonding with the ligands.

■ *Instability of  $d^4$ .* The ion  $\text{Cr}^{2+}$  ( $d^4$ ) is a powerful reducing agent that is oxidized to a  $d^3$  arrangement. Also a  $d^4$  ion,  $\text{Mn}^{3+}$  is an equally powerful oxidant and is reduced to a  $d^5$  ion. And  $\text{Co}^{5+}$ , likewise with a  $d^4$  structure, does not form any stable compounds at all. Any theory of bonding in coordination complexes will have to interpret this extreme instability of the  $d^4$  configuration.

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## 20-2 NOMENCLATURE FOR COORDINATION COMPOUNDS

Many complex transition-metal salts have common names that were given to them before their chemical identities were known. Some of the names are slightly informative: *potassium ferricyanide* for  $\text{K}_3\text{Fe}(\text{CN})_6$  and *potassium ferrocyanide* for  $\text{K}_4\text{Fe}(\text{CN})_6$ . *Luteocobaltic chloride* for  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  and *praseocobaltic chloride* for *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are informative only if you know the Latin and Greek for yellow (*luteus*) and green (*praseos*). Luteoiridium chloride,  $\text{Ir}(\text{NH}_3)_6\text{Cl}_3$ , is not even yellow, and was given that name only because it has the analogous chemical formula to the cobalt salt. And *Reinecke's salt*, *Erdmann's salt*, and *Zeise's salt* are completely useless names.

Systematic nomenclature is gradually replacing these older names. The following rules are used:

1. In naming the entire complex, the name of the cation is given first and the name of the anion is given second (just as for sodium chloride), whether the cation or the anion is the complex species.

2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom. Special ligand names are *aquo* for water, *ammine* for  $\text{NH}_3$ , and *carbonyl* for CO.

3. Ligand names generally end in *-o* if the ligand is negative (*chloro* for  $\text{Cl}^-$ , *ciano* for  $\text{CN}^-$ ) and *-ium* in the rare cases in which the ligand is positive (*hydrazinium* for  $\text{NH}_2\text{NH}_3^+$ ). The names are unmodified if the ligand is neutral (*methylamine* for  $\text{CH}_3\text{NH}_2$ , *ethylenediamine* for  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ).

4. A Greek prefix (*mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on) indicates the number of each ligand (*mono-* is often omitted for a single ligand of a given type). If the name of the ligand itself contains the terms *mono-*, *di-*, and so forth (*ethylenediamine*, abbreviated *en*; *diethylenetriamine*, abbreviated *dien*), then the ligand name is enclosed in parentheses and its number is given with the alternative prefixes *bis-* and *tris-* instead of *di-* and *tri-*. Hence, for example,  $\text{Pt}(\text{en})_3\text{Br}_4$  is tris(ethylenediamine)platinum(IV) bromide.

5. A Roman numeral or a zero in parentheses indicates the oxidation number of the central metal atom.



6. If the complex ion is negative, the name of the metal ends in *-ate*.  
 7. If more than one ligand is present in a species, the order of ligands in the name is negative, neutral, and positive.

Some examples of systematic nomenclature are

$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$	Hexaammineplatinum(IV) chloride
$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	Chloropentaammineplatinum(IV) chloride
$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	Trichlorotriammineplatinum(IV) chloride
$\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	Tetrachlorodiammineplatinum(IV)
$\text{KPt}(\text{NH}_3)\text{Cl}_5$	Potassium pentachloromonoammine-platinate(IV)
$\text{K}_2\text{PtCl}_4$	Potassium tetrachloroplatinate(II)
$\text{K}_2\text{CuCl}_4$	Potassium tetrachlorocuprate(II)
$\text{Fe}(\text{CO})_5$	Pentacarbonyliron(0)
$[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$	Hexaaquonickel(II) perchlorate
$\text{K}_4\text{Fe}(\text{CN})_6$	Potassium hexacyanoferrate(II)
$\text{K}_3\text{Fe}(\text{CN})_6$	Potassium hexacyanoferrate(III)
$[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Br}_2$	Dichlorobis(ethylenediamine)platinum(IV) bromide
$[\text{Pt}(\text{NH}_3)_4](\text{PtCl}_4)$	Tetraammineplatinum(II) tetrachloroplatinate(II)

Some common ligands are listed in Table 20-5. All these ligands are *monodentate*; that is, each ligand binds to the central ion at only one point.

**Table 20-5**

**Common Monodentate Ligands<sup>a</sup>**

Ligand	Name
$\text{F}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	Fluoro, chloro, bromo, iodo
$:\text{NO}_2^-$ and $:\text{ONO}^-$	Nitro and nitrito
$:\text{CN}^-$	Cyano
$:\text{SCN}^-$ and $:\text{NCS}^-$	Thiocyanato and isothiocyanato
$:\text{OH}^-$	Hydroxo
$\text{CH}_3\text{COO}^-$	Acetato
$\text{H}_2\text{O}$	Aquo
$\text{NH}_3$	Ammine
$\text{CO}$	Carbonyl
$\text{NO}^+$	Nitrosyl
py	Pyridine, $\text{C}_5\text{H}_5\text{N}$

<sup>a</sup>The electron pairs are shown to remind you which atom bonds to the central metal. They ordinarily would not be shown.

Table 20-6

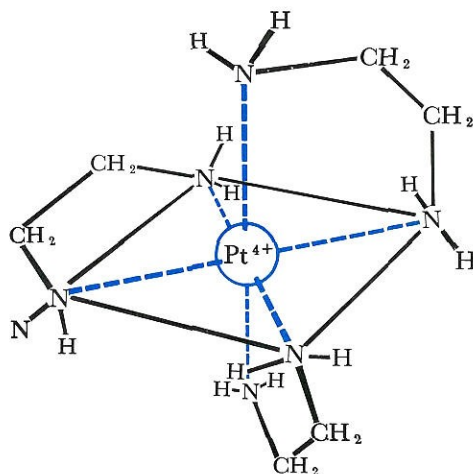
## Common Chelating Agents or Multidentate Ligands

Symbol	Ligand name	Formula	Bonds
en	Ethylenediamine	$\ddot{\text{N}}\text{H}_2-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$	2
pn	Propylenediamine	$\text{NH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{NH}_2$	2
dien	Diethylenetriamine	$\ddot{\text{N}}\text{H}_2-\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}-\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}_2$	3
trien	Triethylenetetraamine	$\text{NH}_2-\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}-\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}-\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}_2$	4
EDTA	Ethylenediaminetetraacetate	$\begin{array}{c} \text{---} \text{OOC} - \text{CH}_2 \qquad \qquad \text{CH}_2 - \text{COO} :^- \\   \qquad \qquad \qquad   \\ : \text{N} - \text{CH}_2\text{CH}_2 - \text{N} : \\   \qquad \qquad \qquad   \\ \text{---} \text{OOC} - \text{CH}_2 \qquad \qquad \text{CH}_2 - \text{COO} :^- \\   \qquad \qquad \qquad   \\ \text{---} \text{OOC} - \text{COO} :^- \end{array}$	6
ox	Oxalate	$\text{---} \text{OOC} - \text{COO} :^-$	2

Other ligands are bi-, tri-, or even hexacentate (Table 20-6). Three molecules of ethylenediamine,  $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , can coordinate octahedrally to Pt to produce the cation illustrated in Figure 20-4. The ethylenediaminetetraacetato ion listed in Table 20-6 can wrap itself around a metal ion and coordinate with all six octahedral positions at once (Figure 20-5). Ethylenediaminetetraacetate, or EDTA, is so efficient a scavenger for Ca, Mg, Mo, Fe, Cu, and Zn that it will remove the essential metal atom from an enzyme and completely block its enzymatic activity. EDTA is also a useful scavenger in removing traces of metals from distilled and purified

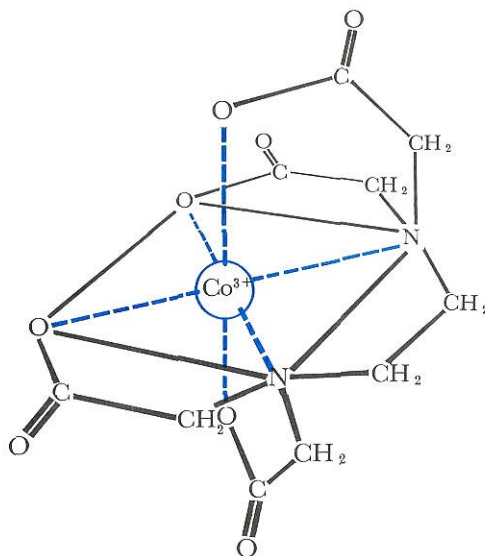
Figure 20-4

The structure of the tris(ethylenediamine)platinum(IV) ion. Each molecule of ethylenediamine,  $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , coordinates to the platinum ion at two points. Such bidentate and multidentate ligands are called *chelating agents*, and the compounds are called *chelates*, from the Greek *chela*, "claw."



**Figure 20-5**

One molecule of EDTA, or ethylenediaminetetraacetate, can completely enclose a metal ion in octahedral coordination. EDTA's attraction for metals is so strong that it will remove metals from enzymes and will inhibit their catalytic activity completely.



water. A molecule or ion that coordinates more than once with a metal ion is called a **chelating agent**, and the total complex is called a **chelate**.

### Isomerism

Three types of isomers are found in coordination complexes: structural, geometrical, and optical isomers. **Structural isomers** have the same overall chemical formula but different ways of connecting component parts. Ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and dimethyl ether ( $\text{H}_3\text{C}-\text{O}-\text{CH}_3$ ) are structural isomers. The material with the formula  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  exists in three structural isomers:

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Hexaaquochromium(III) chloride
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Chloropentaaquochromium(III) chloride monohydrate
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	Dichlorotetraaquochromium(III) chloride dihydrate

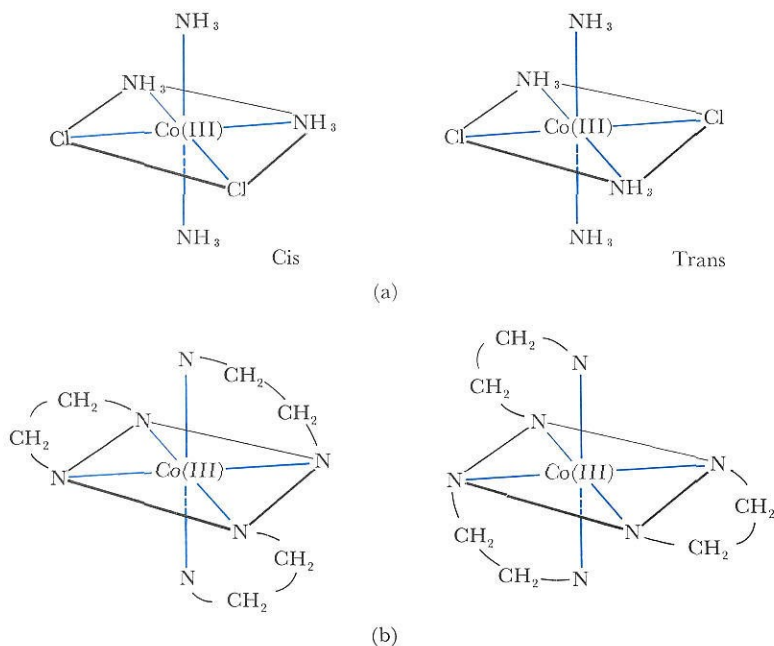
The first of these is violet, the second is light green, and the third is dark green. Their structures can be demonstrated by precipitation of  $\text{Cl}^-$  with  $\text{Ag}^+$  and by elimination of zero, one, or two waters of hydration by drying over  $\text{H}_2\text{SO}_4$ .

As we saw earlier, **geometrical isomers** differ in the arrangement of groups around the same center. The prefix *cis*- indicates that two identical groups are adjacent; *trans*- means that they are across from one another, or at least not adjacent. In Figure 20-6a, the two chlorines in the *cis* isomer are adjacent to one another along one edge of the octahedron, whereas in the *trans* isomer they are across a diagonal through the octahedron.

**Optical isomers** have the same groups connected in the same relative arrangement, but in the reverse sense as your right hand is to your left. Optical isomers arising from the arrangement of groups about a central atom always occur in pairs, one of which is the mirror image of the other. These pairs are called **enantiomers**. An example of two enantiomers is the two  $\text{Co(en)}_3^{3+}$  complexes shown in Figure 20-6b. A central atom around which such isomers can be formed is called an **asymmetric center** or **chiral center**. Another example of a pair of enantiomers is L- and D-alanine, shown in Figure 21-15. Many optical isomers can be formed when several asymmetric carbon atoms are connected in a chain.

## 20-3 THEORIES OF BONDING IN COORDINATION COMPLEXES

The maximum number of  $\sigma$  bonds that can be constructed with  $s$  and  $p$  valence orbitals is 4. Thus, 4 is the highest coordination number commonly encountered in the representative elements in Period 2. These elements do not have filled  $d$  orbitals or access to empty  $d$  orbitals in the next higher shell. For example, in  $\text{CH}_4$  the central carbon atom is “saturated” with four



**Figure 20-6**

Geometrical and optical isomers of octahedral complexes. (a) *cis*- and *trans*-dichlorotetraamminecobalt(III) ions are geometrical isomers. (b) The two optical isomers of the tris(ethylenediamine)cobalt(III) ion. Can you prove to your own satisfaction that, for each ion, only two such isomers exist?



$\sigma$  bonds. However, with a first-row transition metal as the central atom, there are five  $d$  valence orbitals in addition to the four  $s$  and  $p$  orbitals.

If the central metal made full use of its  $d$ ,  $s$ , and  $p$  valence orbitals in  $\sigma$  bonding, a total of *nine* ligands could be attached. However, because of the bulkiness of most ligands it is extremely difficult to achieve a coordination number of 9. With rhenium (Re), a large third-row transition-metal atom, and H, a small ligand, the coordination number of 9 is found in the complex  $\text{ReH}_9^{3-}$ . The structure of this interesting complex is illustrated in Figure 20-7.

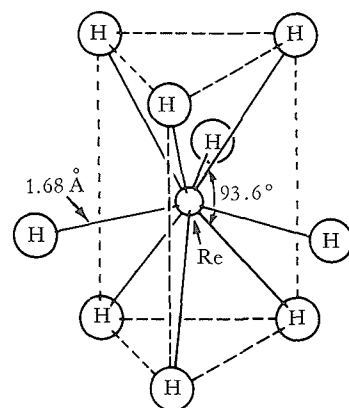
The bonds in most coordination complexes, however, use fewer than the nine atomic orbitals from the metal. We shall turn now to the theories that have been developed to explain this bonding and the properties of the complexes formed. There have been four stages in the development of transition-metal bonding theory. These are the simple **electrostatic theory**, the **valence bond** or **localized-molecular-orbital theory**, the **crystal field theory**, and the **ligand field** or **delocalized-molecular-orbital theory**. Each of these theories is an improvement on its predecessor. Considered together, they provide a good case study of how bonding ideas develop, and how the same physical facts can be explained by different and seemingly contradictory assumptions.

