

# NONMETALS, METALLOIDS, METALS, AND METAL COMPLEXES

21

A chemical found in many brands of shampoo is EDTA, which is able to form stable complexes with ions found in hard water. These ions, which include  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , can interfere with the action of soaps and some detergents and inhibit the formation of a nice lather, like the one shown here. Complexes of metal ions with EDTA and other substances are studied in detail in this chapter. (*Beauty Photo studio/Age Fotostock America, Inc.*)



## CHAPTER OUTLINE

**21.1** Nonmetals and metalloids are found as free elements and in compounds

**21.2** Nonmetallic elements in their free states have structures of varying complexity

**21.3** Metals are prepared from compounds by reduction

**21.4** Metallurgy is the science and technology of metals

**21.5** Complex ions are formed by many metals

**21.6** The nomenclature of metal complexes follows an extension of the rules developed earlier

**21.7** Coordination number and structure are often related

**21.8** Isomers of coordination complexes are compounds with the same formula but different structures

**21.9** Bonding in transition metal complexes involves  $d$  orbitals

**21.10** Metal ions serve critical functions in biological systems

**THIS CHAPTER IN CONTEXT** In previous chapters you learned many of the concepts that chemists have used to develop their understanding of how the elements react with each other and the kinds of compounds they produce. For example, in our discussions of chemical kinetics, you learned how various factors affect the rates of reactions, and in our study of thermodynamics you learned how enthalpy and entropy changes affect the possibility of observing chemical changes. Our focus, however, was primarily on the concepts themselves, with examples of chemical behavior being used to reinforce and justify them. With these concepts available to us now, we will direct

our emphasis in the opposite direction and examine some of the physical and chemical properties of the elements and their compounds.

Our intent in this chapter is not to be encyclopedic. Instead, we will concentrate our attention on several aspects of the chemistries of the elements. We will study how the elements occur in nature and explore the methods used to obtain them in their free (uncombined) states. For metals, their extraction from compounds constitutes a vast commercial enterprise under the general heading of *metallurgy*.

In their free states, the nonmetallic elements exist in a broad range of structures, ranging from simple atoms to very complex molecular forms. We will study how the relative tendencies of the nonmetals to form strong  $\sigma$  and  $\pi$  bonds influences the kinds of structures observed.

The last part of the chapter is devoted to an in-depth look at complex ions of metals, a topic first introduced in Chapter 17. These substances, which have applications from food preservatives to catalyzing biochemical reactions, have a variety of structures and colors. We will study the kinds of substances that combine with metals to form complexes with various geometries, how complexes are named, and how the electronic structures and colors of complexes can be explained.

## 21.1 NONMETALS AND METALLOIDS ARE FOUND AS FREE ELEMENTS AND IN COMPOUNDS

As you learned in Chapter 2, the nonmetals and metalloids are located at the right side of the periodic table (Figure 21.1). As suggested by their positions in the table, metalloids have properties that place them between those of metals and nonmetals. For instance, metalloids have a sheen that gives them the appearance of a metal, and they exhibit weak electrical conductivity (many are semiconductors). Chemically, however, they behave more like nonmetals. For example, metalloids combine with the more active metals in Groups IA and IIA to form compounds that are saltlike, containing anions such as  $\text{Si}^{4-}$ ,  $\text{As}^{3-}$ , and  $\text{Te}^{2-}$  (more complex anions are also formed), and they also combine with nonmetals to form molecular compounds in which their oxidation numbers are positive.

### Nonmetals occur in compounds and in the free state

Most chemical compounds contain one or more nonmetals. In compounds involving metals, nonmetals occur as either simple anions or in polyatomic anions. Many other compounds are composed of only nonmetals in combinations that range from simple (such as HCl) to very complex (such as DNA).

It is difficult to make general statements about the preparation of the elemental nonmetals. The noble gases, for example, are always found uncombined in nature. The atmosphere is the major source of the noble gases, even though their concentrations in air



A sample of crystalline elemental silicon exhibits a metallic sheen. (Jeff J. Daby/*Fundamental Photographs*.)

																		Nonmetals																						
H																	He																							
Li	Be											B	C	N	O	F	Ne																							
Na	Mg											Al	Si	P	S	Cl	Ar																							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																							
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																							
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																							
Fr	Ra																																							
												Metals					Metalloids																							

FIG. 21.1 Distribution of nonmetals and metalloids in the periodic table.

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▣ Noble gas atoms have completed *s* and *p* subshells in their outer shells and are very unreactive. They have very little tendency to form bonds to other atoms.

**Elemental sulfur in nature.**

Sulfur is one of the substances released from the earth during volcanic eruptions. Here we see molten sulfur pouring from a vent in the Kawah Ijen volcano in Indonesia. (© API/Explorer/Photo Researchers.)

▣ Remember, the larger the reduction potential, the greater is the tendency of the substance to acquire electrons and, therefore, to be an oxidizing agent.

are very small. Physical methods are used to separate them from other gases with which they're mixed. Of the noble gases, only helium and radon are not obtained primarily from the atmosphere. Helium is found in gaseous deposits beneath the earth's crust where it has collected after being produced by the capture of electrons by alpha particles (helium nuclei,  $\text{He}^{2+}$ ), which are formed during the radioactive decay of elements such as uranium. Radon itself is radioactive and is produced by the radioactive decay of radium.



Since radon spontaneously decomposes into other elements relatively quickly ( $t_{1/2} = 3.8$  days), it occurs only in minute quantities in nature.

Other nonmetals, while present in many naturally occurring compounds, also are found extensively in the free state as well. For instance, our atmosphere is composed primarily of elemental nitrogen,  $\text{N}_2$  (about 80%), and oxygen,  $\text{O}_2$  (about 20%). Although nitrogen and oxygen are also found in a vast number of compounds, certainly their most economical source is simply the air itself. Sulfur and carbon are two other elements that occur naturally in both the combined and free states. There are, for instance, many naturally occurring sulfates (for example,  $\text{BaSO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and sulfides ( $\text{FeS}_2$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{PbS}$ , and  $\text{ZnS}$ ). In the free state, sulfur has been found in large underground deposits from which it is mined by forcing superheated water under pressure into the sulfur, causing the sulfur to melt. Once molten, the sulfur–water mixture is foamed to the surface using compressed air. Sulfur is also deposited on rock surfaces near volcanic vents and is called *brimstone*.

Turning to carbon, we find that most of its naturally occurring compounds are carbonates, for example, limestone ( $\text{CaCO}_3$ ). In the free state most carbon is found in either of its two principal forms, diamond and graphite.

**Nonmetals are obtained from compounds by either oxidation or reduction**

Because nonmetals combine with each other as well as with metals, no simple generalizations can be made concerning their recovery from compounds. When combined with a metal, the nonmetal is found in a negative oxidation state, so an oxidation must be brought about to generate the free element. For example, the halogens  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  can be conveniently prepared in the laboratory by reacting one of their salts with an oxidizing agent such as  $\text{MnO}_2$  in an acidic solution:



where  $X = \text{Cl}, \text{Br}, \text{or I}$ .

As you learned in Chapter 19, chlorine is a very important industrial chemical, and vast quantities (approximately 10 million tons annually) are produced by electrolysis of  $\text{NaCl}$ , both aqueous and molten. Chlorine is used in large amounts in water treatment, in the manufacture of pharmaceuticals, pesticides, and solvents, and in the production of vinyl chloride, which is used to manufacture vinyl plastics.

The halogens themselves can also serve as oxidizing agents in replacement reactions. Since the tendency to acquire electrons (electronegativity) decreases as we proceed downward in a group, the ability of the halogen to serve as an oxidizing agent decreases too. This is seen in their reduction potentials (Table 21.1), which decrease from fluorine to iodine. As a result, a given halogen is a better oxidizing agent than the other halogens below it in Group VIIA and is able to displace them from their binary compounds with metals. Thus

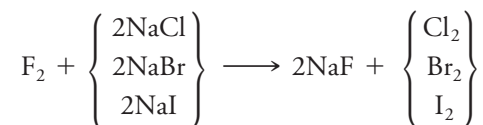
**TABLE 21.1** Reduction Potentials of the Halogens

Reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{F}^-(\text{aq})$	2.87
$\text{Cl}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	1.36
$\text{Br}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	1.07
$\text{I}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{I}^-(\text{aq})$	0.54

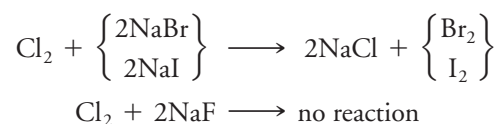
## 21.1 Nonmetals and Metalloids Are Found as Free Elements and in Compounds 857

F<sub>2</sub> will displace Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, while Cl<sub>2</sub> will displace only Br<sup>-</sup> and I<sup>-</sup> but not F<sup>-</sup>, and so on. This is illustrated by the following typical reactions.

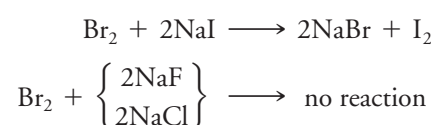
For fluorine:



For chlorine:



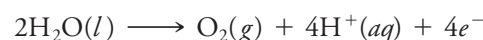
For bromine:



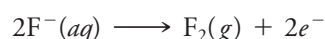
■ Iodine cannot displace any of the other halogens from their compounds.

The relative oxidizing power of the halogens is used in the commercial preparation of Br<sub>2</sub>. Bromine is isolated from seawater and brine solutions pumped from deep wells by passing Cl<sub>2</sub>, followed by air, through the liquid. The Cl<sub>2</sub> oxidizes the Br<sup>-</sup> to Br<sub>2</sub> and the air sweeps the volatile Br<sub>2</sub> from the solution.

Fluorine, because of its position as the most powerful chemical oxidizing agent, can only be obtained by electrolytic oxidation. This process must be carried out in the absence of water because water is more easily oxidized than the fluoride ion. In an aqueous solution, therefore, the oxidation

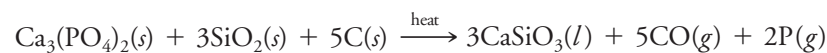


will occur in preference to



In practice, a molten mixture of KF and HF, which has a lower melting point than KF alone, is electrolyzed, producing H<sub>2</sub> at the cathode and F<sub>2</sub> at the anode.

Nonmetals can also be extracted from their compounds by reduction if the nonmetal happens to exist in a positive oxidation state. For instance, elemental phosphorus is produced from a phosphate such as Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, where it exists in the +5 oxidation state. To obtain the phosphorus, the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is heated to approximately 1500 °C in an electric furnace with a mixture of carbon and SiO<sub>2</sub> (sand).<sup>1</sup>



In this reaction, the SiO<sub>2</sub> is present to combine with the calcium to form calcium silicate, CaSiO<sub>3</sub>, a compound with a relatively low melting point. Because the reduction of SiO<sub>2</sub> by carbon requires much higher temperatures (>1900 °C), only the phosphorus is reduced to the element at the lower temperatures used in the reaction.

### Metalloids are found in nature in compounds

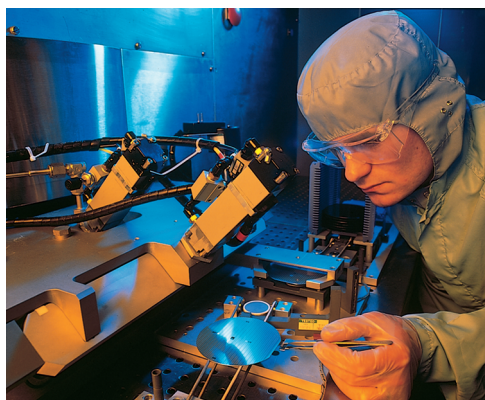
In most of their compounds, the metalloids are combined with nonmetals, either in a molecular structure such as SiO<sub>2</sub> (found in silica sand) or in an oxoanion such as those found in the silicates (found in many kinds of rocks). In such combinations, the

■ H<sup>+</sup> is more easily reduced than K<sup>+</sup>, which is why H<sub>2</sub> appears at the cathode.

■ Most metal silicates contain polymeric anions with oxygen bridges between silicon atoms. Silicon dioxide itself has a complex structure consisting of SiO<sub>4</sub> tetrahedra in which each oxygen atom is shared by two silicon atoms.

<sup>1</sup>Phosphorus was first produced in 1669 when alchemist Hennig Brandt heated a mixture of sand and dried urine. He condensed the vapors by passing them through water to give the new element. It was named phosphorus from the Greek *phosphoros* (light bringer) because the solid in a sealed bottle glowed in the dark. The glow is actually the result of slow oxidation of the phosphorus surface by residual oxygen in the container.

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**Uses of silicon as a semiconductor.** A technician checks a silicon wafer during one stage in the manufacture of computer “chips.” The silicon disk contains hundreds of individual chips, each consisting of thousands of electronic components. After all of the individual components have been added, the disk will be cut up to give separate chips that will be incorporated into parts for computer circuits. (David Parker/Photo Researchers.)

There are few aspects of modern life that are not impacted significantly by computer circuits embedded in silicon or germanium.

metalloid has a lower electronegativity than the nonmetal, so the metalloid exists in a positive oxidation state. To obtain the metalloid in its elemental state, therefore, a chemical reduction must be carried out. This is usually accomplished with either hydrogen or carbon as the reducing agent. For example, boron is obtained by passing a mixture of  $\text{BCl}_3$  vapor and hydrogen gas over a hot wire, on which the following reaction takes place.

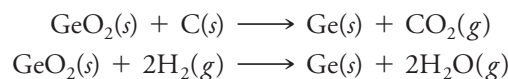


On the other hand, elemental silicon is produced by heating  $\text{SiO}_2$  with carbon in an electric furnace, where the reaction

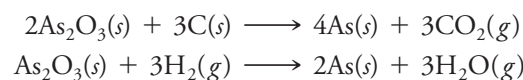


occurs once the temperature exceeds approximately  $3000^\circ\text{C}$  (below this temperature the reverse reaction is actually favored).