We shall devote most of the discussion to octahedral coordination because it is both the most common and the easiest to understand. Keep in mind the following questions, which we shall try to answer when developing the theories:

1. How can we explain the difference in absorption of energy (manifested in the color) by a complex as the nature of the ligands is changed (recall Table 20-2)?
2. How can we explain that a complex such as  $\text{Co}(\text{NH}_3)_6^{3+}$  is diamagnetic, yet others such as  $\text{CoF}_6^{3-}$  are paramagnetic and have one or several unpaired electrons?

**Figure 20-7**

The structure of the  $\text{ReH}_9^{3-}$  ion. There are six H atoms at the corners of a trigonal prism, and three more H atoms around the Re atom on a plane halfway between the triangular end faces of the prism.



3. The stability of  $d^0$ ,  $d^5$ , and  $d^{10}$  electron arrangements can be explained. But why are  $d^3$  and  $d^6$  so stable (recall  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$ )?

4. Why do certain ions with the  $d^8$  configuration, such as  $\text{Pt(II)}$  and  $\text{Pd(II)}$ , prefer square planar geometry to tetrahedral or octahedral?

### Electrostatic Theory

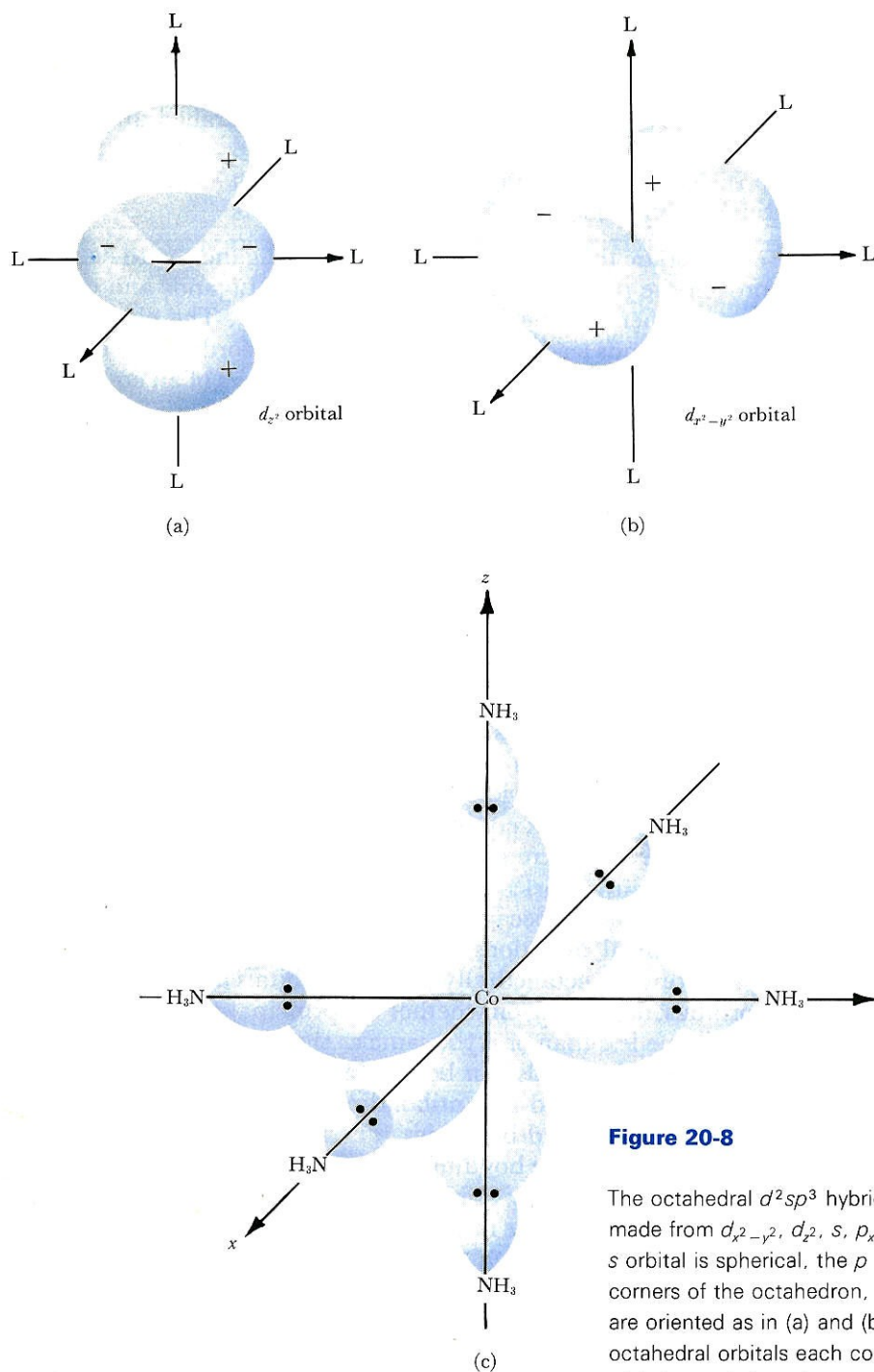
The simple electrostatic theory assumes only that the ligands, with negative charges, approach the positively charged central ion. Ligands and central ion attract one another, but ligands repel one another. The electrostatic repulsion between ligands leads to a prediction that a coordination number of 2 will be linear, and three ligands will lie at the corners of an equilateral triangle with the central atom at the center of the triangle. Four ligands will be tetrahedral, and six will be octahedral. This electrostatic theory cannot explain the existence of square planar complexes. Also, it cannot explain why complexes form with neutral molecules ( $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ) or with positive ions ( $\text{NH}_2\text{NH}_3^+$ ). Finally, the theory does not discuss magnetic properties of complexes or their electronic energy levels as revealed by their colors and spectra.

### Valence Bond (or Localized-Molecular-Orbital) Theory

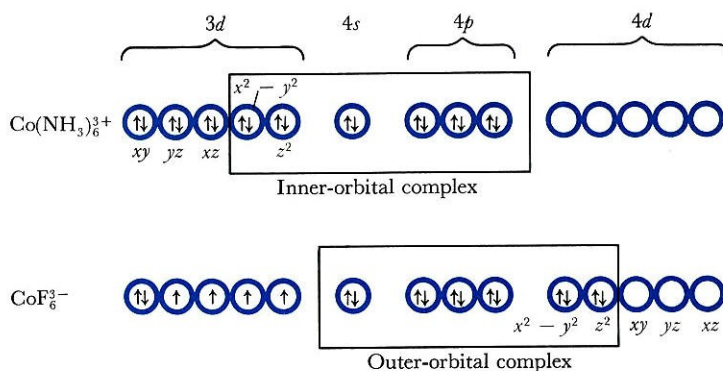
One of the first definite advances toward understanding why octahedral geometry occurs was made when Pauling showed, in 1931, that a set of six  $s$ ,  $p$ , and  $d$  orbitals could be hybridized in a manner similar to the  $sp^3$  and  $sp^2$  hybridization to produce six equivalent orbitals directed to the vertices of an octahedron. The orbitals required are the  $s$ , the three  $p$ , and the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals lying either just below or just above these  $s$  and  $p$  orbitals. The two  $d$  orbitals are chosen because they have lobes of maximum density pointing in the six axial directions of an octahedron, as do the three  $p$  orbitals. The resulting six octahedrally oriented orbitals are called  $d^2sp^3$  or  $sp^3d^2$  hybrid orbitals, depending on whether the principal quantum number of the  $d$  orbitals is one less than or is the same as that of the  $s$  and  $p$  orbitals.

Each of the hybrid orbitals can be combined with an orbital from a ligand to make a bonding and an antibonding orbital, each with  $\sigma$  symmetry around the metal–ligand bond axis. The lone pair of electrons from each ligand orbital goes into the bonding molecular orbital, and six covalent bonds are produced (Figure 20-8). Similarly, four equivalent hybrid orbitals directed to the corners of a square in the  $xy$  plane can be produced from the  $d_{x^2-y^2}$ ,  $s$ ,  $p_x$ , and  $p_y$  metal orbitals.

The valence bond theory has not been successful in making quantitative predictions about energies, but at least it gives a rationalization for the magnetic properties of octahedral complexes. Pauling proposed that two types of complexes could be prepared: **outer-orbital**  $sp^3d^2$  complexes in which the  $d$  orbitals lie above the  $s$  and  $p$  orbitals, and **inner-orbital**  $d^2sp^3$

**Figure 20-8**

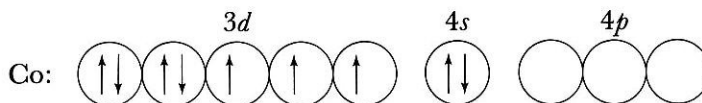
The octahedral  $d^2sp^3$  hybrid atomic orbitals are made from  $d_{x^2-y^2}$ ,  $d_{z^2}$ ,  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  orbitals. The  $s$  orbital is spherical, the  $p$  orbitals point to the corners of the octahedron, and the two  $d$  orbitals are oriented as in (a) and (b). The six hybrid octahedral orbitals each combine with a ligand orbital containing a lone pair of electrons (c). (The symbol L represents a ligand.)

**Figure 20-9**

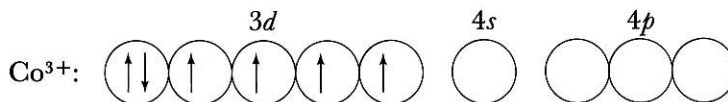
The valence bond theory postulates that in inner-orbital complexes of cobalt such as  $\text{Co}(\text{NH}_3)_6^{3+}$ , six electrons from the metal are spin-paired in  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals; the octahedral hybrid orbitals are produced from  $s$ , three  $p$ , and the two  $d$  from the level beneath. In outer-orbital cobalt complexes, all five of the underlevel  $d$  orbitals are used for electrons from the metal, now not completely paired. The octahedral hybrids use two  $d$  orbitals from the same quantum level as  $s$  and  $p$ . In either case, lone-pair electrons on the ligands fill the bonding orbitals formed between ligand orbitals and the six metal orbitals of the octahedral hybrid.

complexes in which they lie below (Figure 20-9). In inner-orbital complexes, the number of  $d$  orbitals left to hold the  $d$  electrons that remain on the metal ion is restricted. Only the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  are available; the other two are used in octahedral hybridization.

We can use cobalt as an example of the valence bond explanation of magnetic properties. The neutral cobalt atom has nine electrons beyond the Ar noble-gas shell, and can be represented as

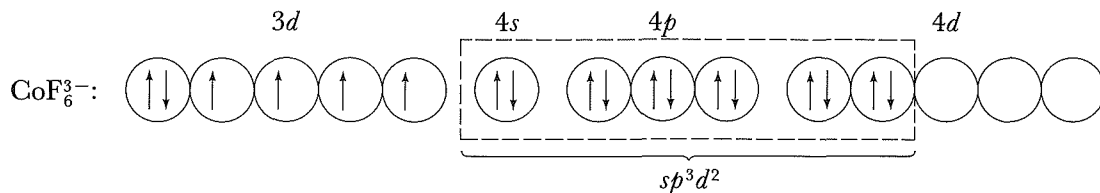


The  $\text{Co}^{3+}$  ion has six electrons, which by Hund's rule will be distributed among all five 3d orbitals:



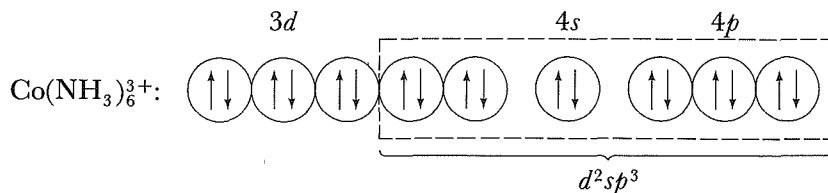
Now let us assume that six ligands, each with an electron pair, are to form six covalent bonds with hybridized metal orbitals that are octahedrally

oriented. If an outer complex is formed with  $4s$ ,  $4p$ , and  $4d$  metal orbitals, the electrons in the  $3d$  orbitals are undisturbed (Figure 20-9):



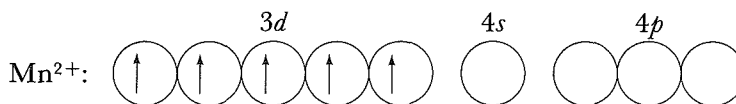
Four electrons will remain unpaired and, by this theory,  $\text{CoF}_6^{3-}$  should be paramagnetic, as it is observed to be.

In contrast, if an inner complex is formed with  $3d$  orbitals in the octahedral hybridization, then only three  $3d$  orbitals will be left for the six valence electrons originally present in the  $\text{Co}^{3+}$  ion:

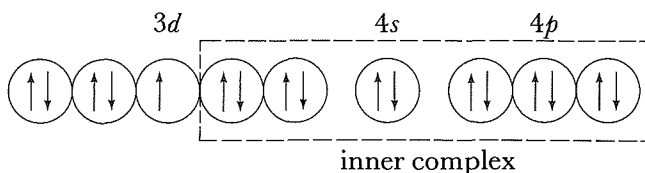


Hence we predict  $\text{Co}(\text{NH}_3)_6^{3+}$  to be diamagnetic, and it is.

In Figure 20-3, the  $\text{Mn}^{2+}$  ion in hexafluoromanganate(II) has a  $d^5$  structure:



If hexafluoromanganate(II) were an inner-orbital complex, its five electrons would be compressed into three  $d$  orbitals and one electron would be unpaired:



Conversely, if it were an outer-orbital complex, all five electrons would be unpaired in the five  $d$  orbitals. Both possible complexes would be paramagnetic, but they would differ in the magnitude of the magnetic moment.



Experimental data indicate that the complex has five unpaired spins, so it must be an outer-orbital complex. The  $\text{Fe}^{3+}$  ion also has a  $d^5$  configuration; however, because magnetic data show that hexacyanoferrate(III) has one unpaired electron, it is described in the valence bond theory as an inner-orbital complex. Ligands such as  $\text{CN}^-$  and  $\text{CO}$  tend to form inner-orbital complexes, and ligands such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  usually form outer-orbital complexes.

The valence bond theory produces the correct two alternatives for the number of unpaired electrons, but it offers little help in making the choice between them. It does predict that inner-orbital complexes will be relatively inert. The experimental observation that outer-orbital complexes *are* usually more labile than inner-orbital complexes gives us confidence that the valence bond theory is at least a step in the right direction. It was a landmark at the time that it was proposed; however, it has been supplanted by crystal field theory and a more complete molecular orbital theory.

## Crystal Field Theory

From a localized-molecular-orbital theory, the pendulum now swings the other way to a purely electrostatic theory that regards the bonding between metal and ligand as ionic. The simple electrostatic theory predicts that octahedral coordination will arise for the same reason that six unit charges, constrained to move on the surface of a sphere, will adopt an octahedral arrangement as the one of lowest energy. This is simply the electron-pair repulsion idea of Section 11-3.

Crystal field theory is more realistic. With this theory we consider what happens to the five metal  $d$  orbitals when six negative charges are brought near the metal in an octahedral array along the three principal axes of the  $d$  orbitals. The negative charges represent the lone pairs on the ligands. They are considered to remain with the ligands rather than being involved in any type of covalent bonding with the metal. Therefore, crystal field theory assumes purely *ionic* bonding.

The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are most affected by the negative charges, which represent the ligands. The orbitals point directly at these charges (Figure 20-10). Any electrons in these  $d$  orbitals will respond to the electrostatic repulsion from the ligand lone pairs. Electrons in these two  $d$  orbitals will have higher energies than those in the other three. In contrast, the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals have their lobes of maximum density directed *between* the ligands (see Figure 8-24). Electrons in these orbitals are more stable. The net result of this electrostatic interaction with the ligands is that the five  $d$  orbitals are split into two energy levels separated by a **crystal-field splitting energy**,  $\Delta_o$ , as shown in Figure 20-11. The lower level is called the  $t_{2g}$  level, and the upper, the  $e_g$ . The names come from group theory, and their origin need not concern us here.

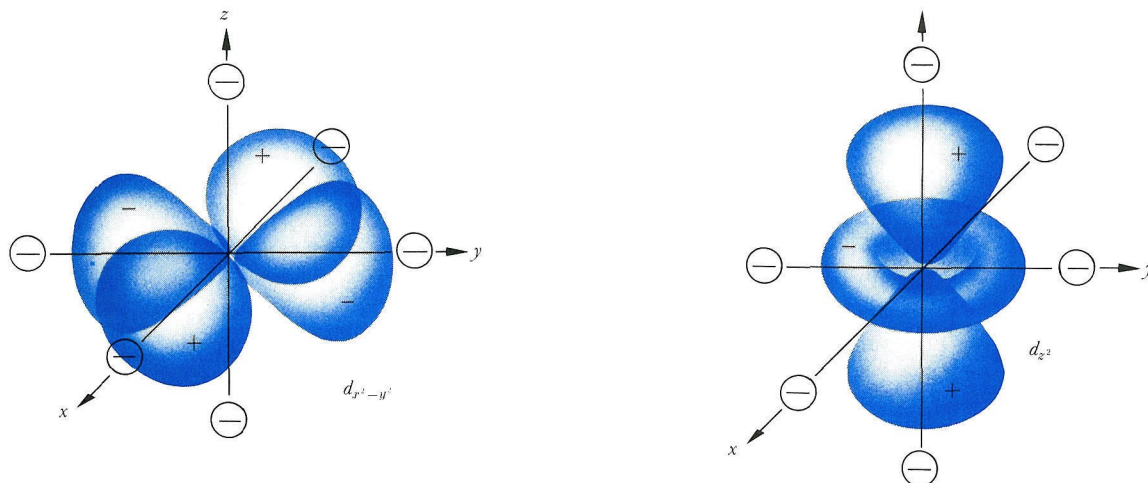
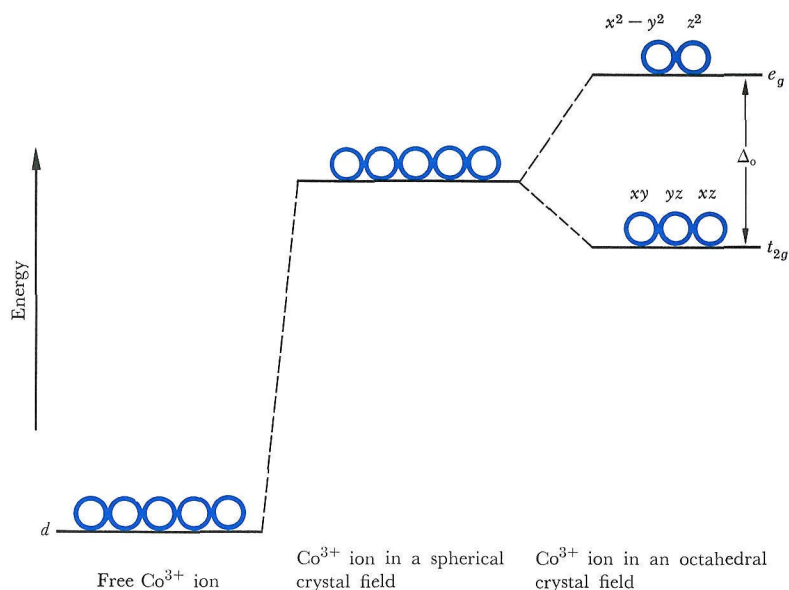


Figure 20-10

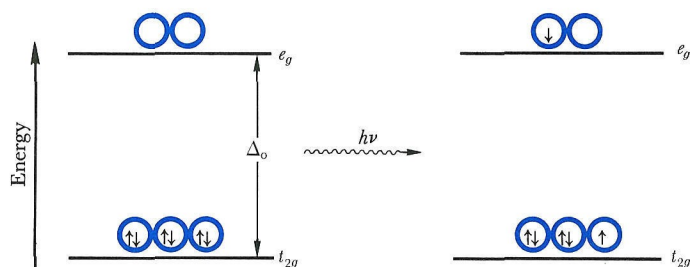
By crystal field theory, the six ligands of an octahedral complex may be represented as six negative charges, which point directly at the electron-density lobes of the metal  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. Any electrons in these two  $d$  orbitals will be repelled by the negative charges. More energy is required to force electrons into these two  $d$  orbitals on the metal than into the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  metal orbitals, all of which point between the ligands.

The crystal-field splitting energy,  $\Delta_o$ , is obtained by measuring the energy absorbed when one electron is promoted from the  $t_{2g}$  level to the  $e_g$  level (Figure 20-12). This splitting energy is crucial in accounting for magnetic properties. If  $\Delta_o$  is small, as in  $\text{CoF}_6^{3-}$ , the six  $d$  electrons of  $\text{Co}^{3+}$  are spread out among all five  $d$  orbitals (Figure 20-13). There is a saving of energy if as few electrons as possible are paired. Conversely, if the splitting constant is large enough to overcome the energy of pairing two electrons in the same orbital, the more stable arrangement will be for the three low-lying orbitals of the  $t_{2g}$  level to contain one pair of electrons each and for the two upper orbitals to be vacant. This is the situation in  $\text{Co}(\text{NH}_3)_6^{3+}$ . Because of the different numbers of unpaired electrons in the two structures,  $\text{Co}(\text{NH}_3)_6^{3+}$  is called a **low-spin complex** and  $\text{CoF}_6^{3-}$  is called a **high-spin complex**.

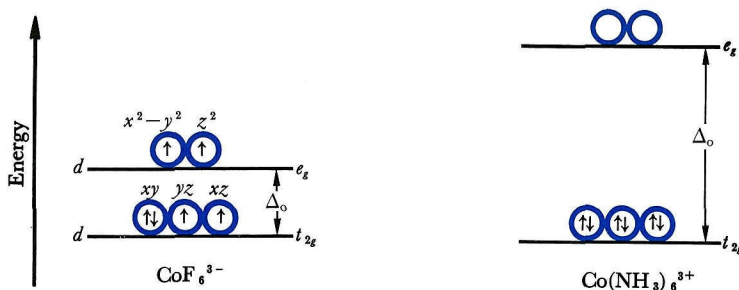
Notice how the same facts are explained by two quite different theories, the valence bond and crystal field theories. Both theories state that low-spin octahedral complexes arise when only three  $d$  orbitals of low energy are available for electrons originally from the central metal ion. High-spin octahedral complexes occur when there are *five* low-lying  $d$  orbitals. However, valence bond theory accounts for the presence of three or five such orbitals in terms of the set of six orbitals used in octahedral hybridization.

**Figure 20-11**

Energy-level diagram for the five  $d$  orbitals of a metal ion in an octahedral crystal field. On the left is the energy of electrons in the  $d$  orbitals of a free ion. In the center is the energy of electrons in the  $d$  orbitals if the ion were surrounded by a spherical cloud of negative charges. On the right is the splitting in energies of the  $d$  orbitals produced if the negative charges are arranged octahedrally around the metal. The three  $d$  orbitals that point between the ligands have lower energies than the two orbitals that point directly at the ligands.

**Figure 20-12**

When  $\text{Co}(\text{NH}_3)_6^{3+}$  absorbs a photon of violet light and transmits those frequencies that give it its yellow color, the electronic configuration goes from the one at the left to the one at the right.

**Figure 20-13**

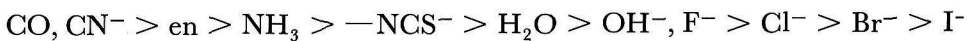
Crystal field theory explanations of high-spin and low-spin complexes. The crystal-field splitting produced by the  $\text{F}^-$  ion is small, and the energy required to place two electrons in the upper level is less than the energy required to pair them with others. Therefore, the high-spin  $\text{CoF}_6^{3-}$  complex spreads its electrons among all five orbitals, and has four unpaired spins. The  $\text{NH}_3$  group produces such a large crystal-field splitting that it is easier to pair electrons in the bottom three orbitals. The low-spin  $\text{Co}(\text{NH}_3)_6^{3+}$  complex has no unpaired electrons.

In contrast, crystal field theory invokes a small or a large energy gap between a low-lying set of three  $d$  orbitals and a less stable set of two. In the valence bond theory, the operating factor is hybridization of orbitals from the metal, and the bonds to the ligands are entirely covalent. In the crystal field theory, the operating factor is electrostatic repulsion between ligand electron pairs and electrons on the metal ion, and the bonds to the ligands are entirely ionic. The effects are the same, but the explanations are radically different. Which theory is true?

Some chemists dislike the word *true* and prefer circumlocutions such as “successful in accounting for the facts.” But unless the chemist is also a mystic who believes in some sort of inner reality beyond that which can be apprehended by the senses, the two sets of terminology are equivalent. No theory can ever be proven to be true in the absolute sense. All we can say is that one theory is “truer” than another because it can account for more observed properties of its subject than another theory. By this criterion, crystal field theory is better than valence bond theory. The common ligands can be ranked according to the magnitude of crystal-field splitting,  $\Delta_o$ , that they produce, and this order can be justified to a certain extent.

The stronger the electrostatic field created by the ligand, the greater the splitting should be. Small ions with their lone pairs concentrated in one place, as in  $\text{F}^-$ , should produce a greater effect than larger groups with electrons diffused over a larger volume, as in  $\text{Cl}^-$ . Beyond this size-related argument, we can list the ligands in order but cannot explain the order:





strong-field ligands	intermediate-field ligands	weak-field ligands
-------------------------	-------------------------------	-----------------------

We write the isothiocyanate ion as  $\text{—NCS}^-$  to emphasize that the metal–ligand bond is through the N atom in these cobalt(III) complexes discussed in this chapter.

Without spectroscopes or prisms, we can quickly check the order of ligands in this list merely by looking at the colors of complexes with these ligands. The absorption of visible light during the excitation of metal  $d$  electrons from  $t_{2g}$  to  $e_g$  orbitals is the other important source of color in transition-metal complexes in addition to charge-transfer absorption. For metals in +2 and +3 oxidation states, the charge-transfer absorption is usually in the ultraviolet, and the colors we see are from crystal-field splitting. These colors are not as intense as the charge-transfer absorption colors of  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$ . In Table 20-2 is a list of cobalt complexes, their colors, the colors absorbed in the electronic transition of lowest energy, and the approximate wavelengths and energies involved. Replacing even one  $\text{NH}_3$  in the complex by  $\text{—NCS}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\text{Cl}^-$  decreases the energy difference between levels, or the transition energy, in the order given. Substituting  $\text{Br}^-$  for  $\text{—NCS}^-$  in the ethylenediamine complex lowers the transition energy by approximately 10% and changes the ion from blue to green. Replacing  $\text{—NCS}^-$  by a halide,  $\text{Cl}^-$ , in the presence of five  $\text{NH}_3$  also lowers the transition energy by 10% and changes the salt from orange to purple.

Why is this list of relative strengths in energy-level splittings as it is? We cannot say from crystal field theory. But if the orbitals on the ligands are taken into account, both those that contain the electron pairs to be shared with the metal and those that contain lone pairs not directly associated with the metal, we can explain more of the order of splitting energies. This extended molecular orbital theory contains both crystal field and valence bond theories as extreme cases, and it is commonly called the **ligand field theory**.

### Ligand Field (or Delocalized-Molecular-Orbital) Theory

With ligand field theory we take into account the orbitals on the ligands, and consider the ligands as something more than mere spherical charges. In the delocalized-molecular-orbital treatment, six ligand orbitals, assumed as a first approximation to have  $\sigma$  symmetry around the metal–ligand bond lines, are combined with six of the nine metal  $s$ ,  $p$ , and  $d$  orbitals:  $d_{x^2-y^2}$ ,  $d_{z^2}$ ,  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$ . These are the same orbitals that Pauling used to synthesize his six hybrid orbitals. Now we shall combine all of them with the six ligand atomic orbitals to produce six delocalized bonding orbitals and six antibonding orbitals (Figure 20-14). The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals, having the wrong symmetry for combining with  $\sigma$ -like ligand orbitals, are *nonbonding*.