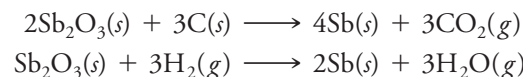
The remaining metalloids may be obtained from their oxides by heating them with either carbon or hydrogen; for example,



Similarly, we have



and



As you may recall, in very pure form, silicon and germanium have widespread applications in the electronics industry, where they are used in transistors and photoconduction devices. Sophisticated electronic circuits embedded in tiny wafers of silicon make possible a myriad of computer-controlled devices that we’ve come to take for granted, such as laptop computers; CD, DVD, and MP3 players; handheld computer games; computers that enable automobile engines to manage exhaust emission; cell phones; and digital cameras (and the list goes on).

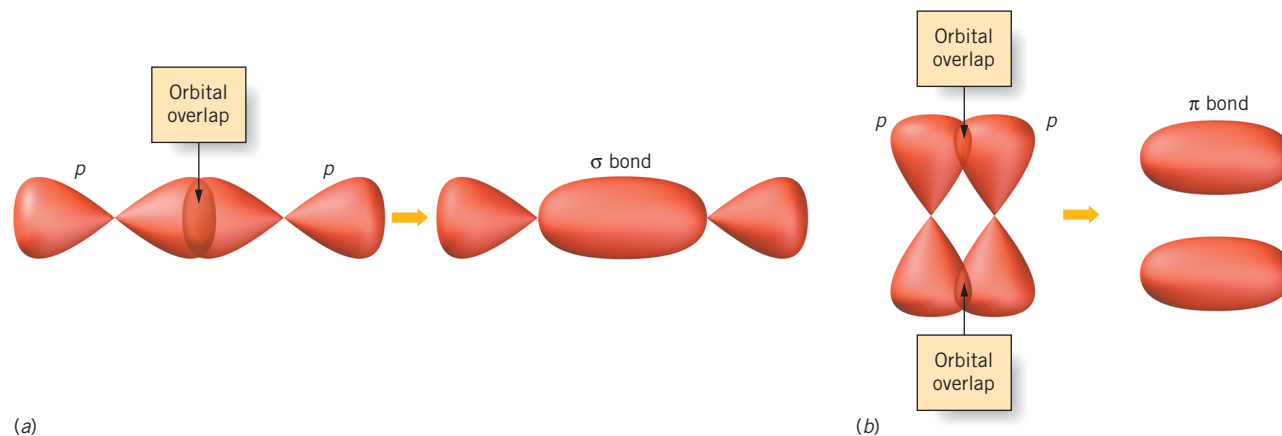
## 21.2 NONMETALLIC ELEMENTS IN THEIR FREE STATES HAVE STRUCTURES OF VARYING COMPLEXITY

Only the noble gases exist in nature as single atoms. All the other nonmetallic elements are found in more complex forms in their free states—some as diatomic molecules and the rest in more complex molecular structures. In this section we will study what these structures are and use bonding theory to understand them. Let’s begin by reviewing how atoms form covalent bonds.

You learned in Chapter 9 that atoms are able to share electrons in two basic ways. One is by the formation of  $\sigma$  bonds, which can involve the overlap of  $s$  orbitals or an end-to-end overlap of  $p$  orbitals or hybrid orbitals. The second kind of covalent bond is the  $\pi$  bond, which normally requires the sideways overlap of unhybridized  $p$  orbitals (Figure 21.2). (Pi bonds can also be formed by  $d$  orbitals, but we do not discuss them in this book.)

Not all atoms have the same tendency to form  $\pi$  bonds. The ability of an atom to form  $\pi$  bonds determines its ability to form multiple bonds, and this in turn greatly affects the kinds of molecular structures that the element produces. One of the most striking illustrations of this is the molecular structures of the elemental nonmetals and metalloids.

## 21.2 Nonmetallic Elements in Their Free States Have Structures of Varying Complexity 859



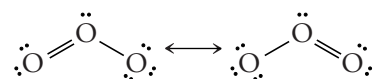
**FIG. 21.2** Formation of sigma and pi bonds. (a) Sigma bonds formed by the head-to-head overlap of  $p$  orbitals. (b) Pi bonds formed by the side-by-side overlap of  $p$  orbitals.

### Nonmetals in Period 2 form multiple bonds relatively easily

One of the controlling factors in determining the complexity of the molecular structures of the nonmetals and metalloids is their ability to form multiple bonds. Small atoms, such as those in Period 2, are able to approach each other closely. As a result, effective sideways overlap of their  $p$  orbitals can occur, and these atoms form strong  $\pi$  bonds. Therefore, carbon, nitrogen, and oxygen are able to form multiple bonds about as easily as they are able to form single bonds. On the other hand, when the atoms are large—which is the case for atoms from Periods 3, 4, and so on— $\pi$ -type overlap between their  $p$  orbitals is relatively ineffective, so  $\pi$  bonds formed by large atoms are relatively weak compared to  $\sigma$  bonds. Therefore, rather than form a double bond consisting of one  $\sigma$  bond and one  $\pi$  bond, these elements prefer to use two separate  $\sigma$  bonds to bond their atoms together. This leads to a useful generalization: *Elements in Period 2 are able to form multiple bonds fairly readily, while elements below them in Periods 3, 4, 5, and 6 have a tendency to prefer single bonds.* Let's see how this affects the structures of the elemental nonmetallic elements.

Oxygen and nitrogen have six and five electrons, respectively, in their valence shells. This means that an oxygen atom needs two electrons to complete its valence shell, and a nitrogen atom needs three. Although a perfectly satisfactory Lewis structure for  $O_2$  can't be drawn, experimental evidence suggests that the oxygen molecule does possess a double bond. The molecular orbital theory, which provides an excellent explanation of the bonding in  $O_2$ , also tells us that there is a double bond in the  $O_2$  molecule. The nitrogen molecule, which we discussed earlier, contains a triple bond. Oxygen and nitrogen, because of their small size, are capable of multiple bonding because they are able to form strong  $\pi$  bonds. This allows them to form a sufficient number of bonds with just a single neighbor to complete their valence shells, so they are able to form diatomic molecules.

Oxygen, in addition to forming the stable species  $O_2$  (dioxygen), also can exist in another very reactive molecular form called **ozone**, which has the formula  $O_3$ . The structure of ozone can be represented as a resonance hybrid



This unstable molecule can be generated by the passage of an electric discharge through ordinary  $O_2$ , and the pungent odor of ozone can often be detected in the vicinity of high-voltage electrical equipment. It is also formed in limited amounts in the upper atmosphere by the action of ultraviolet radiation from the sun on  $O_2$ . The presence of ozone in the upper atmosphere shields the earth and its creatures from exposure to intense and harmful ultraviolet light from the sun.

■  $\Delta G_f^\circ$  for  $O_3$  is  $+163 \text{ kJ mol}^{-1}$ , which indicates that the molecule has a strong tendency to decompose to give  $O_2$ .

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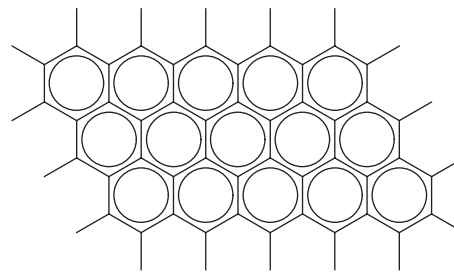
The existence of an element in more than one form, either as the result of differences in molecular structure as with  $O_2$  and  $O_3$ , or as the result of differences in the packing of molecules in the solid, is a phenomenon called **allotropy**. The different forms of the element are called **allotropes**. Thus,  $O_2$  is one allotrope of oxygen and  $O_3$  is another. Allotropy is not limited to oxygen, as you will soon see.

**Carbon forms four allotropes**

An atom of carbon, another Period 2 element, has four electrons in its valence shell, so it must share four electrons to complete its octet. There is no way for carbon to form a quadruple bond, so a simple  $C_2$  species is not stable under ordinary conditions. Instead, carbon completes its octet in other ways, leading to four allotropic forms of the element. One of these is **diamond**, in which each carbon atom uses  $sp^3$  hybrid orbitals to form covalent bonds to four other carbon atoms at the corners of a tetrahedron (Figure 21.3a).

In its other allotropes, carbon employs  $sp^2$  hybrid orbitals to form ring structures with delocalized  $\pi$  systems covering their surfaces. The most stable form of carbon is **graphite**, which consists of layers of carbon atoms, each composed of many hexagonal “benzene-like” rings fused together in a structure reminiscent of chicken wire.

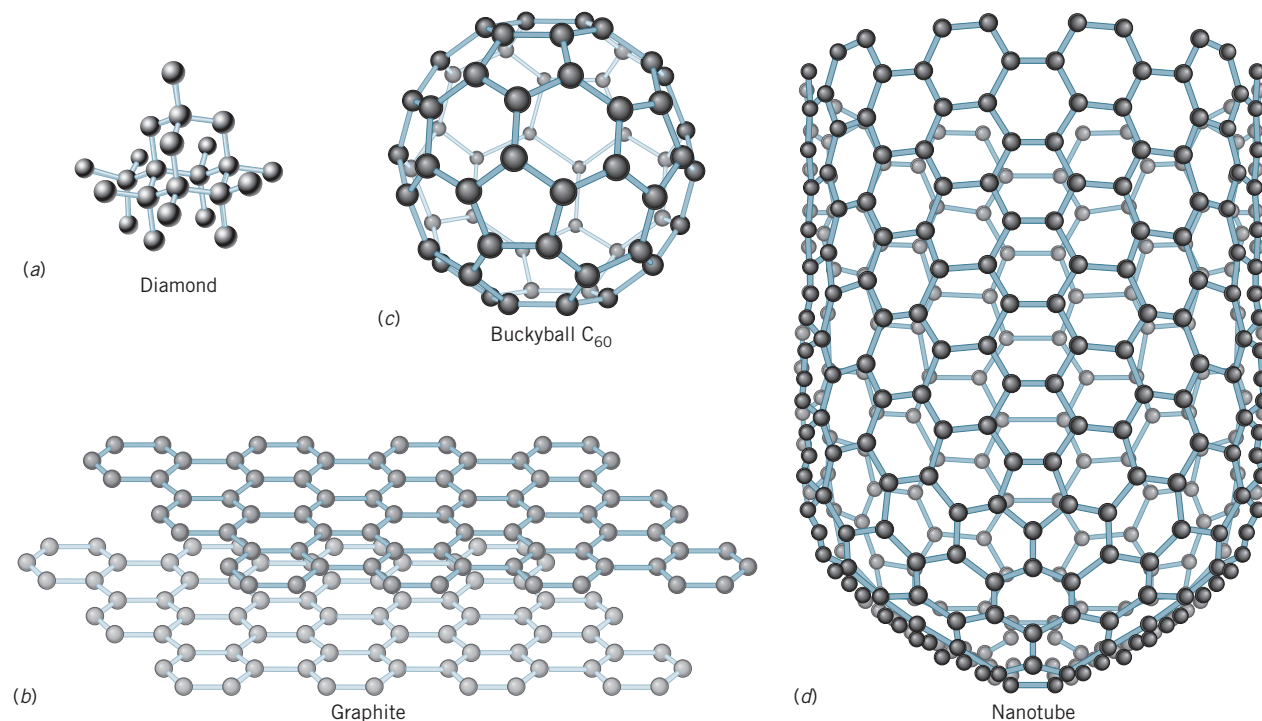
Graphite is able to serve as a lubricant because the layers of carbon atoms in the structure are able to slide over each other relatively easily.



A fragment of a carbon layer in graphite

Another figure showing the layer structure of graphite can be found on the rear cover of the book.

In graphite, these layers are stacked one on top of another, as shown in Figure 21.3b. Graphite is an electrical conductor because of the delocalized  $\pi$  electron system that extends across the layers. Electrons can be pumped in at one end of a layer and removed from the other.



**FIG. 21.3 Molecular forms of carbon.** (a) Diamond. (b) Graphite. (c) Buckminsterfullerene, or “buckyball,”  $C_{60}$ . (d) A portion of a carbon nanotube showing one closed end.

## 21.2 Nonmetallic Elements in Their Free States Have Structures of Varying Complexity 861

In 1985, a new form of carbon was discovered that consists of tiny balls of carbon atoms, the simplest of which has the formula  $C_{60}$  (Figure 21.3c). They were named **fullerenes** and the  $C_{60}$  molecule itself was named **buckminsterfullerene** (nickname **buckyball**) in honor of R. Buckminster Fuller, the designer of a type of structure called a geodesic dome. The bonds between carbon atoms in the buckyball occur in a pattern of five- and six-membered rings arranged like the seams in a soccer ball as well as the structural elements of the geodesic dome.

**Carbon nanotubes**, discovered in 1991, are another form of carbon that is related to the fullerenes. They are formed, along with fullerenes, when an electric arc is passed between carbon electrodes. The nanotubes consist of tubular carbon molecules that we can visualize as rolled up sheets of graphite (with hexagonal rings of carbon atoms). The tubes are capped at each end with half of a spherical fullerene molecule, so a short tube would have a shape like a hot dog. A portion of a carbon nanotube is illustrated in Figure 21.3d. Carbon nanotubes have unusual properties that have made them the focus of much research in recent years.

### Boron forms a complex structure containing $B_{12}$ units

In Period 2 there is still one element whose structure we have not considered, namely, boron. This element, found in Group IIIA, is quite unlike any of the others, since there is no simple way for it to complete its valence shell. The boron atom has just three electrons in its valence shell. Crystalline boron contains clusters of 12 boron atoms located at the vertices of an icosahedron (a 20-sided geometric figure) as shown in Figure 21.4. In the solid, each of these is also joined to yet another boron atom outside the cluster (Figure 21.4b). The electrons available for bonding are therefore delocalized to a large extent over many boron atoms.