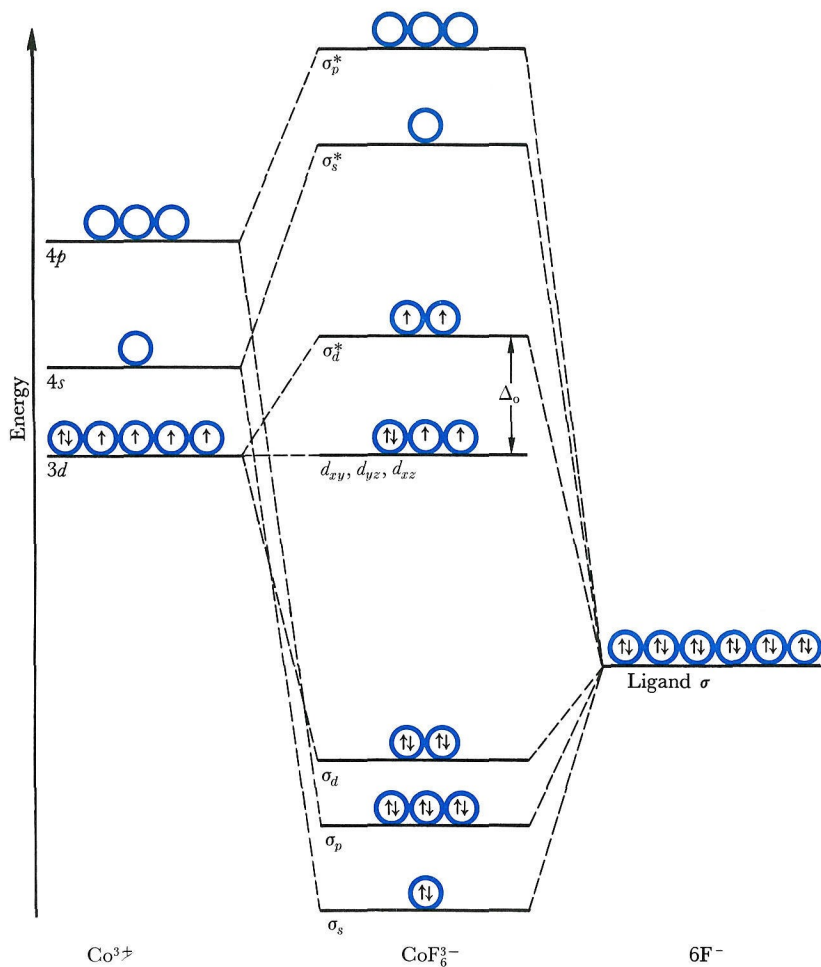


Figure 20-14

In the delocalized-molecular-orbital treatment of octahedral coordination, the same six metal orbitals that were used in the valence bond theory ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ,  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$ ) now combine with the six lone-pair-containing ligand orbitals to produce six bonding molecular orbitals ( $\sigma_s$ ,  $\sigma_p$ , and  $\sigma_d$ ) and six antibonding orbitals ( $\sigma_d^*$ ,  $\sigma_s^*$ , and  $\sigma_p^*$ ). The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  metal orbitals are nonbonding. The low-lying six bonding orbitals fill with the electron pairs from the ligand to make six electron-pair bonds between metal and ligand. The  $d$  electrons of the metal ion are in the nonbonding and lowest antibonding levels, which are separated by the energy  $\Delta_o$ . These two levels correspond to those in Figure 20-11, but the explanation of their origin is different.

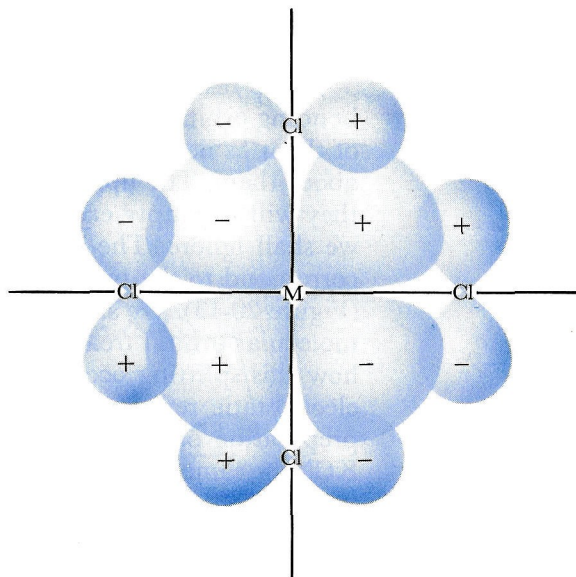
Electron pairs in these orbitals have no effect on holding ligands and metal together, and are described as *metal lone pairs*.

The resulting energy-level diagram appears in Figure 20-14. The six bonding orbitals at the bottom are filled with electron pairs. We can think of them as being the six pairs donated by the ligands, and we can forget about them. The upper four antibonding orbitals are similarly irrelevant; they will be empty except in extreme cases of electronic excitation, which we shall ignore. The nonbonding level and the lowest antibonding level correspond to the two levels,  $t_{2g}$  and  $e_g$ , produced by crystal-field splitting (Figure 20-13). We shall continue to call them by these names, even in the molecular orbital treatment. But note the difference in the explanation of how this splitting occurs. In crystal field theory, it is the consequence of electrostatic repulsion; in ligand field theory, it is a consequence of the preparation of molecular orbitals. As we saw in Chapter 12 for HF and KCl, the same molecular orbital theory can accommodate everything from purely ionic to purely covalent bonding. The choice between these two theories is accordingly a pseudochoice, a consequence of being committed to two extreme models. In  $\text{CoF}_6^{3-}$  there is a certain ionic character to the bonding, because, as you can see in Figure 20-14, the ligand orbitals are lower than those of the metal and closer in energy to the bonding molecular orbitals. Therefore, the bonding orbitals will have more of the character of the ligand orbitals, and there will be a displacement of negative charge toward the ligands. Thus, the bonds will be partially ionic.

With the molecular orbital theory, we can do a much better job of predicting which ligands will cause large energy differences between the  $t_{2g}$  and  $e_g$  levels in octahedral coordination, and which will produce small splittings. For this prediction we must look at the interactions of  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals in the  $t_{2g}$  level with atomic orbitals on ligands that have  $\pi$  symmetry around the metal–ligand bond.

The crystal field theory assumes that there are no such ligand orbitals and that each ligand is a featureless sphere of charge. Ligand field theory considers the ligand orbitals that form bonds to the metal ion, and also the two unhybridized  $p$  orbitals at right angles to the metal–ligand bond. These unhybridized  $p$  orbitals strongly influence the ligand-field splitting energy,  $\Delta_o$ .

Figure 20-15 depicts four of these chloride  $p$  orbitals overlapping one of the three  $d$  orbitals in the  $t_{2g}$  energy level. If there are electrons in this  $d$  orbital, they are repelled by the lone-pair electrons in these  $p$  orbitals, and the energy of the  $t_{2g}$  level is raised. Any ligand with filled orbitals having such  $\pi$  symmetry around the ligand–metal axis decreases the ligand-field splitting energy,  $\Delta_o$ . If we retain the crystal field theory terminology, such ligands ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) are called **weak-field ligands**. Fluoride ion is not as efficient at this process because it holds its electrons so tightly. Such an interaction is a ligand-to-metal( $\pi$ ) or  $\text{L} \rightarrow \text{M}(\pi)$  interaction.

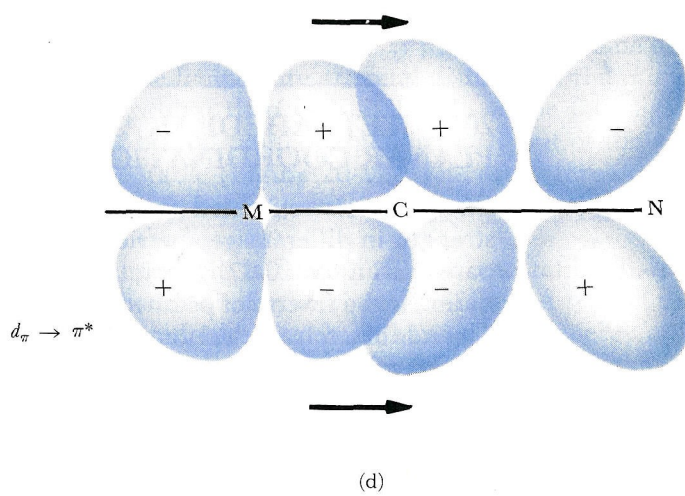
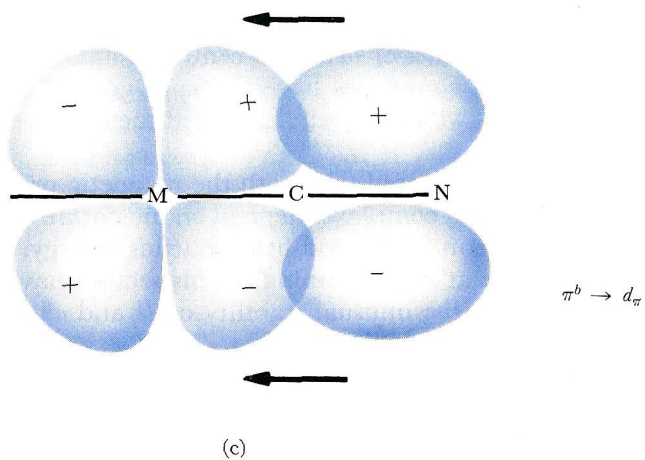
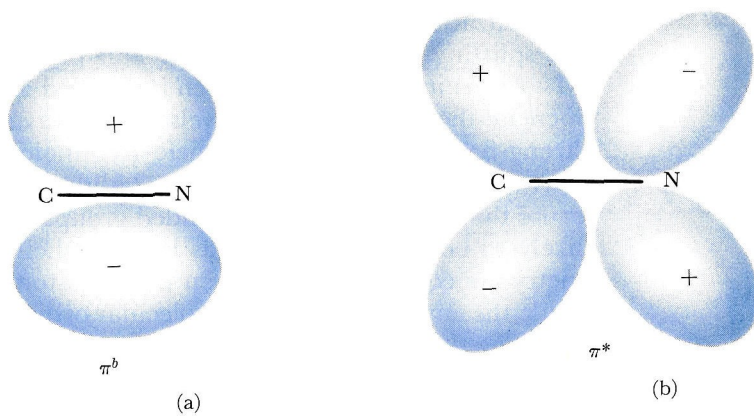
**Figure 20-15**

The lone-pair electrons in the  $\pi$  orbitals of  $\text{Cl}^-$  repel electrons in the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals of the metal (M), thereby making the levels less stable. The  $t_{2g}$  level in Figure 20-11 rises and the splitting energy,  $\Delta_o$ , decreases.

Polyatomic groups that have an unfilled antibonding orbital with  $\pi$  symmetry behave differently. The cyanide ion (Figure 20-16) has a triple bond made from one bonding  $\sigma^b$  orbital and two bonding  $\pi^b$  molecular orbitals. One of these  $\pi^b$  bonding orbitals is shown in Figure 20-16a. This orbital destabilizes or raises the  $t_{2g}$  level by a  $\text{L} \rightarrow \text{M}(\pi)$  process just as in  $\text{Cl}^-$ . But most of the electron density of the  $\pi^b$  orbital lies between the C and the N, *not* in the direction of the metal atom. It is the antibonding  $\pi^*$  orbital (Figure 20-16b) that interacts more with the metal  $t_{2g}$  level. Here the effect is the reverse of that in  $\text{Cl}^-$ . Electrons in the metal  $t_{2g}$  orbitals can become partially delocalized and flow into the  $\pi^*$  orbital on the ligand. This

**Figure 20-16**

The effect of  $\pi$  bonding in cyano complexes. (a) In the  $\text{CN}^-$  ion, the bonding  $\pi^b$  molecular orbital contains an electron pair, and the antibonding  $\pi^*$  orbital (b) is empty. (c) The metal orbitals of the  $t_{2g}$  type are more stable in the presence of simple  $\sigma$  symmetrical ligands because the  $t_{2g}$  orbitals do not concentrate their electrons in the directions of the ligands. But if the ligand has filled  $\pi$  orbitals, then these orbitals interact with the metal  $t_{2g}$  orbitals and make them less stable. The splitting constant decreases. (d) If the metal has filled  $t_{2g}$  orbitals that interact with the empty antibonding  $\pi$  ligand orbitals, then the metal electrons are delocalized, the energy of the orbitals falls, and the splitting energy increases. This last effect predominates in most  $\text{CN}^-$  complexes, and we say that  $\text{CN}^-$  produces a large ligand-field splitting. ►





delocalization stabilizes the  $t_{2g}$  orbital and lowers its energy. Therefore, the splitting energy,  $\Delta_o$ , increases. This process is a metal-to-ligand ( $\pi$ ) or  $M \rightarrow L(\pi)$  interaction, and often it is called  **$\pi$  back bonding**. Ligands that increase the splitting of the levels in this way ( $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ) are called **strong-field ligands** in crystal field terminology. Single atoms with many lone pairs of electrons, such as the halide ions, are weak-field ligands because they donate electrons. Bonded groups of atoms such as  $\text{CO}$  are more likely to be strong-field ligands because their bonding orbitals of  $\pi$  symmetry are concentrated between pairs of atoms and away from the metal, while the empty antibonding molecular orbitals extend closer to the metal.

The nature of the metal itself also has a large influence on the size of the ligand-field splitting. Metal atoms or ions utilizing  $4d$  and  $5d$  valence orbitals give rise to much larger splittings than in corresponding complexes involving  $3d$ -orbital metals. For example, the  $\Delta_o$  values for  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\text{Rh}(\text{NH}_3)_6^{3+}$ , and  $\text{Ir}(\text{NH}_3)_6^{3+}$  are  $22,900\text{ cm}^{-1}$ ,  $34,100\text{ cm}^{-1}$ , and  $40,000\text{ cm}^{-1}$ , respectively. Presumably the  $4d$  and  $5d$  valence orbitals of the ion are more suitable for  $\sigma$  bonding with the ligands than are the  $3d$  orbitals, but the reason for this is not well understood. An important consequence of the much larger  $\Delta_o$  values of  $4d$  and  $5d$  central metal ions is that *all* second- and third-row metal complexes have low-spin ground states, even complexes such as  $\text{RhBr}_6^{3-}$ , which contain ligands at the weak-field end of the spectrochemical series.

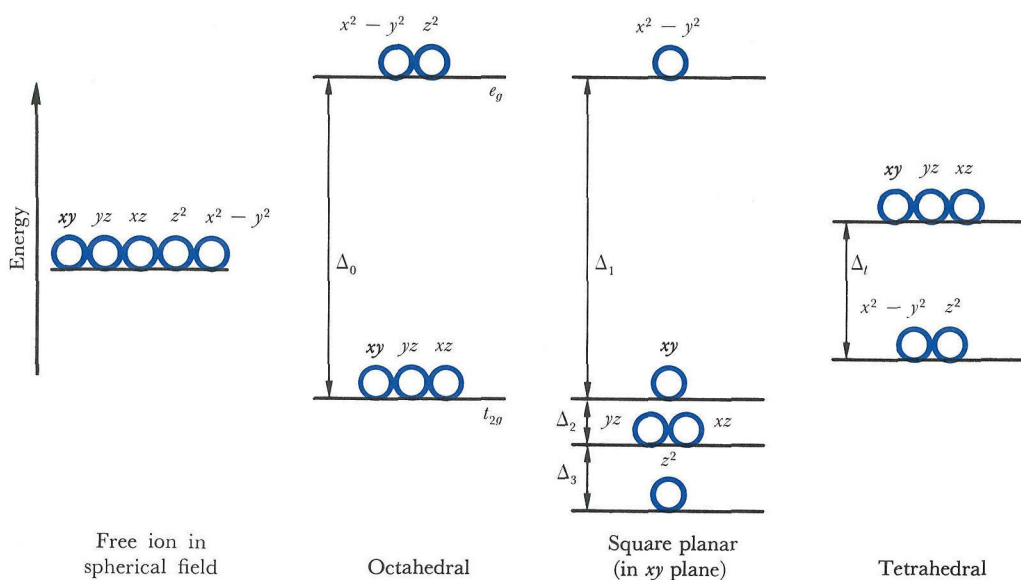
We have discovered that both the magnetic properties and the colors of transition-metal complexes depend on the nature of the ligand and metal by their effects on the ligand-field splitting energy,  $\Delta_o$ . Thus, two of the questions listed at the beginning of this section have been answered. We can also explain the unusual stability of  $d^3$  and  $d^6$  configurations in complexes with strong-field ligands. The  $d^3$  and  $d^6$  arrangements are half-filled and completely filled  $t_{2g}$  levels. When the level splitting is large, these arrangements have the same significance in terms of stability that  $d^5$  and  $d^{10}$  configurations do when all five  $d$  levels have the same energy. The stability of  $d^5$  and  $d^{10}$  arrangements is most noticeable in weak-field complexes, when the ligand-field splitting is small.

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## 20-4 TETRAHEDRAL AND SQUARE PLANAR COORDINATION

Energy levels estimated from ligand field theory for ligands of a given strength in different geometrical arrangements around the metal are compared in Figure 20-17. The relative order of energies in tetrahedral coordination is the reverse of octahedral, and it is not difficult to understand why. Ligands in a tetrahedral complex approach the metal from four of the eight corners of a cube (Figure 20-2b). It is precisely the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals that do *not* point to the corners of the cube around the metal atom. As you



**Figure 20-17**

Energy levels for the five  $d$  orbitals in the free ion in a spherical field of electrical charge and in the three common coordination geometries, all calculated for the same strength ligand. The relative order of levels is explained in the text. The ligand-field splitting energies are represented by  $\Delta_0$ ,  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$ , and  $\Delta_t$ .

can verify from Figure 8-24, the density lobes of the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals point to the midpoints of the 12 edges of a cube, whereas the other two point to the midpoints of the six faces. The set of three  $d$  orbitals, being closer to the tetrahedral ligands, will be less stable, even though the splitting is not as pronounced as for octahedral geometry.

Square planar splitting is almost as straightforward. Since we usually work with  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals, let us take the  $xy$  plane as the plane of the complex, and assume that the ligands are at equal distance in the  $\pm x$  and  $\pm y$  directions. The  $d_{x^2-y^2}$  orbital then points directly at the four ligands and is least stable. The  $d_{z^2}$  orbital points perpendicularly out of the plane of the ligands and is most stable (Figure 20-17). The other three orbitals have intermediate stability;  $d_{yz}$  and  $d_{xz}$  are more stable than  $d_{xy}$  because they are out of the plane of the ligands.

The octahedral arrangement is intrinsically more stable than the square planar because six bonds are formed instead of four. A typical covalent single bond and a typical ionic bond both have a bond energy of 200 to 400 kJ mole<sup>-1</sup>. This corresponds to 17,000 to 33,000 cm<sup>-1</sup> in the units in which splitting energies are given in Table 20-7. An octahedral complex,

**Table 20-7****Ligand-Field Splitting Energies for Representative Metal Complexes**

<b>Octahedral complexes</b>	$\Delta_o$ (cm <sup>-1</sup> )	<b>Octahedral complexes</b>	$\Delta_o$ (cm <sup>-1</sup> )
Ti(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	20,300	CoF <sub>6</sub> <sup>3-</sup>	13,000
TiF <sub>6</sub> <sup>3-</sup>	17,000	Co(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	18,200
V(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	17,850	Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	22,900
V(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	12,400	Co(CN) <sub>6</sub> <sup>3-</sup>	34,500
Cr(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	17,400	Co(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	9,300
Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	21,600	Ni(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	8,500
Cr(CN) <sub>6</sub> <sup>3-</sup>	26,600	Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	10,800
Cr(CO) <sub>6</sub>	32,200	RhCl <sub>6</sub> <sup>3-</sup>	22,800
Fe(CN) <sub>6</sub> <sup>3-</sup>	35,000	Rh(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	34,100
Fe(CN) <sub>6</sub> <sup>4-</sup>	33,800	RhBr <sub>6</sub> <sup>3-</sup>	19,000
Fe(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	13,700	IrCl <sub>6</sub> <sup>3-</sup>	27,600
Fe(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	10,400	Ir(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	40,000

<b>Tetrahedral complexes</b>	$\Delta_t$ (cm <sup>-1</sup> )
VCl <sub>4</sub>	9010
CoCl <sub>4</sub> <sup>2-</sup>	3300
CoBr <sub>4</sub> <sup>2-</sup>	2900
CoI <sub>4</sub> <sup>2-</sup>	2700
Co(NCS) <sub>4</sub> <sup>2-</sup>	4700

<b>Square planar complexes</b>	$\Delta_1$ (cm <sup>-1</sup> )	$\Delta_2$ (cm <sup>-1</sup> )	$\Delta_3$ (cm <sup>-1</sup> )	<b>Total <math>\Delta</math> (cm<sup>-1</sup>)</b>
PdCl <sub>4</sub> <sup>2-</sup>	23,600	3900	7400	34,900
PtCl <sub>4</sub> <sup>2-</sup>	29,700	4700	6800	41,200

with two more bonds than either square planar or tetrahedral, has an intrinsic energy advantage of 35,000 to 65,000 cm<sup>-1</sup>. Although it appears from Figure 20-17 that square planar coordination is preferable for  $d^1$  through  $d^6$ , the extra bond energy causes octahedral coordination to predominate. However, the seventh and eighth electrons are forced into the high-energy  $e_g$  orbitals in octahedral coordination, whereas the much more stable  $d_{xy}$  is available in square planar. This extra stability is decisive for  $d^8$  configurations in which the ligand-field splitting is large: They are found in square planar coordination. The ligand-field splitting is larger at higher

atomic numbers. Hence, Pt(II) and Pd(II) regularly have square planar coordination, whereas Ni(II) is usually octahedral. The ninth and tenth electrons tip the balance back in favor of octahedral because of the extra stability gained from the two additional bonds.

Tetrahedral coordination is seldom preferred and is relatively rare. In addition to the smaller number of bonds in comparison with octahedral, the tetrahedral coordination also suffers from the double disadvantage of a less stable lower level and the necessity of commencing the upper level at the third electron rather than the fourth (in the high-spin complexes).

A selection of measured ligand-field splitting energies for all three coordinations is given in Table 20-7. See whether the octahedral data are compatible with the order of ligand splitting strengths given previously in this section. Also, note how close our guess for the splitting of  $\text{Co}(\text{NH}_3)_6^{3+}$ , based purely on color (Table 20-2), really was.

## 20-5 EQUILIBRIA INVOLVING COMPLEX IONS

When we write  $\text{Co}^{2+}$  to represent an ion in aqueous solution, we understand implicitly that the bare ion is not present, but that water molecules of hydration are coordinated to the metal. Therefore, the chemistry of complex ions in solution is the chemistry of the substitution of one ligand molecule or ion for another in the coordination shell around a metal. Nevertheless, it is customary, for simplicity, to write the formation of the ammine complex of  $\text{Co}^{2+}$ , for example, as if it were the addition of  $\text{NH}_3$  to dipositive cobalt ions:



We can write an equilibrium constant for this reaction:

$$K_f = \frac{[\text{Co}(\text{NH}_3)_6^{2+}]}{[\text{Co}^{2+}][\text{NH}_3]^6} \quad (20-2)$$

Since the equilibrium concerns the formation of a complex,  $K_f$  is known as a formation constant. For the formation of hexamminecobalt(II),  $K_f = 1 \times 10^5$ .

There is no difference in principle between the mathematics of formation-constant problems and that of dissociation of acids or bases. The parallel would be somewhat more apparent if equation 20-1 were written as a dissociation of  $\text{Co}(\text{NH}_3)_6^{2+}$  rather than as an association, and if a dissociation constant that is the inverse of  $K_f$  were used. Formation constants, however, are customary.

As soon as  $\text{NH}_3$  is added to a solution of  $\text{Co}^{2+}$ , some of it combines with  $\text{Co}^{2+}$  and produces some complex ions. At equilibrium after the addition of  $\text{NH}_3$ , the concentrations of the complex ion,  $\text{NH}_3$ , and free  $\text{Co}^{2+}$  (actually hydrated) can be calculated from equation 20-2.

**Example 1**

Enough  $\text{NH}_3$  is added to a  $0.100M$  solution of  $\text{Ag}^+$  to make the initial concentration of  $\text{NH}_3$   $1 \text{ mole liter}^{-1}$ . After equilibrium is restored, what will be the concentrations of  $\text{Ag}^+$  and of  $\text{Ag}(\text{NH}_3)_2^+$ ?

**Solution**

The formation constant for  $\text{Ag}(\text{NH}_3)_2^+$  is given in Table 20-8 as  $K_f = 1 \times 10^8$ . Therefore, the equilibrium-constant expression is

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1 \times 10^8$$

Because the formation constant is so large, we can assume that the formation reaction is effectively complete and that the concentration of  $\text{Ag}(\text{NH}_3)_2^+$  is equal to the initial concentration of  $\text{Ag}^+$ . Since this quantity is appreciable, the concentration of  $\text{NH}_3$  remaining at equilibrium is the original concentration less the amount reacted with  $\text{Ag}^+$ :

$$\begin{aligned} [\text{Ag}(\text{NH}_3)_2^+] &= 0.100 \text{ mole liter}^{-1} \\ [\text{NH}_3] &= 1.000 - 0.200 = 0.800 \text{ mole liter}^{-1} \end{aligned}$$

(Two moles of  $\text{NH}_3$  react for every mole of  $\text{Ag}(\text{NH}_3)_2^+$  produced.) Therefore, the concentration of silver ion left at equilibrium is

$$[\text{Ag}^+] = \frac{0.100}{(0.800)^2} \times 1 \times 10^{-8} = 2 \times 10^{-9} \text{ mole liter}^{-1}$$

The assumption that the formation reaction is effectively complete is justified by the small  $\text{Ag}^+$  concentration.

**Example 2**

What will be the final concentration of  $\text{Ni}^{2+}$  hydrated ion if 50 ml of  $2.00M$   $\text{NH}_3$  solution are added to 50 ml of  $0.200M$   $\text{Ni}^{2+}$  solution?

**Solution**

The formation-constant expression is

$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6} = 6 \times 10^8$$

We assume that the concentration of  $\text{Ni}(\text{NH}_3)_6^{2+}$  at equilibrium is approximately  $0.100 \text{ mole liter}^{-1}$ . The concentration of unbound  $\text{NH}_3$  is then  $1.00 - 6(0.100) = 0.40 \text{ mole liter}^{-1}$ . Thus we have

$$\begin{aligned} \frac{[0.100]}{x[0.40]^6} &= 6 \times 10^8 \\ x &= 4 \times 10^{-8} \text{ mole liter}^{-1} \end{aligned}$$

Table 20-8

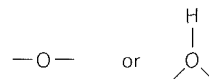
# Overall Formation Constants for Some Complexes in Aqueous Solution<sup>a</sup> at 298 K

Complex, $ML_n$	$K_f, [ML_n]/[M][L]^n$	Complex, $ML_n$	$K_f, [ML_n]/[M][L]^n$
<b>L = NH<sub>3</sub></b>		<b>L = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (en)</b>	
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	1 × 10 <sup>8</sup>	Mn(en) <sub>3</sub> <sup>2+</sup>	5 × 10 <sup>5</sup>
Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	1 × 10 <sup>12</sup>	Fe(en) <sub>3</sub> <sup>3+</sup>	4 × 10 <sup>9</sup>
Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	5 × 10 <sup>8</sup>	Co(en) <sub>3</sub> <sup>2+</sup>	8 × 10 <sup>13</sup>
Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	1 × 10 <sup>7</sup>	Ni(en) <sub>3</sub> <sup>2+</sup>	4 × 10 <sup>18</sup>
Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	6 × 10 <sup>8</sup>	Cu(en) <sub>2</sub> <sup>2+</sup>	1.6 × 10 <sup>20</sup>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	1 × 10 <sup>5</sup>	Zn(en) <sub>3</sub> <sup>2+</sup>	1.2 × 10 <sup>13</sup>
<b>L = F<sup>-b</sup></b>		<b>L = Cl<sup>-</sup></b>	
AlF <sub>6</sub> <sup>3-</sup>	7 × 10 <sup>19</sup>	MgCl <sup>+</sup>	4.0
SnF <sub>3</sub> <sup>-</sup>	8 × 10 <sup>9</sup>	CuCl <sup>+</sup>	1.0
SnF <sub>6</sub> <sup>2-</sup>	10 <sup>25</sup>	CuCl <sub>4</sub> <sup>2-</sup>	10 <sup>-5</sup>
ZnF <sup>+</sup>	5.0	AgCl <sub>2</sub> <sup>-</sup>	1 × 10 <sup>2</sup>
FeF <sub>2</sub> <sup>+</sup>	3 × 10 <sup>5</sup>	HgCl <sub>4</sub> <sup>2-</sup>	1.6 × 10 <sup>16</sup>
MgF <sup>+</sup>	65	TiCl <sub>4</sub> <sup>-</sup>	7.5 × 10 <sup>18</sup>
HgF <sup>+</sup>	10	BiCl <sub>6</sub> <sup>3-</sup>	4 × 10 <sup>6</sup>
CuF <sup>+</sup>	10	SnCl <sub>4</sub> <sup>2-</sup>	1.1 × 10 <sup>2</sup>
<b>L = OH<sup>-c</sup></b>		PbCl <sub>4</sub> <sup>2-</sup>	4 × 10 <sup>2</sup>
Cr(OH) <sub>2</sub> <sup>2+</sup>	1 × 10 <sup>10</sup>	FeCl <sub>2</sub> <sup>+</sup>	3.0
Fe(OH) <sub>2</sub> <sup>2+</sup>	1 × 10 <sup>11</sup>	FeCl <sub>4</sub> <sup>-</sup>	6 × 10 <sup>-2</sup>
Co(OH) <sub>2</sub> <sup>2+</sup>	1 × 10 <sup>12</sup>	<b>L = CN<sup>-</sup></b>	
Al(OH) <sub>2</sub> <sup>2+</sup>	2 × 10 <sup>28</sup>	Fe(CN) <sub>6</sub> <sup>3-</sup>	10 <sup>31</sup>
In(OH) <sub>4</sub> <sup>-</sup>	1.5 × 10 <sup>35</sup>	Fe(CN) <sub>6</sub> <sup>4-</sup>	10 <sup>24</sup>
Mn(OH) <sup>+</sup>	3 × 10 <sup>4</sup>	Ni(CN) <sub>4</sub> <sup>2-</sup>	10 <sup>30</sup>
Fe(OH) <sub>2</sub> <sup>+</sup>	1 × 10 <sup>7</sup>	Zn(CN) <sub>4</sub> <sup>2-</sup>	5 × 10 <sup>16</sup>
Co(OH) <sup>+</sup>	2.5 × 10 <sup>4</sup>	Cd(CN) <sub>4</sub> <sup>2-</sup>	6 × 10 <sup>18</sup>
Ni(OH) <sup>+</sup>	1 × 10 <sup>5</sup>	Hg(CN) <sub>4</sub> <sup>2-</sup>	4 × 10 <sup>41</sup>
Cu(OH) <sup>+</sup>	1 × 10 <sup>7</sup>	Ag(CN) <sub>2</sub> <sup>-</sup>	10 <sup>21</sup>
Zn(OH) <sup>+</sup>	1 × 10 <sup>5</sup>		
Ag(OH)	1 × 10 <sup>3</sup>		
Zn(OH) <sub>4</sub> <sup>2-</sup>	5 × 10 <sup>14</sup>		
Pb(OH) <sub>3</sub> <sup>-</sup>	8 × 10 <sup>13</sup>		

<sup>a</sup>In a strict sense, values should be accompanied by a more detailed description of solvent media and method of measurement. These values are approximate and are useful only for comparisons of similar species. For  $n = 1$  assume that three or five water molecules are also in the complex.