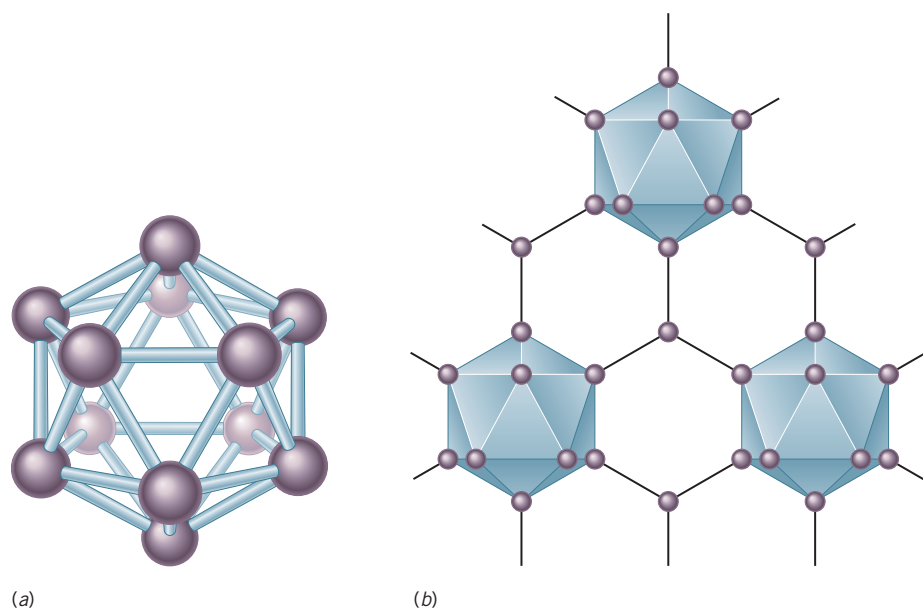
The linking together of  $B_{12}$  units produces a large three-dimensional covalent solid that is very difficult to break down. As a result, boron is very hard (it is the second hardest element) and has a very high melting point (about 2200 °C).

### Nonmetallic elements below Period 2 have structures containing single bonds

In graphite, carbon exhibits multiple bonding, as do nitrogen and oxygen in their molecular forms. As we noted earlier, their ability to do this reflects their ability to form strong  $\pi$  bonds—a requirement for the formation of a double or triple bond. When we move to

■ The front cover of the book illustrates the structure and formation of a carbon nanotube.

■ Weight for weight, carbon nanotubes are about 100 times stronger than stainless steel and about 40 times stronger than the carbon fibers used to make tennis rackets and shafts for golf clubs.



**FIG. 21.4** The structure of elemental boron. (a) The arrangement of 12 boron atoms in a  $B_{12}$  cluster. (b) The element boron consists of an interconnecting network of  $B_{12}$  clusters that produces a very hard and high-melting solid.

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the third and successive periods, a different state of affairs exists. Here, we have much larger atoms that are able to form relatively strong  $\sigma$  bonds but much weaker  $\pi$  bonds. Because their  $\pi$  bonds are so weak, these elements prefer single bonds ( $\sigma$  bonds), and the molecular structures of the free elements reflect this.

### Elements of Group VIIA

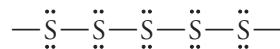
Each of the elements in Group VIIA is diatomic in the free state. This is because  $\pi$  bonding is not necessary in any of their molecular structures. Chlorine, for example, requires just one electron to complete its octet, so it only needs to form one covalent bond with another atom. Therefore, it forms one  $\sigma$  bond to another chlorine atom and is able to exist as diatomic  $\text{Cl}_2$ . Bromine and iodine form diatomic  $\text{Br}_2$  and  $\text{I}_2$  molecules for the same reason. The structures of the remaining nonmetals and metalloids are considerably more complex, however.

### Elements of Group VIA

Below oxygen in Group VIA is sulfur, which has the Lewis symbol



A sulfur atom requires two more electrons to obtain an octet, so it must form two covalent bonds. But sulfur doesn't form  $\pi$  bonds well to other sulfur atoms; instead, it prefers to form two stronger single bonds to *different* sulfur atoms. Each of these also prefers to bond to two different sulfur atoms, and this gives rise to a



sequence. Actually, in sulfur's most stable form, called **orthorhombic sulfur**, the sulfur atoms are arranged in an eight-membered ring to give a molecule with the formula  $\text{S}_8$  (properly named cyclooctasulfur). The  $\text{S}_8$  ring has a puckered crownlike shape, which is illustrated in Figure 21.5. Another allotrope is **monoclinic sulfur**, which also contains  $\text{S}_8$  rings that are arranged in a slightly different crystal structure.

Selenium, below sulfur in Group VIA, also forms  $\text{Se}_8$  rings in one of its allotropic forms. Both selenium and tellurium also can exist in a gray form in which there are long  $\text{Se}_x$  and  $\text{Te}_x$  chains (where the subscript  $x$  is a large number).

### Elements of Group VA

Like nitrogen, the other elements in Group VA all have five valence electrons. Phosphorus is an example.



To achieve a noble gas structure, the phosphorus atom must acquire three more electrons. Because there is little tendency for phosphorus to form multiple bonds, as nitrogen does when it forms  $\text{N}_2$ , the octet is completed by the formation of three single bonds to three *different* phosphorus atoms.

The simplest elemental form of phosphorus is a waxy solid called **white phosphorus** because of its appearance. It consists of  $\text{P}_4$  molecules in which each phosphorus atom lies at a corner of a tetrahedron, as illustrated in Figure 21.6. Notice that in this structure each phosphorus is bound to three others. This allotrope of phosphorus is very reactive, partly because of the very small  $\text{P}-\text{P}-\text{P}$  bond angle of  $60^\circ$ . At this small angle, the  $p$  orbitals of the phosphorus atoms don't overlap very well, so the bonds are weak. As a result, breaking a  $\text{P}-\text{P}$  bond occurs easily. When a  $\text{P}_4$  molecule reacts, this bond breaking is the first step, so  $\text{P}_4$  molecules are readily attacked by other chemicals, especially oxygen. White phosphorus is so reactive toward oxygen that it ignites and burns spontaneously in air. For this reason, white phosphorus is used in military incendiary devices, and you've probably seen movies in which exploding phosphorus shells produce arching showers of smoking particles.

A second allotrope of phosphorus that is much less reactive is called **red phosphorus**. At the present time, its structure is unknown, although it has been suggested that it contains  $\text{P}_4$  tetrahedra joined at the corners as shown in Figure 21.7. Red phosphorus is also used in explosives and fireworks, and it is mixed with fine sand and used on the

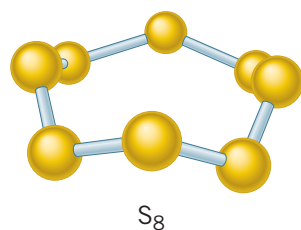


FIG. 21.5 The structure of the puckered  $\text{S}_8$  ring.

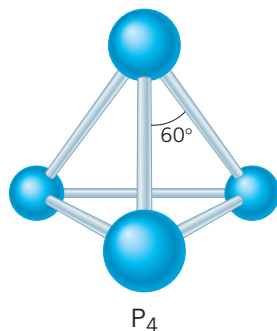
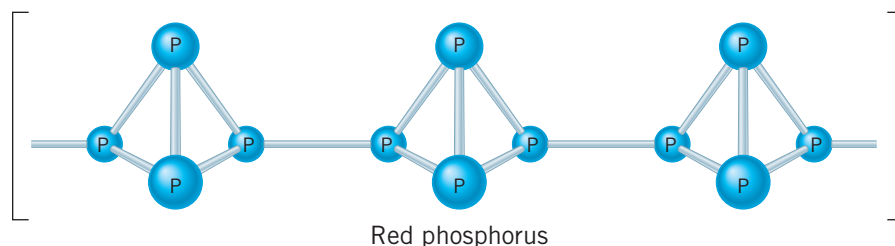


FIG. 21.6 The molecular structure of white phosphorus,  $\text{P}_4$ . The bond angles of  $60^\circ$  make the phosphorus–phosphorus bonds quite weak and causes the molecule to be very reactive.

▣ The preferred angle between bonds formed by overlap of  $p$  orbitals is  $90^\circ$ . Each face of the  $\text{P}_4$  tetrahedron is a triangle, however, with  $60^\circ$  angles between edges. This produces less than optimum overlap between the  $p$  orbitals in the bonds.

## 21.3 Metals Are Prepared from Compounds by Reduction 863



**FIG. 21.7** Proposed molecular structure of red phosphorus. Red phosphorus is believed to be composed of long chains of  $P_4$  tetrahedra connected at their corners.

striking surfaces of matchbooks. As a match is drawn across the surface, friction ignites the phosphorus, which then ignites the ingredients in the tip of the match.

A third allotrope of phosphorus is called **black phosphorus**, which is formed by heating white phosphorus at very high pressures. This variety has a layered structure in which each phosphorus atom in a layer is covalently bonded to three others in the same layer. As in graphite, these layers are stacked one atop another, with only weak forces between the layers. As you might expect, black phosphorus has many similarities to graphite.

The elements arsenic and antimony, which are just below phosphorus in Group VA, are also able to form somewhat unstable yellow allotropic forms containing  $As_4$  and  $Sb_4$  molecules, but their most stable forms have a metallic appearance with structures similar to black phosphorus.

#### Elements of Group IVA

Finally, we look at the heavier nonmetallic elements in Group IVA, silicon and germanium. To complete their octets, each must form four covalent bonds. Unlike carbon, however, they have very little tendency to form multiple bonds, so they don't form allotropes that have a graphite structure. Instead, each of them forms a solid with a structure similar to diamond.

### 21.3 METALS ARE PREPARED FROM COMPOUNDS BY REDUCTION

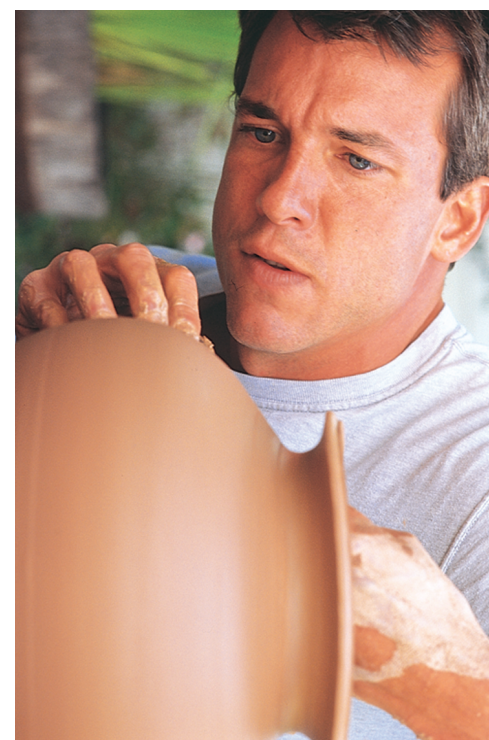
When metals form compounds, they almost always lose electrons (become oxidized) and exist in positive oxidation states. Therefore, isolating metals from compounds generally involves reduction. In this section we will look at some of the ways this can be accomplished. Before we do this, however, let's take a brief look at where in nature we find metal compounds.

#### Metals come from both the earth and the sea

Most metals are reactive enough that they do not occur as free elements in nature. Instead, they are found combined with other elements in compounds. Where we find such compounds depends a great deal on their solubilities in water. For example, you learned that salts of the alkali metals (metals of Group IA) are soluble in water. It is no surprise, therefore, to find  $Na^+$  and  $K^+$  ions in the sea. In fact, the oceans provide a huge storehouse of many minerals, as illustrated by the table in the margin. Sodium and magnesium (as  $Na^+$  and  $Mg^{2+}$ ) are the metal ions in largest concentration in seawater, partly because their natural abundance among the elements is large,<sup>2</sup> and also because their sulfates, halides, and carbonates are water soluble.

Oxygen is the earth's most abundant element, and because it is so reactive it is able to combine with nearly all metals. As you learned when studying the solubility rules in Chapter 4, most metal oxides are insoluble in water (exceptions are the oxides of the alkali metals and some of the oxides of the Group IIA metals). Because of these facts, many metals occur in nature as insoluble oxides found buried in the ground. An example is iron(III) oxide, which gives its rich rust-red color to iron ores and various clay minerals that contain  $Fe_2O_3$  (Figure 21.8).

<sup>2</sup>On the earth, sodium is the fourth most abundant element on an atom basis (approximately 2.6% of the atoms on earth are Na); magnesium is the seventh most abundant (about 1.8%).



**FIG. 21.8** The color of iron oxide. Red  $Fe_2O_3$  gives the clay used by this sculptor its rich color. (Dan Boler/Stone/Getty Images.)

#### Concentrations of Ions in Seawater

Ion	Molarity
Chloride	0.550
Sodium	0.468
Magnesium	0.055
Sulfate	0.029
Calcium	0.011
Potassium	0.011
Bicarbonate	0.002

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As you learned in Chapter 4, nearly all metal carbonates are also insoluble, and the ability of sea creatures, such as clams, oysters, and coral, to extract carbonate ions from seawater to construct their shells accounts for the large formations of carbonate minerals of calcium and magnesium present in many locations around the planet. Over eons of time, the calcium carbonate skeletons of these creatures have built up and then been moved by upheavals in the earth's crust. Such movements have often lifted them to heights far above sea level and at times subjected them to tremendous compressive forces that transformed them into limestone and marble.

□ In most soils, phosphorus is the limiting nutrient, so phosphate fertilizers are essential to produce good crops.

Other anions yield insoluble compounds with metal ions as well, which accounts for deposits of metal sulfides, such as copper sulfides ( $\text{CuS}$  and  $\text{Cu}_2\text{S}$ ), lead sulfide ( $\text{PbS}$ ), and calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ . The latter mineral is the chief source of phosphate fertilizers, without which farmers could not hope to maintain the large crop harvests required to feed the world's growing population.

A few metals, most notably gold and platinum, do occur in the uncombined state in nature. These are metals with very low degrees of reactivity. Although they form many compounds, the metals are found free in nature because their compounds are not particularly stable and are easily decomposed by heat.

### Reactive metals are often produced by electrolysis

□ Recall that for metals, reactivity is a measure of how easily oxidized they are.

The method used to extract a metal from its compounds depends on how “reactive” the metal is. Metals that are easily oxidized, such as the alkali and alkaline earth metals, form compounds that are correspondingly difficult to reduce, and it is difficult and expensive to find chemical reducing agents that are up to the job. For this reason, electrolysis is usually the procedure used. For example, in Chapter 19 we described the electrolytic production of two reactive metals, sodium and aluminum. Sodium is formed by electrolysis of its molten chloride, whereas aluminum is produced from its oxide by dissolving it in a salt such as  $\text{Na}_3\text{AlF}_6$  which has a lower melting point.

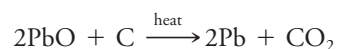
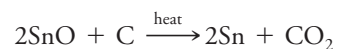
In an interesting application of Le Châtelier's principle, potassium is usually made by passing sodium vapor over molten potassium chloride at high temperature. Although potassium ions are more difficult to reduce than sodium ions, the equilibrium



is shifted to the right because potassium has a higher vapor pressure than sodium. The less volatile sodium condenses as potassium vapor is swept away, thereby gradually shifting the position of equilibrium. The same procedure is used to make metallic rubidium and cesium.

### Many metals can be made using a chemical reducing agent

When a metal is of intermediate reactivity, it can be economically extracted from its compounds by reaction with a chemical reducing agent. For example, one of the most common agents used for the reduction of metal oxides is carbon. Tin and lead, for example, can be produced by heating their oxides with carbon, a process called **smelting**.



Carbon is used in large quantities in commercial metallurgy (Section 21.4) because of its abundance and low cost.

Hydrogen is another reducing agent that can be used to liberate metals of moderate chemical activity. For instance tin and lead oxides are also reduced when heated under a stream of  $\text{H}_2$ .



**Marble is a favorite stone of sculptors.** The type of stone called marble is composed of calcium carbonate, which was deposited by sea creatures long ago and then transformed by heat and pressure caused by movements of the earth's crust. How fortunate for us, because it enabled the great sculptor Michelangelo to create this masterpiece known as *La Pietà*. (*Art Resource.*)

## FACETS OF CHEMISTRY

## 21.1

**Polishing Silver—The Easy Way**

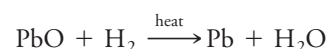
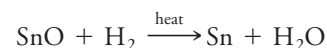
Using an active metal to reduce a compound of a less active metal has a number of practical applications. One that is handy around the home is using aluminum to remove the tarnish from silver. Generally, silver tarnishes by a gradual reaction with hydrogen sulfide, present in very small amounts in the air. The product of the reaction is silver sulfide,  $\text{Ag}_2\text{S}$ , which is black and forms a dull film over the bright metal. Polishing a silver object using a mild abrasive restores the shine, but it also gradually removes silver from the object as the silver sulfide is rubbed away.

An alternative method, and one that requires little effort, involves lining the bottom of a sink with aluminum foil, adding

warm water and detergent (which acts as an electrolyte), and then submerging the tarnished silver object in the detergent–water mixture and placing it in contact with the aluminum (Figure 1). A galvanic cell is established in which the more active aluminum is the anode and the silver object is the cathode. In a short time, the silver sulfide is reduced, restoring the shine and depositing the freed silver metal on the object. As this happens, a small amount of the aluminum foil is oxidized and caused to dissolve. Besides requiring little physical effort, this silver polishing technique doesn't remove silver from the object being polished.



**FIG. 1** Using aluminum to remove tarnish from silver. (a) A badly tarnished silver vase stands next to a container of detergent (Soilax) dissolved in water. The bottom of the container is lined with aluminum foil. (b) The vase, shown partly immersed in the detergent, rests on the aluminum foil. (c) After a short time, the vase is removed, rinsed with water, and wiped with a soft cloth. Where the vase was immersed in the liquid, much of the tarnish has been reduced to metallic silver. (Andy Washnik.)



The use of a more active metal to carry out the reduction is also possible. In Chapter 19 we saw that a galvanic cell could be established between two different metals, for example, Zn and Ag. In that cell the more active reducing agent, Zn, causes the  $\text{Ag}^+$  to be reduced. Aluminum was first prepared in 1825 by the reaction of aluminum chloride with the more active metal, potassium.

**Some metal compounds are thermally unstable**

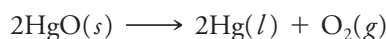
**Thermal decomposition** of a compound involves the conversion of the substance into its elements by heat. Some metal compounds are extremely resistant to such decomposition. For example, magnesium oxide is used to make bricks to line the walls of high-temperature ovens because it has a very high melting point and virtually no tendency to undergo decomposition. On the other hand, mercury(II) oxide decomposes at a relatively low temperature. For example, Joseph Priestley (1733–1804), in his experiments leading to the discovery of oxygen, produced metallic mercury and oxygen from mercury(II) oxide by simply heating it with sunlight focused on the  $\text{HgO}$  by means of a magnifying glass.

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**FIG. 21.9 Thermal decomposition of mercury(II) oxide.** Heated to a temperature of only 400 °C, HgO turns black and releases oxygen. Drops of mercury metal begin to collect on the walls of the test tube as mercury vapor condenses on the cooler parts of the tube. (Richard Megna/Fundamental Photographs.)

In this case, HgO decomposes quite spontaneously at elevated temperatures (Figure 21.9). The equation for the decomposition is.



The practicality of using a thermal decomposition reaction of this type to produce a free metal depends on the extent to which the reaction proceeds to completion at a given temperature.

In Chapter 18 you learned that at 25 °C the position of equilibrium in a reaction is roughly governed by  $\Delta G_{298}^\circ$ . If  $\Delta G_{298}^\circ$  is negative,  $K > 1$  and appreciable amounts of products will be expected at equilibrium. Taking  $\Delta G_T^\circ$  to be the equivalent of  $\Delta G_{298}^\circ$ , but at a higher temperature, we have the relationship

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

For decomposition,  $\Delta S_T^\circ$  is positive (decomposition leads to formation of more particles). Most compounds have negative values of  $\Delta H_f^\circ$ , so we expect the  $\Delta H_T^\circ$  for the decomposition to be positive, too. That makes  $\Delta G_T^\circ$  equal to the difference between two positive quantities,  $\Delta H_T^\circ$  and  $T\Delta S_T^\circ$ . If  $\Delta H_T^\circ$  is not *too* positive, the temperature  $T$  needed to make  $\Delta G_T^\circ$  negative is not very large, and thermal decomposition should proceed to a significant degree at a reasonable temperature. *Stated another way, if  $\Delta H_f^\circ$  for a compound is not too negative, it should be susceptible to thermal decomposition at a reasonably low temperature.*

**EXAMPLE 21.1**
**Calculating the Temperature  
Required for Thermal  
Decomposition**

Above what temperature would the decomposition of  $\text{Ag}_2\text{O}$  be expected to proceed to an appreciable extent toward completion? At 25 °C,  $\Delta H_f^\circ$  for  $\text{Ag}_2\text{O}$  is  $-31.1 \text{ kJ mol}^{-1}$ , and  $\Delta S_f^\circ = -66.1 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**ANALYSIS:** The tool that we will use is Equation 18.10 (page 752), which allows us to estimate  $\Delta G_T^\circ$  assuming  $\Delta H_T^\circ$  and  $\Delta S_T^\circ$  are nearly independent of temperature:

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ \quad (\text{Equation 18.10})$$

The decomposition of  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{O}(s) \longrightarrow 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g)$ , is the reverse of its formation. Therefore, for this reaction at 25 °C we can write

$$\begin{aligned}\Delta H_{298}^\circ &= -\Delta H_f^\circ = +31.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^\circ &= -\Delta S_f^\circ = +66.1 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Let's calculate the temperature at which  $\Delta G_T^\circ = 0$ , because above that temperature  $\Delta G_T^\circ$  will be negative and the decomposition reaction will proceed to a significant extent.

**SOLUTION:** We will assume, as stated above, that  $\Delta H_T^\circ$  and  $\Delta S_T^\circ$  are approximately independent of temperature so that we can use  $\Delta H_{298}^\circ$  and  $\Delta S_{298}^\circ$  in the equation for  $\Delta G_T^\circ$ .

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ$$

When  $\Delta G_T^\circ = 0$

$$0 = \Delta H_{298}^\circ - T\Delta S_{298}^\circ$$

Solving for  $T$  gives

$$\begin{aligned}T &= \frac{\Delta H_{298}^\circ}{\Delta S_{298}^\circ} \\ &= \frac{31,100 \cancel{\text{ J mol}^{-1}}}{66.1 \cancel{\text{ J mol}^{-1} \text{ K}^{-1}}} \\ &= 470 \text{ K}\end{aligned}$$

This corresponds to a Celsius temperature of 197 °C.

Because  $\Delta H_{298}^{\circ}$  and  $\Delta S_{298}^{\circ}$  are both positive,  $\Delta G_T^{\circ}$  will become negative at temperatures above 197 °C. This means that above 197 °C the reaction should become feasible, with much of the  $\text{Ag}_2\text{O}$  undergoing decomposition.

**IS THE ANSWER REASONABLE?** There is no simple check on this answer, although we can check to be sure that the units cancel properly, and they do. Notice that we were careful to change the units of  $\Delta H_{298}^{\circ}$  from kilojoules to joules. If we had not done that, the units would not have canceled properly.

**Practice Exercise 1:** Above what temperature would  $\text{Au}_2\text{O}_3$  decompose to give Au and  $\text{O}_2$ ? At 25 °C,  $\Delta H_f^{\circ} = +80.8 \text{ kJ mol}^{-1}$  for  $\text{Au}_2\text{O}_3$ . Also, for  $\text{Au}_2\text{O}_3$ ,  $S^{\circ} = 125 \text{ J mol}^{-1} \text{ K}^{-1}$ ; for Au,  $S^{\circ} = 47.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ; for  $\text{O}_2$ ,  $S^{\circ} = 205 \text{ J mol}^{-1} \text{ K}^{-1}$ . (Hint: Can the absolute temperature be negative?)

**Practice Exercise 2:** Calculate the temperature required to observe a significant amount of thermal decomposition of MgO. At 25 °C, magnesium oxide has  $\Delta H_f^{\circ} = -601.7 \text{ kJ mol}^{-1}$ ; for Mg,  $S^{\circ} = 32.5 \text{ J mol}^{-1} \text{ K}^{-1}$ , and for  $\text{O}_2$ ,  $S^{\circ} = 205 \text{ J mol}^{-1} \text{ K}^{-1}$ . For MgO,  $S^{\circ} = 26.9 \text{ J mol}^{-1} \text{ K}^{-1}$ .

## 21.4 METALLURGY IS THE SCIENCE AND TECHNOLOGY OF METALS

Metals played an important role in the growth and development of civilization even before the beginning of recorded history. Archaeological evidence indicates that gold was used in making eating utensils and ornaments as early as 3500 BC. Silver was discovered at least as early as 2400 BC, and iron and steel have been used as construction materials since about 1000 BC. Since these earliest times, the methods for obtaining metals from their naturally occurring deposits have evolved, and today they constitute the subject we call metallurgy.

As the title of this section proclaims, **metallurgy** is defined as the science and technology of metals. In modern terms, it is primarily concerned with the procedures and chemical reactions that are used to separate metals from their ores and the preparation of metals for practical use. An **ore** is simply a mineral deposit that has a desirable component in a sufficiently high concentration to make its extraction economically profitable. The economics of the recovery operation, though, is what distinguishes an ore from just another rock. For example, magnesium is found in the mineral *olivine*, which has the formula  $\text{Mg}_2\text{SiO}_4$ . This compound contains over 30% magnesium, but there is no economical way to extract the metal from it. Instead, most magnesium is obtained from seawater, even though its concentration is a mere 0.13%. Although the concentration is much less in the water, a profitable method of obtaining the magnesium has been developed, so seawater is the principal source of magnesium.

Because of the wide variety of sources and the varying nature of the metal compounds in ores, no single method can be applied to the production of all metals. Nevertheless, the sequence of metallurgical processes can be divided into three principal steps.

1. **Concentration.** Ores that contain substantial amounts of impurities, such as rock, must often be treated to concentrate the metal-bearing component. Pretreatment of an ore is also carried out to convert some metal compounds into substances that can be more easily reduced.
2. **Reduction.** The particular procedure employed to reduce the metal compound to give the metal depends on how easily the compound is reduced.

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3. *Refining.* Often, during reduction, substantial amounts of impurities become incorporated into the metal. Refining is the process whereby these impurities are removed and the composition of the metal adjusted (alloys formed) to meet the needs of specific applications.

### Ores are often treated to enrich the metal-bearing component

When the source of a metal is an ore that is dug from the ground, considerable amounts of sand and dirt are usually mixed in with the ore. To reduce the volume of material that must be processed, the ore is normally concentrated before the metal is separated from it. How this is done depends on the physical and chemical properties of the ore itself, as well as those of the impurities.

■ Gangue is pronounced “gang.”

In some cases, the unwanted rock and sand, called **gangue**, can be removed simply by washing the material with a stream of water. This flushes away the waste and leaves the enriched ore behind. Some iron ores are treated in this way. This procedure also forms the basis for the well-known technique called “panning for gold” that you’ve probably seen in movies. A sample of sand that might also contain gold is placed into a shallow pan partially filled with water. As the water is swirled around, it washes the less dense sand over the rim of the pan, but leaves any of the more dense bits of gold behind.

**Flotation** is a method commonly used to enrich the sulfide ores of copper and lead. The ore is crushed, mixed with water, and ground into a souplike slurry which is then transferred to flotation tanks (Figure 21.10) where it is mixed with detergents and oil. The oil adheres to the particles of sulfide ore, but not to the particles of sand and dirt. Air is blown through the mixture and the rising air bubbles become attached to the oil-coated ore particles, bringing them to the surface where they are held in a froth. The detergents in the mixture stabilize the bubbles long enough for the froth and its load of ore particles to be skimmed off. Meanwhile, the sand and dirt settle to the bottom of the tanks and are removed.