<sup>b</sup>Many stable complexes such as SiF<sub>6</sub><sup>2-</sup> and AsF<sub>6</sub><sup>-</sup> form, but they hydrolyze in water to give oxyanions or oxides.

<sup>c</sup>Most polypositive metal ions tend to form polynuclear complexes with



bridges in the presence of OH<sup>-</sup>, as in Fe—O—Fe<sup>4+</sup>, Bi<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup>, Cr<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, and so on, not to mention extremely insoluble hydroxide precipitates.



**Example 3**

What will be the final concentration of  $\text{Ni}^{2+}$  hydrated ion if 50 ml 2.00M ethylenediamine (en) solution are added to 50 ml of 0.200M  $\text{Ni}^{2+}$  solution?

**Solution**

The formation-constant expression is

$$K_f = \frac{[\text{Ni(en)}_3^{2+}]}{[\text{Ni}^{2+}][\text{en}]^3} = 4 \times 10^{18}$$

Under the same assumptions made in Example 2, we have

$$\frac{[0.100]}{x[0.70]^3} = 4 \times 10^{18}$$

$$x = 7 \times 10^{-20} \text{ mole liter}^{-1}$$

These exercises illustrate the considerably greater attraction that a chelating agent has for a metal ion as compared with a related ligand. Formation constants for ethylenediamine complexes in Table 20-8 are 8 to 10 orders of magnitude, or about a billion times, as large as formation constants for  $\text{NH}_3$  complexes of the same metal ion. The bonding of ammonia and amine chelating agents to the metal is similar; in both cases the lone-pair electrons on an ammonia or amine nitrogen atom interact with the metal. The difference in formation constants between  $\text{NH}_3$  and ethylenediamine reflects the increased stability when the bonding atoms of ligands are combined in a chelate molecule. This increased stability is sometimes called the **chelate effect**. However, the cyanide ion,  $\text{CN}^-$  (which bonds through the carbon), has an intrinsically stronger attraction for metals than does an amine nitrogen atom. As Table 20-8 shows, the formation constants for cyanide complexes are 3 to 13 orders of magnitude greater even than those of the corresponding ethylenediamine complexes!

Because formation constants are usually so large, we can ordinarily assume in complex-ion equilibrium problems that the concentration of the complex is the same as the total concentration of metal ion, as we have in the previous examples. However, for complexes of  $\text{F}^-$  this approximation is incorrect.

**Example 4**

What are the final concentrations of  $\text{F}^-$ ,  $\text{Hg}^{2+}$ , and  $\text{HgF}^+$  if 50 ml of a solution 2.00M in  $\text{F}^-$  are added to 50 ml of a solution 0.200M in  $\text{Hg}^{2+}$ ?

**Solution**

It is best to begin with a table:

	$\text{F}^-$	+	$\text{Hg}^{2+}$	$\rightleftharpoons$	$\text{HgF}^+$
Initial conditions:	1.00		0.100		0 mole liter <sup>-1</sup>
At equilibrium:	$1.00 - x$		$0.100 - x$		$x$ mole liter <sup>-1</sup>

$$K_f = \frac{x}{(1.00 - x)(0.100 - x)} = 10$$

Solve the equation for  $x$  by using the quadratic formula;  $x = 0.090$  mole liter<sup>-1</sup> =  $[\text{HgF}^+]$ ;  $[\text{F}^-] = 0.910$  mole liter<sup>-1</sup>; and  $[\text{Hg}^{2+}] = 0.010$  mole liter<sup>-1</sup>.

## Summary

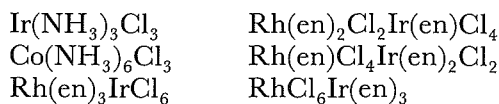
This chapter has been a brief introduction to a rich area of chemistry, that of transition-metal complexes. Much of the richness (and the confusion) in their chemistry results from the presence of closely spaced energy levels involving  $d$  orbitals of the metal. The key to understanding transition-metal chemistry is the explanation of how the ligands perturb these metal energy levels. **Valence bond theory** and **crystal field theory** offer partial explanations, but currently the most successful theory is **ligand field theory**.

The story of these theories is an illustration of the dictum, "You can always prove a theory wrong, but you can never prove it right." The success of valence bond theory in accounting for the coordination geometry and magnetic properties is no guarantee that the theory is right, or even that this way of looking at the problem is correct. For example, does the splitting of  $t_{2g}$  and  $e_g$  levels come about because of the formation of molecular orbitals (ligand field theory), electrostatic repulsion (crystal field theory), or the choice of six orbitals for hybridization (valence bond theory)? Or are all three theories incomplete, and will we some day regard ligand field theory with the same skeptical tolerance with which we now view the old valence bond theory?

For the present, ligand field theory works in many ways and accounts for much of the behavior of transition-metal complexes. Using it, we can explain the absorption of light and the observed magnetic properties of ions. It accounts successfully for the effect of the ligand on the splitting of energy levels. It explains why the  $d^3$  and low-spin  $d^6$  electronic configurations are especially favored in octahedral complexes, and why  $d^8$  leads to square planar geometry.

## Self-Study Questions

1. How can you account for the series of compounds with the formulas  $\text{CrCl}_3$ ,  $\text{CrCl}_3 \cdot 3\text{NH}_3$ ,  $\text{CrCl}_3 \cdot 4\text{NH}_3$ ,  $\text{CrCl}_3 \cdot 5\text{NH}_3$ , and  $\text{CrCl}_3 \cdot 6\text{NH}_3$ ? Why would you not expect to find the missing members of the series  $\text{CrCl}_3 \cdot 2\text{NH}_3$  and  $\text{CrCl}_3 \cdot \text{NH}_3$ ?
2. If you found the compound  $\text{CrCl}_3 \cdot \text{NaCl} \cdot x\text{NH}_3$ , what would you expect  $x$  to be?
3. How many different isomers of this compound,  $\text{CrCl}_3 \cdot \text{NaCl} \cdot x\text{NH}_3$ , would you expect to find?
4. What assumption about the geometry of bonding around the Cr molecule did you make in answering Question 3?
5. How does the number of isomers of a compound distinguish between the possible geometrical arrangements around the central metal ion? Illustrate with tetrahedral and square planar geometry.
6. What is the difference between paramagnetic and diamagnetic compounds? How are these distinguished from one another by experiment?
7. What is the difference between stability and inertness? Can a chemical system be stable yet not be inert? Can it be inert yet not be stable?
8. Why are complexes with electronic configurations of  $d^5$  or  $d^{10}$  on the central metal atom stable? Why are complexes with  $d^3$  and  $d^6$  arrangements stable? Which configurations would you predict to be more important for stability in complexes with ligands of large splitting energies? Of small splitting energies?
9. How would you name the following compounds in a systematic way:



10. Sketch each of the four Rh–Ir complexes of Question 9.
11. Sketch each of the following complex ions or molecules:

*cis*-dichlorotetraamminechromium(III) ion  
*trans*-dichlorotetraamminechromium(III) ion

Indicate the charge on each complex.

12. What is the difference between structural, geometrical, and optical isomers? Find examples in Questions 9 and 11 of structural and geometrical isomers.
13. Why do complexes in which the central metal ion has the  $d^8$  electronic configuration exist with square planar geometry?
14. What will be the number of unpaired electrons in  $\text{FeCl}_6^{3-}$ ? In  $\text{Fe}(\text{CN})_6^{3-}$ ?
15. All octahedral complexes of vanadium(III) have the same number of unpaired electrons, no matter what the nature of the ligand. Why is this so?

16. What is the difference in the way that valence bond theory and crystal field theory explain the magnetic properties of complex ions?
17. How does ligand field theory account for the observed order of ligands in terms of the sizes of their splitting energies?
18. Why, in the crystal field theory, are the five  $d$  orbitals on the metal atom divided into two energy levels in the way they are? Where do the corresponding energy levels come from in the molecular orbital theory of complex ion structure?
19. Why are the same groupings of the five  $d$  orbitals made in tetrahedral coordination as in octahedral, but with the relative energies of these two groups reversed?
20. What is a chelate? If porphyrin is a tetradentate chelating group, and ethylenediamine is a bidentate chelating group, how would triethylenetetraamine, diethylenetriamine, and EDTA be described?
21. What is a heme group? How does it function in hemoglobin and in cytochrome  $c$ ?

## Problems

### Stoichiometry

1. A student was given 1.00 g of ammonium dichromate for the preparation of a coordination compound. The sample was ignited, thereby producing chromium(III) oxide, water, and nitrogen gas. The chromium(III) oxide was allowed to react at  $600^{\circ}\text{C}$  with carbon tetrachloride to yield chromium(III) chloride and phosgene ( $\text{COCl}_2$ ). Upon treatment with excess liquid ammonia, the chromium(III) chloride reacted to produce hexaamminechromium(III) chloride. Calculate the maximum amount of hexaamminechromium(III) chloride that the student could prepare from the 1.00-g sample of ammonium dichromate.
2. When silver nitrate is added to a solution of a substance with the empirical formula  $\text{CoCl}_3 \cdot 5\text{NH}_3$ , how many moles of  $\text{AgCl}$  will be precipitated per mole of cobalt present? Why?
3.  $\text{Co(III)}$  occurs in octahedral complexes with the general empirical formula  $\text{CoCl}_m \cdot n\text{NH}_3$ . What values of  $n$  and  $m$  are possible? What are the values of  $n$  and  $m$  for the complex that precipitates 1 mole of  $\text{AgCl}$  for every mole of  $\text{Co}$  present?
4. How many ions per mole will you expect to find in solution when a compound with the empirical formula  $\text{PtCl}_4 \cdot 3\text{NH}_3$  is dissolved in water? What about  $\text{PtCl}_2 \cdot 3\text{NH}_3$ ? Draw diagrams of each of the complex cations.
5. Each of the following is dissolved in water to make a  $0.001M$  solution. Rank the compounds in order of decreasing conductivity of their solutions:  $\text{K}_2\text{PtCl}_6$ ,  $\text{Co(NH}_3)_6\text{Cl}_3$ ,  $\text{Cr(NH}_3)_4\text{Cl}_3$ ,  $\text{Pt(NH}_3)_6\text{Cl}_4$ . Rewrite each compound by using brackets to distinguish the complex ion present in aqueous solution.

## Formulas and nomenclature

6. Give the systematic names of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ ,  $\text{K}_3\text{Cr}(\text{CN})_6$ , and  $\text{Na}_2\text{CoCl}_4$ .
7. Write the formulas for each of the following compounds by using brackets to distinguish the complex ion from the other ions: (a) hexaaquanickel(II) perchlorate; (b) trichlorotriammineplatinum(IV) bromide; (c) dichlorotetraammineplatinum(IV) sulfate; (d) potassium monochloropentacyanoferrate(III).
8. Write the formula for each of the following by using brackets to distinguish the complex ion: (a) hydroxopentaaquoaluminum(III) chloride; (b) sodium tricarbonatocobaltate(III); (c) sodium hexacyanoferrate(II), (d) ammonium hexanitrocobaltate(III).

## Isomers

9. How many isomers are there of the compound  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ? Sketch them.
10. Sketch all the geometrical and optical isomers of  $\text{PtCl}_2\text{I}_2(\text{NH}_3)_2$ .
11. How many geometrical and optical isomers are there of the complex ion  $\text{Co}(\text{en})_2\text{Cl}_2^+$ ? Of these, how many pairs of isomers are there differing only by a mirror reflection? How many isomers have a plane of symmetry and hence do not exist in pairs of optical isomers?
12. Repeat Problem 11 with propylenediamine substituted for ethylenediamine. Ignore optical isomers from the propylene carbon.

13. How many different *structural* isomers are there of a substance with the empirical formula  $\text{FeBrCl} \cdot 3\text{NH}_3 \cdot 2\text{H}_2\text{O}$ ? For each different structural isomer, how many different *geometrical* isomers exist? How many of these can be grouped into right-handed and left-handed pairs of *optical isomers*?

## Electronic structure

14. The  $\text{Co}^{2+}$  ion in aqueous solution is octahedrally coordinated and paramagnetic, with three unpaired electrons. Which one or ones of the following statements follow from this observation: (a)  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  is square planar; (b)  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  is tetrahedral; (c)  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  has a  $\Delta_o$  that is larger than the electron-pairing energy; (d) the  $d$  levels are split in energy and filled as follows:  $(t_{2g})^5(e_g)^2$ ; (e) the  $d$  levels are split in energy and filled as follows:  $(t_{2g})^6(e_g)^1$ .
15. The coordination compound potassium hexafluorochromate(III) is paramagnetic. What is the formula for this compound? What is the configuration of the Cr  $d$  electrons?
16. How many unpaired electrons are there in  $\text{Cr}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Co}^{2+}$  in (a) a strong octahedral ligand field and (b) a very weak octahedral field?
17. A low-spin tetrahedral complex has never been reported, although numerous high-spin complexes of this geometry have been prepared. What conclusion may be drawn regarding the magnitude of  $\Delta_t$  from this fact?
18. Certain platinum complexes have been found to be active antitumor agents.