Many ores must undergo a second round of pretreatment before the metal can be obtained from them. For example, after enrichment, sulfide ores are usually heated in air. This procedure, called **roasting**, converts the sulfides to oxides which are more conveniently reduced than sulfides. Typical reactions that occur during roasting are

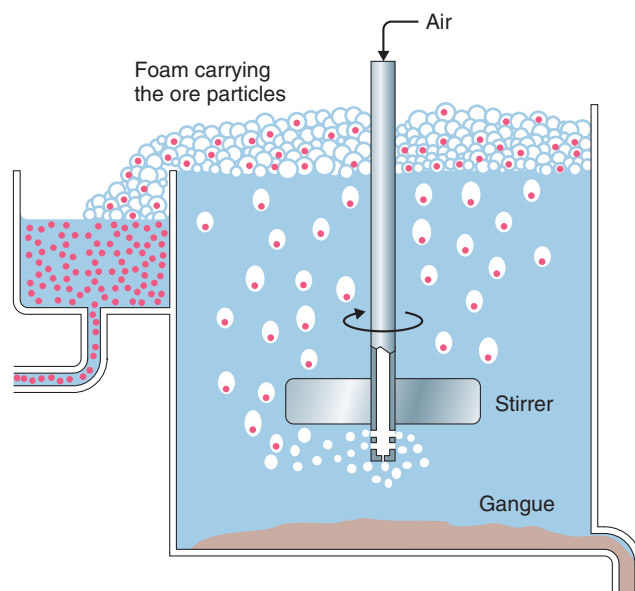
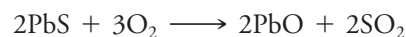
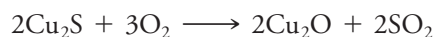


FIG. 21.10 A flotation apparatus.

## 21.4 Metallurgy Is the Science and Technology of Metals 869

A by-product of roasting is sulfur dioxide. In years past this was simply released to the atmosphere and was a major source of air pollution. Today we realize that the  $\text{SO}_2$  cannot be allowed to escape into the air. One way to remove it from the exhaust gases is to allow it to react with calcium carbonate ( $\text{CaCO}_3$ ).



This method creates another problem, however—the disposal of the solid calcium sulfite. Another way to dispose of the  $\text{SO}_2$  is to oxidize it to  $\text{SO}_3$ . The  $\text{SO}_3$  can be converted to sulfuric acid which is then sold.

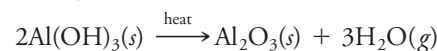
Aluminum ore, called *bauxite*, must also be pretreated before it can be processed. Bauxite contains aluminum oxide,  $\text{Al}_2\text{O}_3$ , but a number of impurities are also present. To remove the impurities, use is made of aluminum oxide's amphoteric behavior. The ore is mixed with a concentrated sodium hydroxide solution, which dissolves the  $\text{Al}_2\text{O}_3$ .



The major impurities, however, are insoluble in base, so when the mixture is filtered, the impurities remain on the filter while the aluminum-containing solution passes through. The solution is then neutralized with acid, which precipitates aluminum hydroxide.



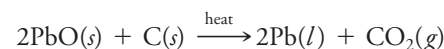
When the precipitate is heated, water is driven off and the oxide is formed.



This purified  $\text{Al}_2\text{O}_3$  then becomes the raw material for the Hall–Héroult process discussed in Section 19.8.

### Most metals are obtained from their ores using chemical reducing agents

Except for very reactive metals such as sodium, magnesium, and aluminum, which are reduced using electrolysis (Section 19.8), most metals are formed from their compounds using chemical reduction. A plentiful, and therefore inexpensive, reducing agent that's often used is carbon, which is usually obtained from coal. When coal is heated strongly in the absence of air, volatile components are driven off and **coke** is formed. Coke is composed almost entirely of carbon. Carbon is an effective reducing agent for metal oxides because it combines with the oxygen to form carbon dioxide. For example, after it is roasted, lead oxide is mixed with coke and heated. As noted earlier, this method for reducing a metal oxide is known as *smelting*.

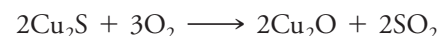


The high thermodynamic stability of  $\text{CO}_2$  serves as one driving force for the reaction. The loss of  $\text{CO}_2$  and the inability to reach an equilibrium is another.

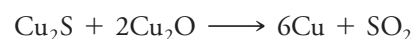
Copper oxide ores can also be reduced with carbon.



This step is unnecessary for some copper sulfide ores if the conditions under which the ore is roasted are properly controlled. For example, heating an ore that contains  $\text{Cu}_2\text{S}$  in air can convert some of the  $\text{Cu}_2\text{S}$  to  $\text{Cu}_2\text{O}$ .



At the appropriate time the supply of oxygen is cut off and the mixture of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  reacts further to give metallic copper.



### Reduction of iron ore is the first step in making steel

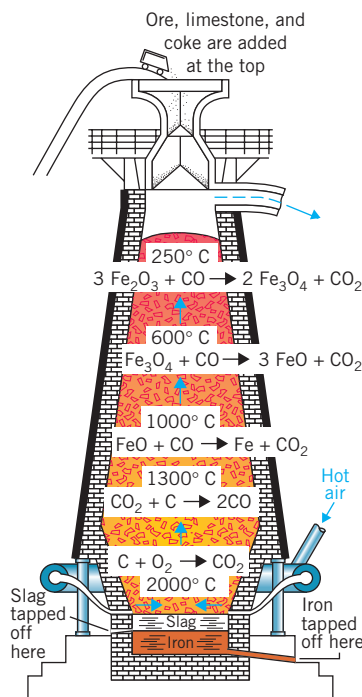
Without question, the most important use of carbon as a reducing agent is in the production of iron and steel. The chemical reactions take place in a huge tower called a **blast furnace**

Aluminum oxide is also called alumina.



**Coke is made from coal.** Coke is made in a battery of side-by-side coke ovens where coal is heated to drive off volatile materials. Here we see a fresh batch of white-hot coke being pushed from one of the ovens into a waiting railroad car. It will be delivered to a blast furnace nearby where it will be used to reduce iron ore to metallic iron. (David M. Campione/Photo Researchers.)

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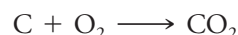
**FIG. 21.11** A typical blast furnace for the reduction of iron ore. To make 1 ton of iron requires 1.75 tons of ore, 0.75 ton of coke, and 0.25 ton of limestone.

- The blast of hot air is what gives the blast furnace its name.
- The active reducing agent in the blast furnace is carbon monoxide.
- The acidic anhydride  $\text{SiO}_2$  reacts with oxide ion in  $\text{CaO}$  to form the silicate ion,  $\text{SiO}_3^{2-}$ , in  $\text{CaSiO}_3$ . It's a Lewis acid–base reaction.

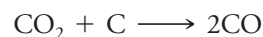
(see Figure 21.11). Some are as tall as a 15-story building and produce up to 2400 tons of iron a day. They are designed for continuous operation, so the raw materials can be added at the top and molten iron can be tapped off at the bottom. Once started, a typical blast furnace may run continuously for two years or longer before it is worn out and must be rebuilt.

The material put into the top of the blast furnace is called the **charge**. It consists of a mixture of iron ore, limestone, and coke. A typical iron ore consists of an iron oxide ( $\text{Fe}_2\text{O}_3$ , for example) plus impurities of sand and rock. The coke is added to reduce the iron oxide to the free metal. The limestone is added to react with the high-melting impurities to form a **slag**, which has a lower melting point. The slag can then be drained off as a liquid at the base of the furnace.

To understand what happens in the furnace, it is best to begin with the reactions that take place near the bottom. Here, heated air is blown into the furnace where carbon (from the coke) reacts with oxygen to form carbon dioxide.



The reaction is very exothermic, and the temperature in this part of the furnace rises to nearly 2000 °C. It is the hottest region of the furnace. The hot  $\text{CO}_2$  rises and reacts with additional carbon to form carbon monoxide.

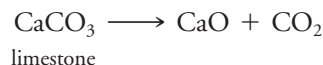


This reaction is endothermic, which causes the temperature higher up in the furnace to drop to about 1300 °C. As the carbon monoxide rises through the charge, it reacts with the iron oxides and reduces them to the free metal. The reactions are

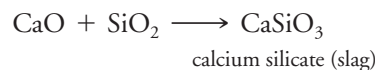


As the charge settles toward the bottom, molten iron trickles down and collects in a well at the base of the furnace.

The high temperature in the furnace also causes the limestone in the reaction mixture to decompose to give calcium oxide.



The calcium oxide reacts with impurities such as silica ( $\text{SiO}_2$ ) in the sand to form the slag.



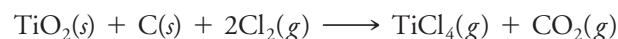
The molten slag also trickles down through the charge. It collects as a liquid layer on top of the more dense molten iron. Periodically, the furnace is tapped and the iron and slag are drawn off. The iron, which still contains some impurities, is called **pig iron**.<sup>3</sup> It is usually treated further to produce steel. The slag itself is a valuable by-product. It is used to make insulating materials and is one of the chief ingredients in the manufacture of Portland cement.

### Preparing metals for use is called refining

Before metals can be used, most must be purified, or **refined**, after they are reduced to the metallic state. Sometimes, reduction and purification can take place in a single step. For example, the ore for titanium (a metal used to make aircraft parts) is its oxide,  $\text{TiO}_2$ . Recovering the metal from the ore is difficult because the metal itself reacts at high temperature with both carbon and nitrogen. The solution is to heat the oxide with carbon

<sup>3</sup>The name pig iron comes from an early method of casting the molten iron into bars for shipment. The molten metal was run through a channel that fed into sand molds. The arrangement looked a little like a litter of pigs feeding from their mother.

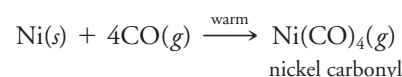
in the presence of chlorine gas, which converts the titanium to  $\text{TiCl}_4$ , a volatile compound that is drawn off as a gas.



The volatility of the  $\text{TiCl}_4$  enables it to be removed from any impurities in the ore. After being separated from the  $\text{CO}_2$ , the  $\text{TiCl}_4$  is allowed to react with magnesium to form essentially pure titanium metal.



The purification of nickel also takes advantage of the volatility of one of its compounds. When nickel is heated mildly in the presence of carbon monoxide, it forms a compound called nickel carbonyl,  $\text{Ni}(\text{CO})_4$ .



Vapors of the  $\text{Ni}(\text{CO})_4$  compound are easily separated from impurities in the nickel, which don't form similarly volatile substances. Later the  $\text{Ni}(\text{CO})_4$  can be heated to high temperature, causing the substance to decompose and deposit highly purified nickel.<sup>4</sup>

For some metals, refining is accomplished by electrolysis. For example, metallic copper that comes from the smelting process is about 99% pure, but before being used in electrical wiring it is purified electrolytically as described in Chapter 19.

#### Refining of iron to make steel involves removing impurities and adding other metals

The conversion of pig iron to steel is the most important commercial refining process. The pig iron from a blast furnace consists of about 95% iron, 3 to 4% carbon, and smaller amounts of phosphorus, sulfur, manganese, and other elements. Steel contains much less carbon as well as certain other ingredients in very definite proportions. Converting pig iron to steel, therefore, involves removing the impurities and much of the carbon, and adding other metals in precisely controlled amounts.

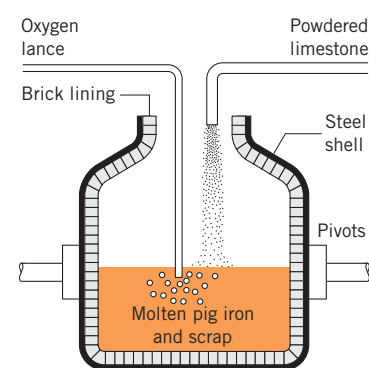
Today, most steel is made by a method called the **basic oxygen process**. It uses a large pear-shaped reaction vessel that is mounted on pivots as shown in Figure 21.12. The vessel is lined with an insulating layer of refractory bricks composed of  $\text{MgCO}_3$  or a mixture of  $\text{MgCO}_3$  and  $\text{CaCO}_3$ . The charge consists of about 30% scrap iron and scrap steel and about 70% molten pig iron. A tube called an *oxygen lance* is dipped into the charge and pure oxygen is blown through the molten metal. The oxygen rapidly burns off the excess carbon and oxidizes impurities to their oxides. The heat generated also melts the scrap iron. The impurities form a slag with calcium oxide that comes from powdered limestone, which is also added. Finally, other metals are introduced in the proper proportions to give a product with the desired properties. After the steel is ready, the reaction vessel can be tipped to pour out its contents. This method of making steel is very fast. A batch of steel weighing 300 tons can be made in less than an hour.

### 21.5 COMPLEX IONS ARE FORMED BY MANY METALS

In Section 17.4 (page 712), we introduced you to **complex ions** (or more simply, **complexes**) of metals. Recall that these are substances formed when molecules or anions become bonded covalently to metal ions to form more complex species. Two examples that were given were the pale blue  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ion and the deep blue  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion. In Chapter 17 we discussed how the formation of complex ions can affect the solubilities of salts, but the importance of these substances reaches far beyond solubility equilibria. The number of complex ions formed by metals, especially the transition metals, is enormous, and the study of the properties, reactions, structures, and bonding in complexes like  $\text{Cu}(\text{NH}_3)_4^{2+}$  has become an important specialty within chemistry. The study of metal

<sup>4</sup>This method of purifying nickel is called the Mond process.

■ Nickel carbonyl is very toxic.



**FIG. 21.12** The basic oxygen process for making steel. The reaction vessel is very large, being capable of holding up to 300 tons of steel.