- Among these are *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>, *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and *cis*-Pt(en)Cl<sub>2</sub> (none of the trans isomers is effective). Use valence bond theory to account for the diamagnetism of these complexes. Are these inner or outer complexes? What kinds of hybrid orbitals are used in bonding?
- What is the *d*-orbital electronic configuration of Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>? How many unpaired electrons are present? If six Br<sup>-</sup> groups were substituted for the six NH<sub>3</sub> groups to give CrBr<sub>6</sub><sup>3-</sup>, would you expect Δ<sub>o</sub> to increase or decrease?
  - Diagram the electronic arrangements in Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> for both the valence bond and crystal field models. Briefly compare these models.
  - For each of the following, sketch the *d*-orbital energy levels and the distribution of *d* electrons among them:
    - Ni(CN)<sub>4</sub><sup>2-</sup> (square planar)
    - Ti(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> (octahedral)
    - NiCl<sub>4</sub><sup>2-</sup> (tetrahedral)
    - CoF<sub>6</sub><sup>3-</sup> (high-spin complex)
    - Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> (low-spin complex)
  - Co(III) can occur in the complex ion Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. (a) What is the geometry of this ion? In the valence bond theory, what Co orbitals are used in making bonds to the ligands? (b) What is the systematic name for the chloride salt of this ion? (c) Using crystal field theory, draw two possible *d*-electron configurations for this ion. Assign to them the labels *high spin*, *low spin*, *paramagnetic*, *diamagnetic*. Which two labels are correct for the ammine complex? (d) Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> can be reduced to Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> by adding an electron. Draw the preferred *d*-electron configuration for this reduced ion. Why is it preferred?
  - Pt(II) can occur in the complex ion PtCl<sub>4</sub><sup>2-</sup>. (a) What is the geometry of this ion? In the valence bond theory, what Pt orbitals are used in making bonds to the Cl<sup>-</sup> ions? (b) What is the systematic name for the sodium salt of this ion? (c) Using crystal field theory, draw the *d*-electron configuration for this ion. Is the ion paramagnetic or diamagnetic? (d) Pt(II) can be oxidized to Pt(IV). Draw the *d*-electron configuration for the chloride complex ion of Pt(IV). Explain the difference between this configuration and that of Pt(II). Is the Pt(IV) chloride complex ion paramagnetic or diamagnetic?

### Formation constants

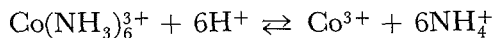
- A solution is prepared that is 0.025*M* in tetraamminecopper(II), Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>. What will be the concentration of Cu<sup>2+</sup> hydrated copper ion if the ammonia concentration is 0.10, 0.50, 1.00, and 3.00*M* respectively? What ammonia concentration is needed to keep the Cu<sup>2+</sup> concentration less than 10<sup>-15</sup>*M*?
- From the data in Table 20-8, calculate the pH of a 0.10*M* solution of Cr<sup>3+</sup> ion. *Hint*: Consider the reactions
 
$$\text{Cr}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Cr}(\text{OH})^{2+} + \text{H}^+ \quad K = ?$$

$$\text{Cr}^{3+} + \text{OH}^- \rightleftharpoons \text{Cr}(\text{OH})^{2+} \quad K_f = 1 \times 10^{10}$$

$$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \quad K_w = ?$$
- From the data in Table 20-8, calculate the pH of 0.10*M* solutions of Mn<sup>2+</sup>, Fe<sup>2+</sup>, and Ag<sup>+</sup>. See Problem 25 if you need help. From the results of these two problems, can you correlate the "acidity" of positive ions with their charge?



27. The ion  $\text{Co}(\text{NH}_3)_6^{3+}$  is very stable, with  $K_f = 2.3 \times 10^{34}$ . If the hydrolysis constant for the ammonium ion,  $K_b$ , is  $5 \times 10^{-10}$ , show that the equilibrium in the reaction

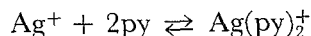


lies far to the right. Then why does  $\text{Co}(\text{NH}_3)_6^{3+}$  remain intact in hot concentrated sulfuric acid?

28. What is the concentration of chromate ion,  $\text{CrO}_4^{2-}$ , when solid  $\text{BaCrO}_4$  is placed in contact with water? What is the chromate ion concentration when solid  $\text{BaCrO}_4$  is placed in contact with a solution of  $0.2M$   $\text{Ba}^{2+}$ ?  $\text{BaCrO}_4$  can be dissolved in a solution of pyridine (py), producing the complex  $\text{Ba}(\text{py})_2^{2+}$ , with a formation constant of  $4 \times 10^{12}$ . If  $0.10M$   $\text{BaCrO}_4$  is dissolved in a solution with a constant pyridine concentration of  $1.0$  mole liter $^{-1}$ , what is the concentration of  $\text{Ba}^{2+}$  ion?
29. What is the solubility of  $\text{Cu}(\text{OH})_2$  in pure water? In buffer at pH 6? Copper(II) forms a complex with  $\text{NH}_3$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$ , with  $K_f = 1.0 \times 10^{12}$ . What concentration of ammonia must be maintained in a solution to dissolve

$0.10$  mole of  $\text{Cu}(\text{OH})_2$  per liter of solution?

30. Calculate the silver ion concentration in a saturated solution of  $\text{AgCl}$  in water. Silver ions react with an excess of  $\text{Cl}^-$  as follows:
- $$\text{Ag}^+ + 2\text{Cl}^- \rightleftharpoons \text{AgCl}_2^- \quad K_f = 1 \times 10^2$$
- Calculate the concentration of  $\text{AgCl}_2^-$  and show that you were justified in ignoring the complex ion formation in calculating the silver ion concentration at the beginning of the problem.
31. The formation constant for the pyridine complex of silver



is  $K_f = 1 \times 10^{10}$ . If a solution is initially  $0.10M$  in  $\text{AgNO}_3$  and  $1.0M$  in pyridine, what are the equilibrium concentrations of silver ion, pyridine, and the complex ion?

32. In  $0.10M$   $\text{NaCl}$ , the concentration of silver ions cannot exceed  $10^{-9}$  mole liter $^{-1}$  because  $\text{AgCl}$  is so slightly soluble. What concentration of pyridine must be added to dissolve  $0.10$  mole of  $\text{AgCl}$  per liter of solution?

## Postscript: Coordination Complexes and Living Systems

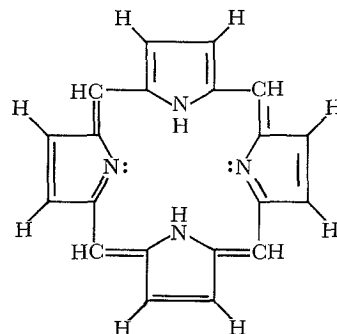
Since we first realized that we lived on a planet circling one sun among many, rather than being fixed at the center of creation, we have wondered whether we were a one-time miracle (or accident) or part of a general pattern of living things. The astronomer Johannes Kepler (1571–1630) wrote a science fiction novel, *Somnium*, in which he described life on the moon as seen with a new invention, the telescope. He imagined intelligent humanoids and fast-growing plant life that sprouted, matured, and died in the course of one lunar day.

Today we know that any humanoids on the moon or Mars will be immigrants. However, it is possible that we will find the remains of simple life forms or the possible precursors of life forms on Mars, and that these will suggest something about how life evolved on earth. For years, scientists have extracted and analyzed organic matter from meteorites. They have debated whether this organic matter is truly meteoric or only terrestrial contamination, and whether it is of biological origin.

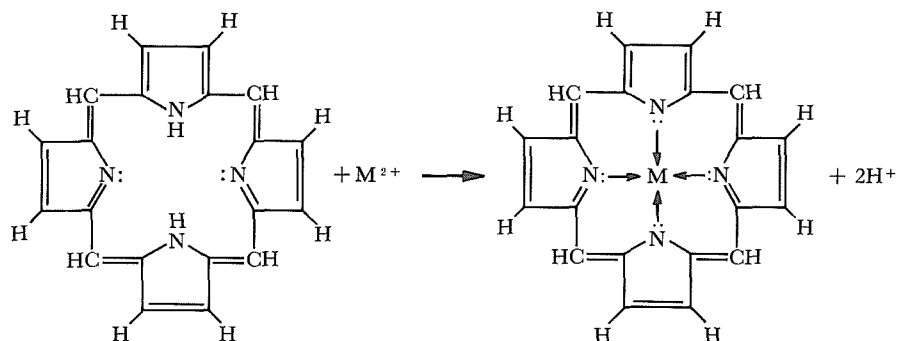
One of the compounds whose presence in meteorite samples is most suggestive of extraterrestrial life is porphin (Figure 20-18), and its derivatives, the *porphyrins*. The porphyrins are flat molecules that can act as tetradentate chelating groups\* for metals such as Mg, Fe, Zn, Ni, Co, Cu, and Ag in a square planar complex as in Figure 20-19. The iron complex with the side chains shown in Figure 20-20 is called *heme*. The magnesium complex of porphyrin, with the organic side chain shown in Figure 20-21, is chlorophyll.

**Figure 20-18**

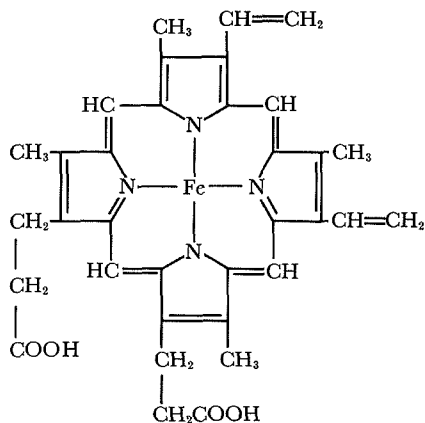
The porphin molecule. Porphin molecules with side groups substituted at the eight outermost hydrogen atoms around the ring are called porphyrins. A vertex where several bond lines meet, without a letter symbol, by convention is assumed to be a carbon atom. The four carbon atoms explicitly shown here by the symbol C could have been left out.



\*The name *chelate* comes from the Greek for “claw”; *tetradentate* literally means “four-toothed.” Chelates with twofold, threefold, or fourfold coordination to the metal ion are called *bidentate*, *tridentate*, or *tetradentate*. It may seem illogical to speak of claws with teeth, but lovers of lobster or crab will appreciate the usage.

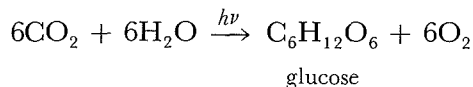
**Figure 20-19**

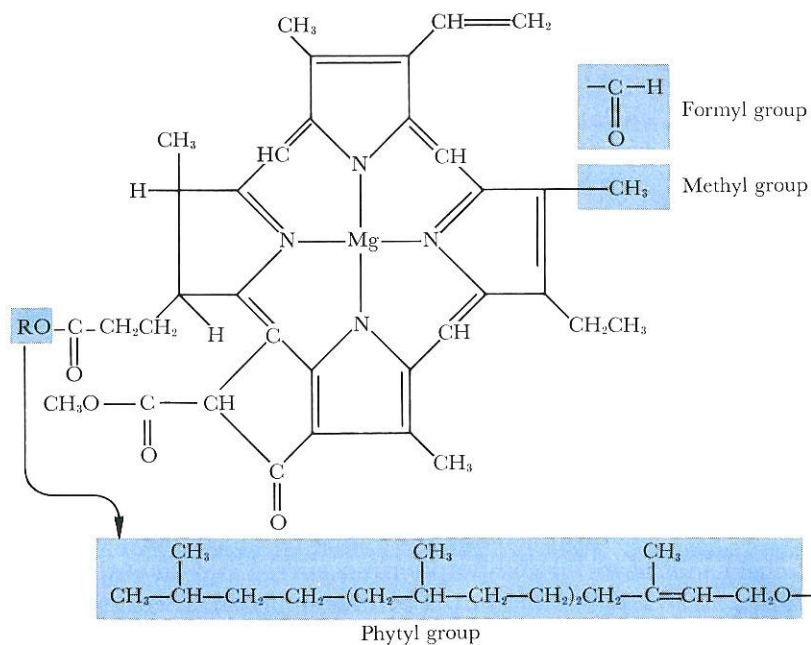
A porphyrin molecule can act as a tetradentate chelating group around an ion of a metal such as Mg, Fe, Zn, or Cu.

**Figure 20-20**

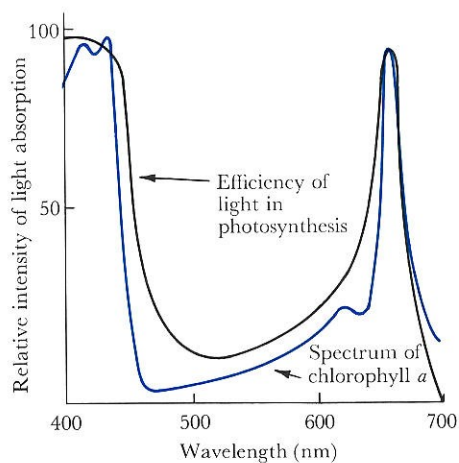
The iron—porphyrin complex with the side chains shown here is called a *heme group*.

These two compounds, chlorophyll and heme, are the key components in the elaborate mechanism by which solar energy is trapped and converted for use by living organisms. We have seen that a peculiar feature of transition-metal complexes is their closely spaced *d* levels, which permit them to absorb light in the visible part of the spectrum and to appear colored. The porphyrin ring around the  $\text{Mg}^{2+}$  ion in chlorophyll serves the same function. Chlorophyll in plants can absorb photons of visible light and go to an excited electronic state (Figure 20-22). This energy of excitation can initiate a chain of chemical synthesis that ultimately produces sugars from carbon dioxide and water:




**Figure 20-21**

The magnesium—porphyrin derivative shown here is called chlorophyll *a*, and is the essential molecule in photosynthesis. Chlorophyll *b* has a formyl group in place of the methyl group.


**Figure 20-22**

Chlorophyll *a* absorbs visible light except in the region around 500 nm (green light), and thus appears green.

Most compounds of the representative elements cannot absorb visible light; there are no electronic energy levels close enough together. Neither can  $\text{Mg}^{2+}$  alone. But the coordination complex of  $\text{Mg}^{2+}$  plus its square planar chelating agent has such levels, and chlorophyll is able to trap light and to use its energy in chemical synthesis.

Scientists now believe that life evolved on earth in the presence of a *reducing* atmosphere, an atmosphere with ammonia, methane, water, and carbon dioxide but *no* free oxygen. Free oxygen would degrade organic compounds faster than they could be synthesized by natural processes (electrical discharge, ultraviolet radiation, heat, or natural radioactivity). In the absence of free oxygen, such organic compounds would accumulate in the oceans for eons until finally a packaged, localized bit of chemicals developed that we would call “living.”

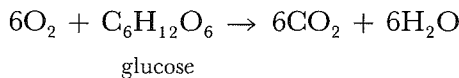
Living organisms, once developed, would exist by degrading these naturally occurring organic compounds for their energy. The amount of life on the planet would be limited severely if this were the only source of energy. Fortunately for us, around 3 billion years ago, the right combination of metal and porphyrin occurred and an entirely new source of energy was tapped—the sun. The first step that lifted life on earth above the humble role of a scavenger of high-energy organic compounds was an application of coordination chemistry.