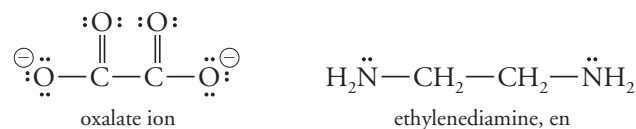


**A molten iron charge is added to a basic oxygen furnace.**  
(James Mejuto Photography.)

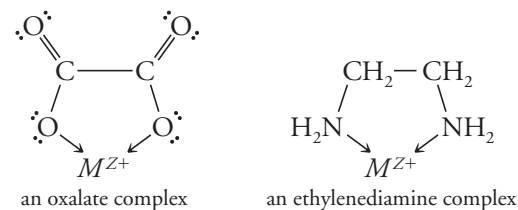


## 21.5 Complex Ions Are Formed by Many Metals 873

There are also many ligands that have two or more donor atoms, and collectively they are referred to as **polydentate ligands**. The most common of these have two donor atoms, so they are called **bidentate ligands**. When they form complexes, *both* donor atoms become attached to the same metal ion. Oxalate ion and ethylenediamine (abbreviated *en* in writing the formula for a complex) are examples of bidentate ligands.



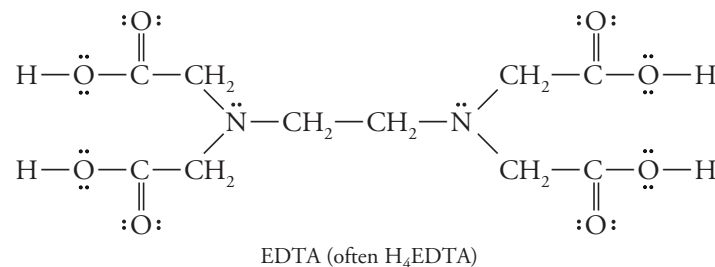
When these ligands become attached to a metal ion, ring structures are formed as shown below. Complexes that contain such ring structures are called **chelates**.<sup>6</sup>



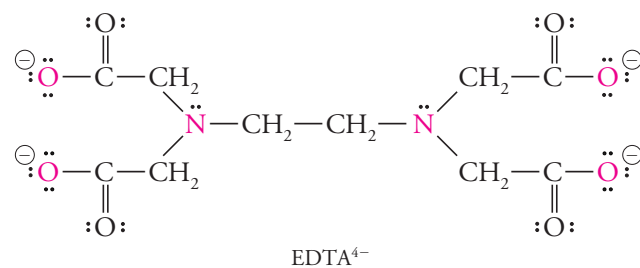
Structures like these are important in “complex ion chemistry,” as we shall see later in this chapter.

One of the most common polydentate ligands is a compound called ethylenediaminetetraacetic acid, mercifully abbreviated EDTA.

■ Sometimes the ligand EDTA is abbreviated using small letters (i.e., edta).

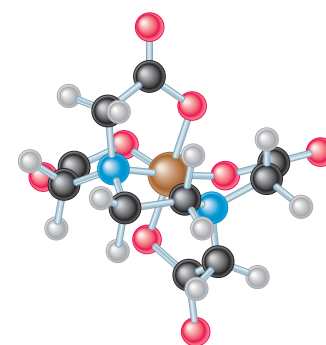


The H atoms attached to the oxygen atoms are easily removed as protons, which gives an anion with a charge of 4−. The structure of the anion, EDTA<sup>4−</sup>, is shown below with the donor atoms in color.



As you can see, the EDTA<sup>4−</sup> ion has six donor atoms, and this permits it to wrap itself around a metal ion and form very stable complexes.

EDTA is a particularly useful and important ligand. It is relatively nontoxic, which allows it to be used in small amounts in foods to retard spoilage. If you look at the labels on bottles of salad dressings, for example, you often will find that one of the ingredients is CaNa<sub>2</sub>EDTA (calcium disodium EDTA). The EDTA<sup>4−</sup> available from this salt forms



**The structure of an EDTA complex.** The nitrogen atoms are blue, oxygen is red, carbon is black, and hydrogen is white. The metal ion is in the center of the complex bonded to the two nitrogens and four oxygens.

■ The *calcium* salt of EDTA is used because the EDTA<sup>4−</sup> ion would otherwise extract Ca<sup>2+</sup> ions from bones, and that would be harmful.

<sup>6</sup>The term *chelate* comes from the Greek *chele*, meaning claw. These bidentate ligands grasp the metal ions with two “claws” (donor atoms) somewhat like a crab holds its prey. (Who says scientists have no imagination?)

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soluble complex ions with any traces of metal ions that might otherwise promote reactions of the salad oils with oxygen, and thereby lead to spoilage.

Many shampoos contain  $\text{Na}_4\text{EDTA}$  to soften water. The  $\text{EDTA}^{4-}$  binds to  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{3+}$  ions, which removes them from the water and prevents them from interfering with the action of detergents in the shampoo (see the photo at the beginning of this chapter). A similar application was described in Facets of Chemistry 17.1 on page 715.

EDTA is also sometimes added in small amounts to whole blood to prevent clotting. It ties up calcium ions, which the clotting process requires. EDTA has even been used as a treatment in cases of poisoning because it can help remove poisonous heavy metal ions, like  $\text{Pb}^{2+}$ , from the body when they have been accidentally ingested.

### Formulas for complexes obey rules

When we write the formula for a complex, we follow rules.



1. The symbol for the metal ion is always given first, followed by the ligands.
2. When more than one kind of ligand is present, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order).
3. The charge on the complex is the algebraic sum of the charge on the metal ion and the charges on the ligands.

For example, the formula of the complex ion of  $\text{Cu}^{2+}$  and  $\text{NH}_3$ , which we mentioned earlier, was written  $\text{Cu}(\text{NH}_3)_4^{2+}$  with the Cu first followed by the ligands. The charge on the complex is  $2+$  because the copper ion has a charge of  $2+$  and the ammonia molecules are neutral. Copper(II) ion also forms a complex ion with four cyanide ions,  $\text{CN}^-$ ,  $\text{Cu}(\text{CN})_4^{2-}$ . The metal ion contributes two ( $+$ ) charges and the four ligands contribute a total of four ( $-$ ) charges, one for each cyanide ion. The algebraic sum is therefore  $-2$ , so the complex ion has a charge of  $2-$ .

The formula for a complex ion is often placed within brackets, with the charge *outside*. The two complexes just mentioned would thus be written as  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{Cu}(\text{CN})_4]^{2-}$ . The brackets emphasize that the ligands are attached to the metal ion and are not free to roam about. One of the many complex ions formed by the chromium(III) ion contains five water molecules and one chloride ion as ligands. To indicate that all are attached to the  $\text{Cr}^{3+}$  ion, we use brackets and write the complex ion as  $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ . When this complex is isolated as a chloride salt, the formula is written  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2$ , in which  $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$  is the cation and so is written first. The formula  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2$  clearly shows that five water molecules and a chloride ion are bonded to the chromium ion, and the other two chloride ions are present to provide electrical neutrality for the salt.

In Chapter 2 you learned about hydrates, and one was the beautiful blue hydrate of copper(II) sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (see page 56). It was much too early then to make the distinction, but the formula should have been written as  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  to show that four of the five water molecules are held in the crystal as part of the complex ion  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ . The fifth water molecule is held in the crystal by being hydrogen bonded to the sulfate ion.

Many other hydrates of metal salts actually contain complex ions of the metals in which water is the ligand. Cobalt salts like cobalt(II) chloride, for example, crystallize from aqueous solutions as hexahydrates (meaning they contain six  $\text{H}_2\text{O}$  molecules per formula unit of the salt). The compound  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Figure 21.14) actually is  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ , and it contains the pink complex  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . This ion also gives solutions of cobalt(II) salts a pink color as can be seen in Figure 21.14. Although most hydrates of metal salts contain complex ions, the distinction is seldom made, and it's acceptable to write the formula for these hydrates in the usual fashion, e.g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  instead of  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

■ Square brackets here do not mean molar concentration. It is usually clear from the context of a discussion whether we intend the brackets to mean molarity.

■ *Hexa-* means “six.”

## EXAMPLE 21.2

## Writing the Formula for a Complex Ion

Write the formula for the complex ion formed by the metal ion  $\text{Cr}^{3+}$  and six  $\text{NO}_2^-$  ions as ligands. Decide whether the complex could be isolated as a chloride salt or a potassium salt, and write the formula for the appropriate salt.

**ANALYSIS:** The rules on page 874 are the tools we'll use to write the formula of the complex ion correctly. If the complex is a positive ion, it would require a negative ion to form a salt, so it could be isolated as a chloride salt; if the complex is a negative ion, then a potassium salt could form.

**SOLUTION:** Six  $\text{NO}_2^-$  ions contribute a total charge of  $6-$ ; the metal contributes a charge of  $3+$ . The algebraic sum is  $(6-) + (3+) = 3-$ . The formula of the complex ion is therefore  $[\text{Cr}(\text{NO}_2)_6]^{3-}$ .

Because the complex is an anion, it requires a cation to form a neutral salt, so the complex could be isolated as a potassium salt, not as a chloride salt. For the salt to be electrically neutral, three  $\text{K}^+$  ions are required for each complex ion,  $[\text{Cr}(\text{NO}_2)_6]^{3-}$ . The formula of the salt would therefore be  $\text{K}_3[\text{Cr}(\text{NO}_2)_6]$ . Notice that in writing the formula for the salt, we've specified the cation ( $\text{K}^+$ ) first, followed by the anion.

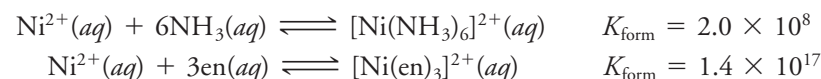
**IS THE ANSWER REASONABLE?** Things to check: Have we written the formula with the metal ion first, followed by the ligands? (Yes.) Have we computed the charge on the complex correctly? (Yes.) Does the formula for the salt correspond to an electrically neutral substance? (Yes.) All seems to be okay.

**Practice Exercise 3:** Write the formula of the complex ion formed by  $\text{Ag}^+$  and two thiosulfate ions,  $\text{S}_2\text{O}_3^{2-}$ . If we were able to isolate this complex ion as its ammonium salt, what would be the formula for the salt? (Hint: Remember, salts are electrically neutral.)

**Practice Exercise 4:** Aluminum chloride crystallizes from aqueous solutions as a hexahydrate. Write the formula for the salt and suggest a formula for the complex ion formed by aluminum ion and water.

### The chelate effect leads to extra stability in complexes

An interesting aspect of the complexes formed by ligands such as ethylenediamine and oxalate ion is their stabilities compared to similar complexes formed by monodentate ligands. For example, the complex  $[\text{Ni}(\text{en})_3]^{2+}$  is considerably more stable than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , even though both complexes have six nitrogen atoms bound to a  $\text{Ni}^{2+}$  ion. We can compare them quantitatively by examining their formation constants.



The ethylenediamine complex is more stable than the ammonia complex by a factor of  $2 \times 10^9$  (2 billion)! This exceptional stability of complexes formed with polydentate ligands is called the **chelate effect**, so named because it occurs in compounds that have these *chelate ring* structures.

There are two related reasons for the chelate effect, which we can understand best if we examine the ease with which the complexes undergo dissociation once formed. One reason appears to be associated with the probability of the ligand being removed from the vicinity of the metal ion when a donor atom becomes detached. If one end of a bidentate ligand comes loose from the metal, the donor atom cannot wander very far because the other end of the ligand is still attached. There is a high probability that the loose end will become reattached to the metal ion before the other end can let go, so overall the ligand appears to be bound tightly. With a monodentate ligand, however, there is nothing to hold the ligand near the metal ion if it becomes detached. The ligand can easily wander off into



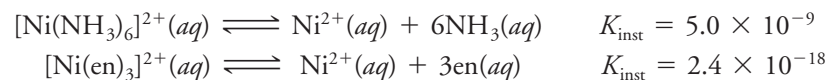
**FIG. 21.14** Color of the cobalt(II) ion in hexahydrate salts. The ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is pink and gives its color both to crystals and to an aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . (Michael Watson.)

Ammonia is a monodentate ligand, and each  $\text{NH}_3$  can supply one donor atom to a metal. Ethylenediamine (en) is a bidentate ligand, and each has two nitrogen donor atoms. Therefore, six ammonia molecules and three ethylenediamine molecules supply the same number of donor atoms.

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the surrounding solution and be lost. As a result, a mono-dentate ligand doesn't behave as if it is as firmly attached to the metal ion as a polydentate ligand.

The second reason is related to the entropy change for the dissociation. In Chapter 18 you learned that when there is an increase in the number of particles in a chemical reaction, the entropy change is positive. Dissociation of both complexes produces more particles, so the entropy change is positive for both of them. However, comparing the two reactions,



we see that dissociation of the ammonia complex gives a net increase of *six* in the number of particles, whereas dissociation of the ethylenediamine complex yields a net increase of *three*. This means the entropy change is more positive for the dissociation of the ammonia complex than for the ethylenediamine complex. The larger entropy change translates into a more favorable  $\Delta G^\circ$  for the decomposition, so at equilibrium the ammonia complex should be dissociated to a greater extent. This is, in fact, what is suggested by the values of their instability constants,  $K_{\text{inst}}$  (recall that  $K_{\text{inst}} = 1/K_{\text{form}}$ ).

■ Recall that  $\Delta G^\circ$  is related to the equilibrium constant. A more favorable  $\Delta G^\circ$  for dissociation should yield a larger equilibrium constant, and, indeed, we find the instability constant is larger for the ammonia complex.

## 21.6

### THE NOMENCLATURE OF METAL COMPLEXES FOLLOWS AN EXTENSION OF THE RULES DEVELOPED EARLIER

The naming of chemical compounds was introduced in Chapter 2 where we discussed the nomenclature system for simple inorganic compounds. This system, revised and kept up to date by the International Union of Pure and Applied Chemistry (IUPAC), has been extended to cover metal complexes. Below are some of the rules that have been developed to name coordination complexes. As you will see, some of the names arrived at by following the rules are difficult to pronounce at first, and may even sound a little odd. However, the primary purpose of this and any other system of nomenclature is to provide a method that gives each unique compound its own unique name and permits us to write the formula of the compound given the name.



Rules for naming complexes

#### Rules of Nomenclature for Coordination Complexes

- Cationic species are named before anionic species.** This is the same rule that applies to other ionic compounds such as NaCl, where we name the cation first followed by the anion (i.e., sodium chloride).
- The names of anionic ligands always end in the suffix -o.**
  - Ligands whose names end in *-ide* have this suffix changed to *-o*.

Anion		Ligand
Chloride	$\text{Cl}^-$	chloro-
Bromide	$\text{Br}^-$	bromo-
Cyanide	$\text{CN}^-$	cyano-
Oxide	$\text{O}^{2-}$	oxo-

- Ligands whose names end in *-ite* or *-ate* become *-ito* and *-ato*, respectively.

Anion		Ligand
Carbonate	$\text{CO}_3^{2-}$	carbonato-
Thiosulfate	$\text{S}_2\text{O}_3^{2-}$	thiosulfato-
Thiocyanate	$\text{SCN}^-$	thiocyanato- (when bonded through sulfur) isothiocyanato- (when bonded through nitrogen)
Oxalate	$\text{C}_2\text{O}_4^{2-}$	oxalato-
Nitrite	$\text{NO}_2^-$	nitrito- (when bonded through oxygen; written ONO in formula for complex) <sup>a</sup>

<sup>a</sup>An exception to this is when the nitrogen of the  $\text{NO}_2^-$  ion is bonded to the metal, in which case the ligand is named nitro-

## 21.6 The Nomenclature of Metal Complexes Follows an Extension of the Rules Developed Earlier 877

3. **A neutral ligand is given the same name as the neutral molecule.** By this rule, the molecule ethylenediamine, when serving as a ligand, is called ethylenediamine in the name of the complex. Two very important exceptions to this, however, are water and ammonia. These are named as follows when they serve as ligands.



4. **When there is more than one of a particular ligand, their number is specified by the prefixes di- = 2, tri- = 3, tetra- = 4, penta- = 5, hexa- = 6, and so forth. When confusion might result by using those prefixes, the following are used instead: bis- = 2, tris- = 3, tetrakis- = 4.** Following this rule, the presence of two chloride ligands in a complex would be indicated as *dichloro-* (notice, too, the ending on the ligand name). However, if two ethylenediamine ligands are present, use of the prefix *di-* might cause confusion. Someone reading the name might wonder whether diethylenediamine means two ethylenediamine molecules or one molecule of a substance called diethylenediamine. To avoid this problem we place the ligand name in parentheses preceded by *bis*; that is, *bis(ethylenediamine)*.
5. **As noted earlier, in the formula of a complex, the symbol for the metal is written first, followed by those of the ligands. Among the ligands, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order). In the name of the complex, the ligands are named first, in alphabetical order without regard to charge, followed by the name of the metal.** For example, suppose we had a complex composed of  $\text{Co}^{3+}$ , two  $\text{Cl}^-$  (chloro- ligands), one  $\text{CN}^-$  (cyano- ligand), and three  $\text{NH}_3$  (ammine- ligands). The formula of the electrically neutral complex would be written  $[\text{CoCl}_2(\text{CN})(\text{NH}_3)_3]$ . In the name of this complex, the ligands would be specified before the metal as *triamminedichlorocyano-* (*triammine-* for the three  $\text{NH}_3$  ligands, *dichloro-* for the two  $\text{Cl}^-$  ligands, and *cyano-* for the  $\text{CN}^-$  ligand). Notice that in alphabetizing the names of the ligands, we ignore the prefixes *tri-* and *di-*. Thus *triammine-* is written before *dichloro-* because *ammine-* precedes *chloro-* alphabetically. For the same reason, *dichloro-* is written before *cyano-*. The complete name for the complex is given below under Rule 7.
6. **Negative (anionic) complex ions always end in the suffix -ate.** This suffix is appended to the English name of the metal atom in most cases. However, if the name of the metal ends in *-ium*, *-um*, or *-ese*, the ending is dropped and replaced by *-ate*.

■ *Bis-* is employed here so that when the name is used in verbal communication it is clear that the meaning is two ethylenediamine molecules.

■ In the formula, the metal ion appears first, followed by the ligands; in the name, the ligands are specified first, followed by the metal.

■ The ligands are alphabetized according to the first letter of the name of the ligand, not the first letter of the prefix.

Metal	Metal as Named in an Anionic Complex
Aluminum	aluminate
Chromium	chromate
Manganese	manganate
Nickel	nickelate
Cobalt	cobaltate
Zinc	zincate
Platinum	platinate
Vanadium	vanadate

For metals whose symbols are derived from their Latin names, the suffix *-ate* is appended to the Latin stem. (An exception, however, is mercury; in an anion it is named *mercurate*.)

Metal	Stem	Metal as Named in an Anionic Complex
Iron	ferr-	ferrate
Copper	cupr-	cuprate
Lead	plumb-	plumbate
Silver	argent-	argentate
Gold	aur-	aurate
Tin	stann-	stannate

For neutral or positively charged complexes, the metal is *always* specified with the English name for the element, *without any suffix*.

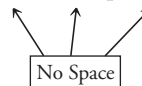
## 878 Chapter 21 Nonmetals, Metalloids, Metals, and Metal Complexes

## 7. The oxidation state of the metal in the complex is written in Roman numerals within parentheses following the name of the metal. For example,

$[\text{CoCl}_2(\text{CN})(\text{NH}_3)_3]$  is triamminedichlorocyanocobalt(III)

$[\text{Co}(\text{NH}_3)_6]^{3+}$  is the hexaamminecobalt(III) ion

$[\text{CuCl}_4]^{2-}$  is the tetrachlorocuprate(II) ion



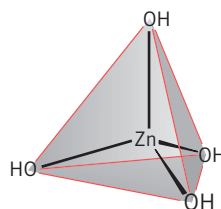
As you learned earlier, the charge on the complex is the algebraic sum of the charges on the ligands and the charge on the metal ion.

Notice that there are no spaces between the names of the ligands and the name of the metal, and that there is no space between the name of the metal and the parentheses that enclose the oxidation state expressed in Roman numerals.

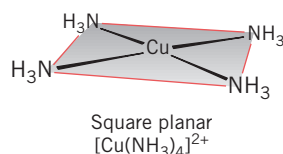
The following are some additional examples. Study them carefully to see how the rules given above apply. Then try the practice exercises that follow.

Notice, once again, that the alphabetical order of the ligands is determined by the first letter in the name of the ligand, not the first letter in the prefix.

$[\text{Ni}(\text{CN})_4]^{2-}$	tetracyanonickelate(II) ion
$\text{K}_3[\text{CoCl}_6]$	potassium hexachlorocobaltate(III)
$[\text{CoCl}_2(\text{NH}_3)_4]^+$	tetraamminedichlorocobalt(III) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	sodium hexanitrocobaltate(III)
$[\text{Ag}(\text{NH}_3)_2]^+$	diamminesilver(I) ion
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	dithiosulfatoargentate(I) ion
$[\text{Mn}(\text{en})_3]\text{Cl}_2$	tris(ethylenediamine)manganese(II) chloride
$[\text{PtCl}_2(\text{NH}_3)_2]$	diamminedichloroplatinum(II)



Tetrahedral  
 $[\text{Zn}(\text{OH})_4]^{2-}$



Square planar  
 $[\text{Cu}(\text{NH}_3)_4]^{2+}$

### FIG. 21.15 Tetrahedral and square planar geometries.

These are structures that occur for complexes in which the metal ion has a coordination number of 4. For the copper complex, we are viewing the square planar structure tilted back into the plane of the paper.

Ordinarily, the VSEPR model isn't used to predict the structures of transition metal complexes because it can't be relied on to give correct results when the metal has a partially filled  $d$  subshell.

**Practice Exercise 5:** Write the formula for each of the following: (a) hexachlorostannate(IV) ion and (b) ammonium diaquatetracyanoferrate(II). (Hint: Divide each name into its various parts.)

**Practice Exercise 6:** Name the following compounds: (a)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and (b)  $[\text{CrCl}_2(\text{en})_2]\text{SO}_4$ .

## 21.7 COORDINATION NUMBER AND STRUCTURE ARE OFTEN RELATED

One of the most interesting aspects of the study of complexes is the kinds of structures that they form. In many ways, this is related to the **coordination number** of the metal ion, which we define as *the number of donor atoms attached to the metal ion*. For example, in the complex  $[\text{Ni}(\text{CN})_4]^{2-}$  the nickel is surrounded by the four carbon atoms that belong to the cyanide ions, so the coordination number of  $\text{Ni}^{2+}$  in the complex is 4. Similarly, the coordination number of  $\text{Cr}^{3+}$  in the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion is 6, and the coordination number of  $\text{Ag}^+$  in  $[\text{Ag}(\text{NH}_3)_2]^+$  is 2.

Sometimes the coordination number isn't immediately obvious from the formula of the complex. For example, you learned that there are many polydentate ligands which contain more than one donor atom that can bind simultaneously to a metal ion. Often, a metal is able to accommodate two or more polydentate ligands to give complexes with formulas such as  $[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$  and  $[\text{Cr}(\text{en})_3]^{3+}$ . In each of these examples, the coordination number of the  $\text{Cr}^{3+}$  is 6. In the  $[\text{Cr}(\text{en})_3]^{3+}$  ion, there are three ethylenediamine ligands that each supply two donor atoms, for a total of 6, and in  $[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ , the two ethylenediamine ligands supply a total of 4 donor atoms and the two  $\text{H}_2\text{O}$  molecules supply another 2, so once again the total is 6.

### Structures of complexes depend on coordination number

For metal complexes, there are certain geometries that are usually associated with particular coordination numbers.

## 21.7 Coordination Number and Structure Are Often Related 879

**Coordination Number 2.** Examples are complexes such as  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Ag}(\text{CN})_2]^-$ . Usually, these complexes have a linear structure such as



(Since the  $\text{Ag}^+$  ion has a filled  $d$  subshell, it behaves as any of the representative elements as far as predicting geometry by VSEPR theory, so these structures are exactly what we would expect based on that theoretical model.)

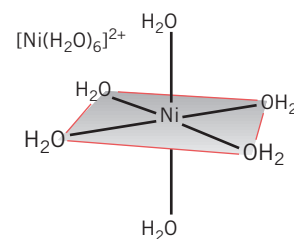
**Coordination Number 4.** Two common geometries occur when four ligand atoms are bonded to a metal ion, namely, tetrahedral and square planar. These are illustrated in Figure 21.15. The tetrahedral geometry is usually found with metal ions that have completely filled  $d$  subshells, such as  $\text{Zn}^{2+}$ . The complexes  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $[\text{Zn}(\text{OH})_4]^{2-}$  are examples.

Square planar geometries are observed for complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and especially  $\text{Pt}^{2+}$ . Examples are  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ , and  $[\text{PtCl}_4]^{2-}$ . The most well-studied square planar complexes are those of  $\text{Pt}^{2+}$ , because they are considerably more stable than the others.

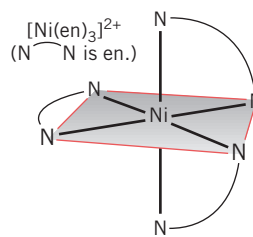
**Coordination Number 6.** The most common coordination number for complex ions is 6. Examples are  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $[\text{Ni}(\text{en})_3]^{2+}$ , and  $[\text{Co}(\text{EDTA})]^-$ . With few exceptions, all complexes with a coordination number of 6 are octahedral. This holds true for those formed from both monodentate and bidentate ligands, as illustrated in Figure 21.16. In describing the shapes of octahedral complexes, most chemists use one of the simplified drawings of the octahedron shown in Figure 21.17.

**Practice Exercise 7:** What is the coordination number of the metal ion in  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ ? (Hint: Identify the ligand and sketch its structure.)

**Practice Exercise 8:** What is the coordination number of the metal ion in (a)  $[\text{CoCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ , (b)  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{en})]^-$ , and (c)  $[\text{Co}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ ?



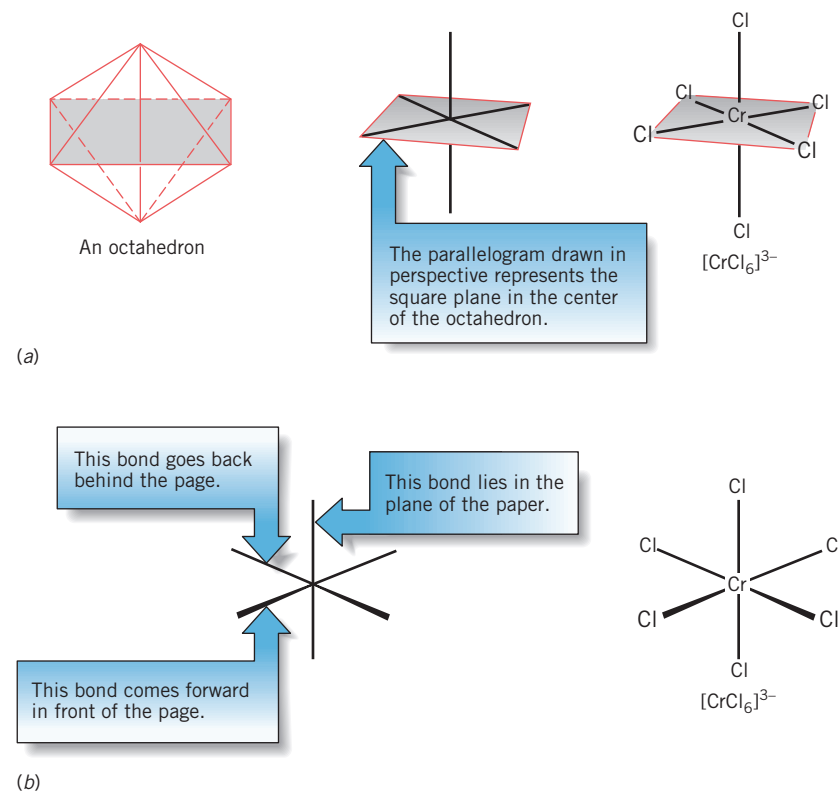
Complex with monodentate ligands



Complex with bidentate ligands

**FIG. 21.16 Octahedral**

**complexes.** Complexes with this geometry can be formed with either monodentate ligands such as water or with polydentate ligands such as ethylenediamine (en). To simplify the drawing of the ethylenediamine complex, the atoms joining the donor nitrogen atoms in the ligand,  $-\text{CH}_2-\text{CH}_2-$ , are represented as the curved line between the N atoms. Also notice that the nitrogen atoms of the bidentate ligand span adjacent positions within the octahedron. This is the case for all polydentate ligands that you will encounter in this book.