Unfortunately, **photosynthesis** (as the chlorophyll photon-trapping process is called) liberates a dangerous by-product, oxygen. Oxygen was not only useless to these early organisms, it competed with them by oxidizing the naturally occurring organic compounds before they could be oxidized within the metabolism of the organisms. Oxygen was a far more efficient scavenger of high-energy compounds than living matter was. Even worse, the ozone ( $\text{O}_3$ ) screen that slowly developed in the upper atmosphere cut off the supply of ultraviolet radiation from the sun and made the natural synthesis of more organic compounds even slower. From all contemporary points of view, the appearance of free oxygen in the atmosphere was a disaster.

As so often happens, life bypassed the obstacle, absorbed it, and turned a disaster into an advantage. The waste products of the original simple organisms had been compounds such as lactic acid or ethanol. These are not nearly so energetic as sugars, but they can release large amounts of energy if oxidized completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Living organisms evolved that were able to “fix” the poisonous  $\text{O}_2$  as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and to gain, in the bargain, the energy of combustion of what were once its waste products. Aerobic metabolism had evolved.

Again, the significant development was an advance in coordination chemistry. The central components in the new machinery for aerobic metabolism, by which the combustion of organic molecules was brought to completion, are the **cytochromes**. These are molecules in which an iron atom is complexed with a porphyrin to make a heme (Figure 20-20), and

the heme is surrounded with protein. The iron atom changes from iron(II) to iron(III) and back again as electrons are transferred from one component in the chain to another. The entire aerobic machinery is a carefully interlocked set of oxidation–reduction or redox reactions, in which the overall result is the reverse of the photosynthetic process:



The energy liberated is stored in the organism for use as needed. The entire, elaborate, chlorophyll–cytochrome system can be regarded as a mechanism for converting the energy of solar photons into stored chemical energy in the muscles of living creatures.

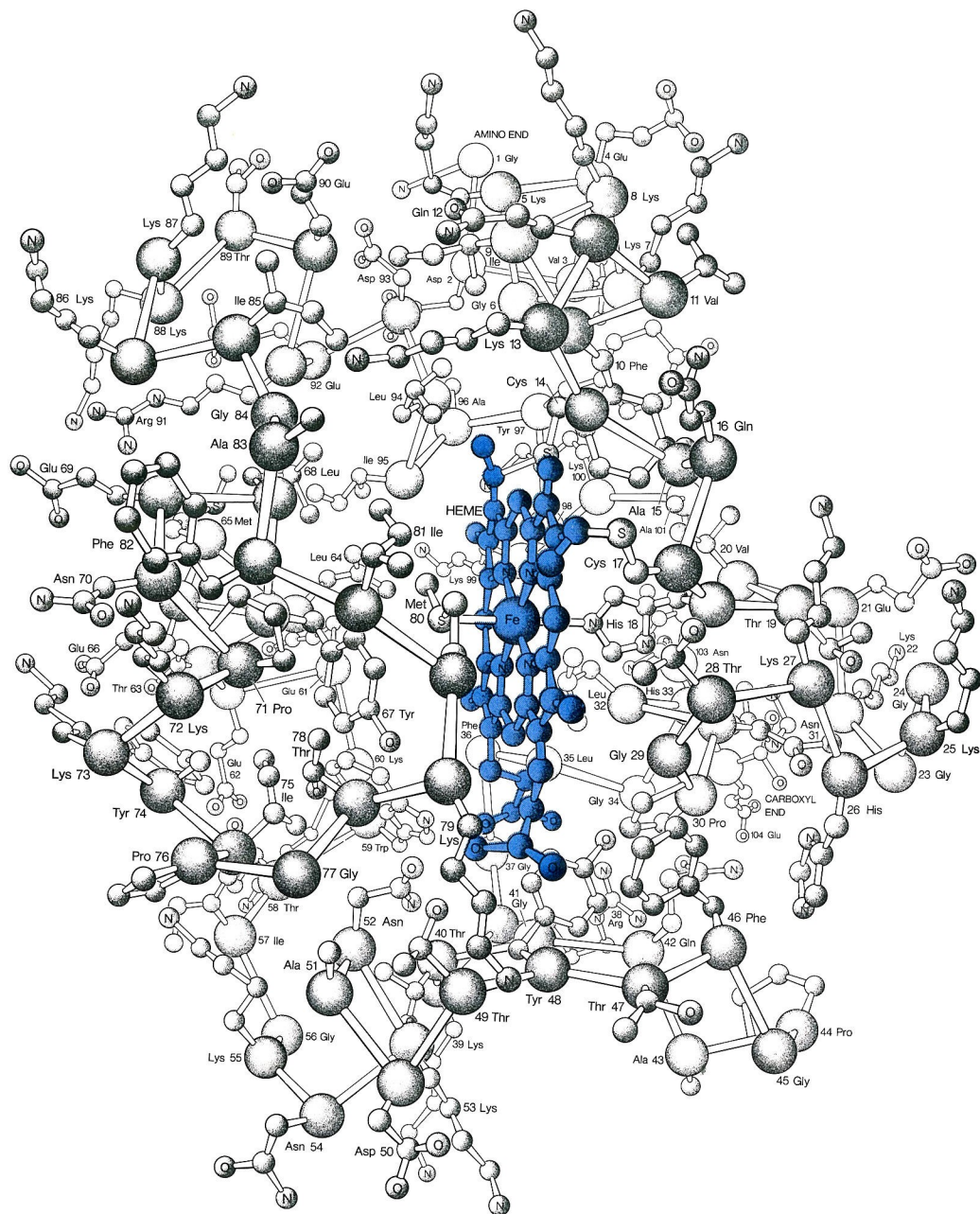
Iron atoms usually exhibit octahedral coordination. What happens to the two coordination positions above and below the plane of the porphyrin ring? In cytochrome *c*, the heme group sits in a crevice in the surface of the protein molecule (Figure 20-23). From each wall of this crevice, one new ligand extends toward the heme: on one side a nitrogen lone electron pair from a *histidine* side chain on the protein, and on the other side a sulfur lone pair from a *methionine* side chain (Figure 20-24). Therefore, the octahedral coordination positions on the iron are directed to five nitrogen atoms and one sulfur atom.

How does the cytochrome *c* molecule operate? This is not yet known. The structure of the version with iron(III) was only determined in 1969 by x-ray diffraction, and that of the reduced iron in 1971. The ligands in the complex around the iron, and the protein wrapped around the whole structure, both modify the redox chemistry of the iron atom and ensure that oxidation and reduction are coupled to the earlier and later links in the terminal oxidation chain.

There is one more step in the story of metal–porphyrin complexes. Parkinson might add a subclause to his well-known law: Organisms expand to accommodate the food supplies available. With the guarantee of new energy sources, multicelled organisms evolved. At this point arose the problem, not of obtaining foods or oxygen, but of transporting oxygen to the proper place in the organism. Simple gaseous diffusion through body fluids will work for small organisms but not for large, multicelled creatures. Again, a natural limit was placed on evolution.

For the third time, the way out of the impasse was found with coordination chemistry. Molecules of iron, porphyrin, and protein evolved, in which the iron could *bind* a molecule of oxygen without being oxidized by it. The oxidation of Fe(II) was, in a sense, “aborted” after the first binding step. Oxygen was merely carried along, to be released under the proper conditions of acidity and oxygen scarcity. Two compounds evolved, *hemoglobin*, which carries O<sub>2</sub> in the blood, and *myoglobin*, which receives and stores O<sub>2</sub> in the muscles until it is needed in the cytochrome process.



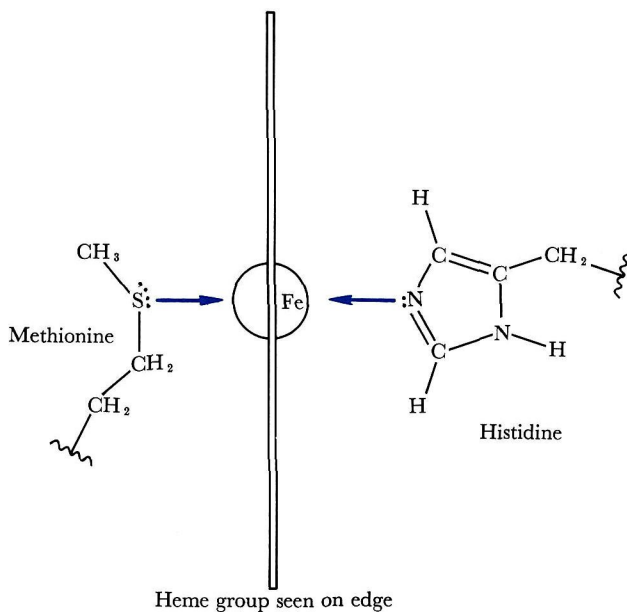


**Figure 20-23**

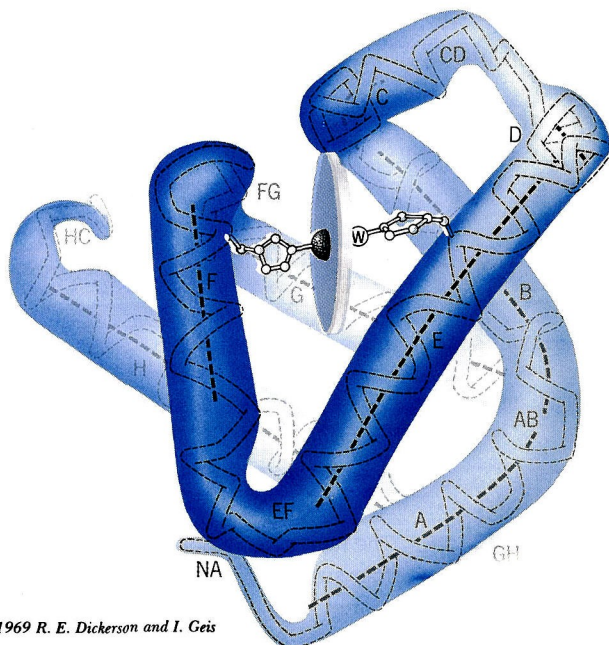
Cytochrome *c* is a globular protein with 104 amino acids in one protein chain and an iron-containing heme group. In this schematic drawing, each amino acid is represented by a numbered sphere, and only key amino acid side chains are shown. The heme group is seen nearly edgewise in a vertical crevice in the molecule. Copyright © 1972 R. E. Dickerson and I. Geis: *Scientific American*, April 1972, page 62.

**Figure 20-24**

The iron atom in cytochrome *c* is octahedrally coordinated through five bonds to nitrogen atoms and one to a sulfur atom. One nitrogen atom and the sulfur atom come from side groups on the protein chain. The other four nitrogen atoms are from the porphyrin ring of the heme.

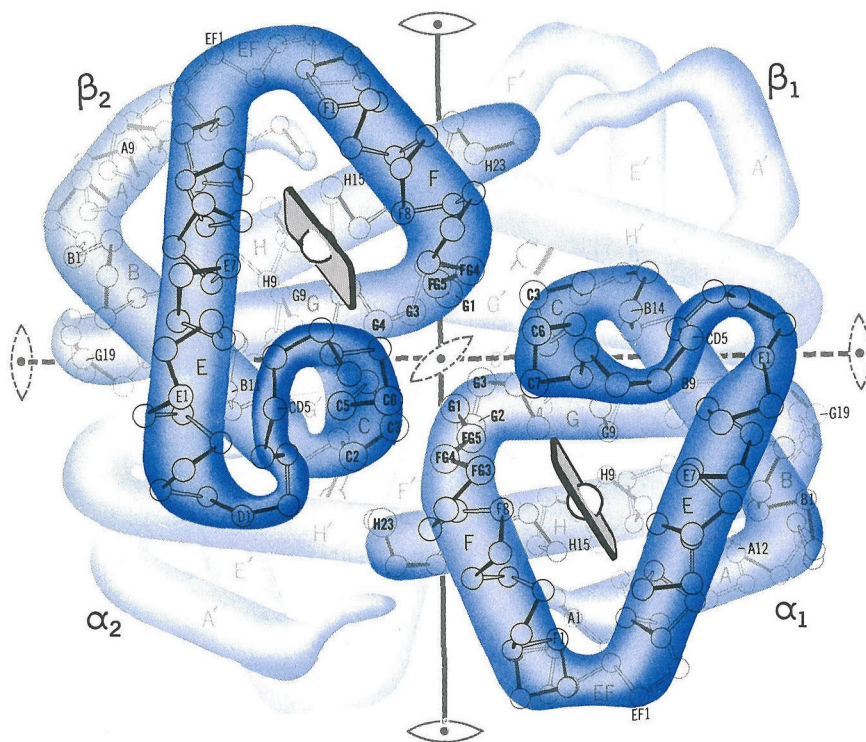

**Figure 20-25**

The myoglobin molecule is a storage unit for an oxygen molecule in muscle tissue. The heme group is represented by a flat disk, and the iron atom by a ball at the center. The circled W marks the binding site for O<sub>2</sub>. The path of the polypeptide chain is shown by double dashed lines.



The myoglobin molecule is depicted in Figure 20-25. As in cytochrome *c*, four of the six octahedral iron positions are taken by heme nitrogen atoms. The fifth position has the nitrogen atom of a histidine. However, the sixth position has *no ligand*. This is the place where the oxygen molecule binds, marked by the circled W. In myoglobin, the iron is in the Fe(II) state. If the iron is oxidized, the molecule is inactivated and a water molecule occupies the oxygen position.

Hemoglobin is a package of four myoglobinlike molecules (Figure 20-26). In the past decade, these two structures have been determined by x-ray crystallography. It has become apparent that the four subunits of hemoglobin shift by 7 Å relative to one another when oxygen binds. Hemoglobin and myoglobin now become a model system for transition-metal chemists to study. Why does binding at the sixth ligand site of the iron



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**Figure 20-26**

The hemoglobin molecule is the carrier of oxygen in the bloodstream. It is built from four subunits, each of which is constructed like a myoglobin molecule. This figure and that of myoglobin are reprinted from R. E. Dickerson and I. Geis, *The Structure and Action of Proteins*, W. A. Benjamin, Menlo Park, Calif., 1969.



complex cause the protein subunits to rearrange? Why does the oxygen molecule fall away from hemoglobin in an acid environment (such as in oxygen-poor muscle tissue)? How is the coordination chemistry of hemoglobin and myoglobin so carefully meshed that myoglobin binds oxygen just as hemoglobin releases it at the tissues?

Heme, or iron porphyrin, is also at the active sites of enzymes such as peroxidase and catalase. Many other transition metals are essential components in enzyme catalysis; we shall discuss some of them in Chapter 21. With the evolution of myoglobin and hemoglobin, the size limitation was removed from living organisms. Thereafter, all the multicelled animals that we ordinarily see around us evolved. In the sense that transition metals and double-bonded organic ring systems such as porphyrin are uniquely suited for absorbing visible light, and their combinations have a particularly rich redox chemistry, life is indeed applied coordination chemistry.

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