**FIG. 21.17 Simplified representations of the octahedral complex,  $[\text{CrCl}_6]^{3-}$ .**

(a) Drawings similar to those you learned to construct in Chapter 9. (b) An alternative method of representing the octahedron.

## 21.8 ISOMERS OF COORDINATION COMPLEXES ARE COMPOUNDS WITH THE SAME FORMULA BUT DIFFERENT STRUCTURES



**Chromium(III) chloride hexahydrate.** The hydrated chromium(III) chloride purchased from chemical supply companies is actually  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ . Its green color in both the solid state and solution is due to the complex ion  $[\text{CrCl}_2(\text{H}_2\text{O})_4]^{+}$ . (Michael Watson.)

■  $\text{Ag}_2\text{SO}_4$  is soluble but  $\text{BaSO}_4$  is insoluble.  $\text{BaBr}_2$  is soluble but  $\text{AgBr}$  is insoluble.

When you write the chemical formula for a compound, you might be tempted to think that you should also be able to predict exactly what the structure of the molecule or ion is. As you may realize by now, this just isn't possible in many cases. Sometimes we can use simple rules to make reasonable structural guesses, as in the discussion of the drawing of Lewis structures in Chapter 8, but these rules apply only to simple molecules and ions. For more complex substances, there usually is no way of knowing for sure what the structure of the molecule or ion is without performing the necessary experiments to determine the structure.

One of the reasons that structures can't be predicted with certainty from chemical formulas alone is that there are usually many different ways that the atoms in the formula can be arranged. In fact, it is frequently possible to isolate two or more compounds that actually have the same chemical formula. For example, three different solids, each with its own characteristic color and other properties, can be isolated from a solution of chromium(III) chloride. All three have the same overall composition, and in the absence of other data, their formulas are written  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . However, experiments have shown that these solids are actually the salts of three different complex ions. Their actual formulas (and colors) are

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	purple
$[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	blue-green
$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	green

*Even though their overall compositions are the same, each of these substances is a distinct chemical compound with its own unique set of properties.*

The existence of two or more compounds, each having the same chemical formula, is known as **isomerism**. In the example above, each salt is said to be an **isomer** of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . For coordination compounds, isomerism can occur in a variety of ways. In the example above, isomers exist because of the different possible ways that the water molecules and chloride ions can be held in the crystals. In one instance, all the water molecules serve as ligands, while in the other two, part of the water is present as water of hydration and some of the chloride is bonded to the metal ion. Another example, which is similar in some respects, is  $\text{Cr}(\text{NH}_3)_5\text{SO}_4\text{Br}$ . This "substance" can be isolated as two isomers.



They can be distinguished chemically by their differing abilities to react with  $\text{Ag}^+$  and  $\text{Ba}^{2+}$ . The first isomer reacts in aqueous solution with  $\text{Ag}^+$  to give a precipitate of  $\text{AgBr}$ , but it doesn't react with  $\text{Ba}^{2+}$ . This tells us that  $\text{Br}^-$  exists as a free ion in the solution. It also suggests the  $\text{SO}_4^{2-}$  is bound to the chromium and is unavailable to react with  $\text{Ba}^{2+}$  to give insoluble  $\text{BaSO}_4$ .

The second isomer,  $[\text{CrBr}(\text{NH}_3)_5]\text{SO}_4$ , reacts in solution with  $\text{Ba}^{2+}$  to give a precipitate of  $\text{BaSO}_4$ , which means there is free  $\text{SO}_4^{2-}$  in the solution. There is no reaction with  $\text{Ag}^+$ , however, because  $\text{Br}^-$  is bonded to the chromium and is not available as free  $\text{Br}^-$  in the solution. Thus, we see that even though both isomers have the same overall composition, they behave chemically in quite different ways and are therefore distinctly different compounds.

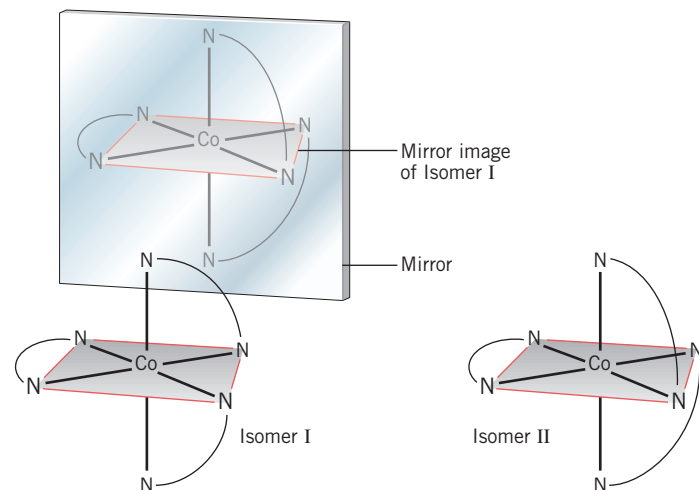
### Stereoisomerism relates to how atoms are arranged in space

One of the most interesting kinds of isomerism found among coordination compounds is called **stereoisomerism**, which is defined as *differences among isomers that arise as a result of the various possible orientations of their atoms in space*. In other words, when stereoisomerism exists, we have compounds in which the same atoms are attached to each other, but they differ in the way those atoms are arranged in space relative to one another.



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**FIG. 21.20** The two isomers of  $[\text{Co}(\text{en})_3]^{3+}$ . Isomer II is constructed as the mirror image of Isomer I. No matter how Isomer II is turned about, it is not superimposable on Isomer I.



Chirality is the technical term for “handedness,” meaning objects structurally related to each other as are our left and right hands.



**Thumbtacks are not chiral.** Thumbtacks and their mirror images are superimposable; they are not chiral and are identical. (Andy Washnik.)

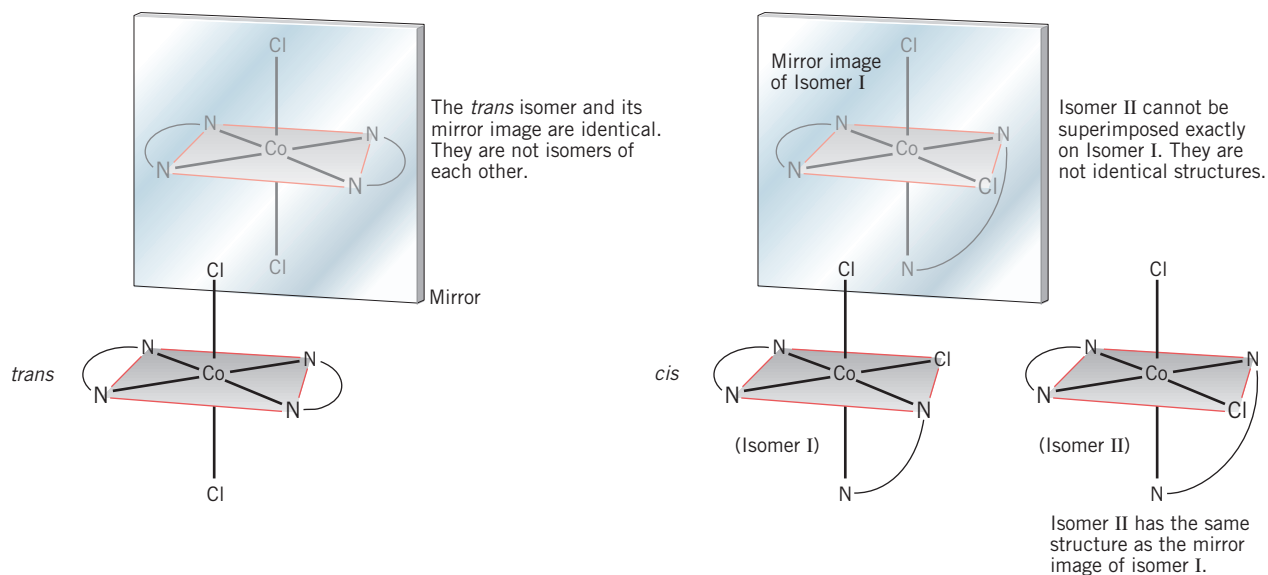
your right-hand glove would fit the reflection of your left hand perfectly. Thus, your two hands are *nonsuperimposable mirror images* of each other.

If two objects are nonsuperimposable mirror images of each other, they are not identical and are said to be **chiral**. Your left and right hands have this property and are not exactly alike. A pair of thumbtacks, however, are mirror images of each other and *are* superimposable, so they are identical. Thumbtacks are not chiral.

#### Some complex ions exhibit chirality

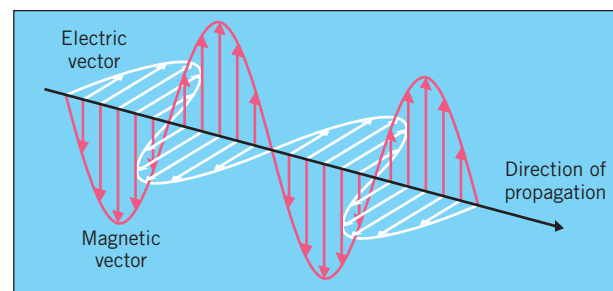
The most common examples of chirality among coordination compounds occur with octahedral complexes that contain two or three bidentate ligands—for instance,  $[\text{CoCl}_2(\text{en})_2]^+$  and  $[\text{Co}(\text{en})_3]^{3+}$ . For the complex  $[\text{Co}(\text{en})_3]^{3+}$ , the two nonsuperimposable isomers, called **enantiomers**, are shown in Figure 21.20. For the complex  $[\text{CoCl}_2(\text{en})_2]^+$ , only the *cis* isomer is chiral, as described in Figure 21.21.

As you can see, chiral isomers differ in only a very minor way from each other. This difference is so subtle that most of the properties of chiral isomers are identical. They have identical melting points and boiling points, and in nearly all of their reactions, their behavior is exactly alike. The only way that the difference between chiral molecules or ions manifests itself is in the way that they interact with physical or chemical “probes” that also

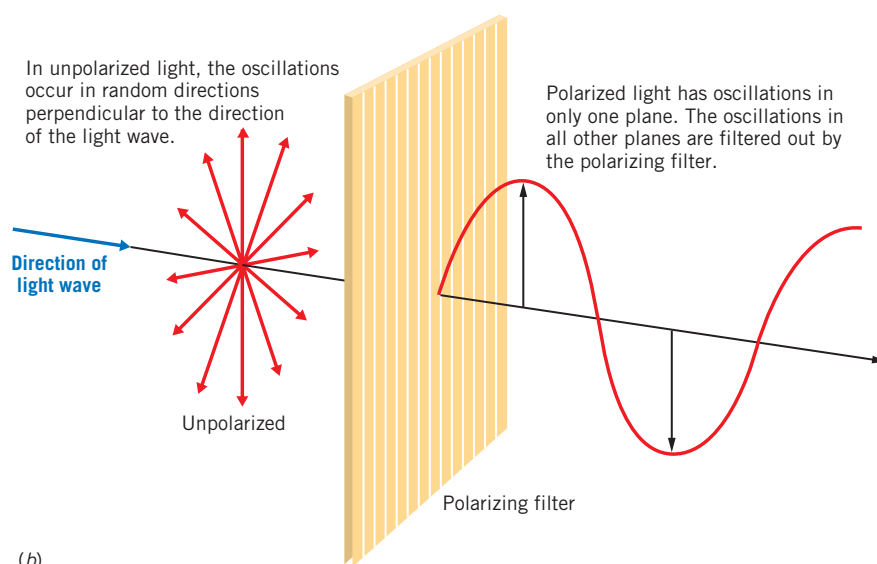


**FIG. 21.21** Isomers of the  $[\text{CoCl}_2(\text{en})_2]^+$  ion. The mirror image of the *trans* isomer can be superimposed exactly on the original, so the *trans* isomer is not chiral. The *cis* isomer (Isomer I) is chiral, however, because its mirror image (Isomer II) cannot be superimposed on the original.

## 21.8 Isomers of Coordination Complexes Are Compounds with the Same Formula but Different Structures 883



(a)



(b)

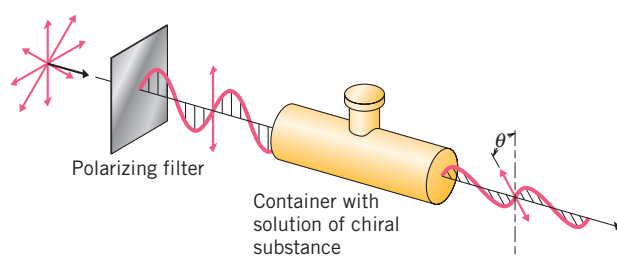
**FIG. 21.22 Unpolarized and polarized light.** (a) Light possesses electric and magnetic components that oscillate perpendicular to the direction of propagation of the light wave. (b) In unpolarized light, the electromagnetic oscillations of the photons are oriented at random angles around the axis of propagation of the light wave. The polarizing filter has the effect of preventing oscillations from passing through unless they are in one particular plane. The result is called plane-polarized light.

have a handedness about them. For example, if two reactants are both chiral, then a given isomer of one of them will usually behave slightly differently toward each of the two isomers of the other reactant. This has very profound effects in biochemical reactions, in which nearly all of the molecules involved are chiral.

#### Chiral isomers can rotate plane-polarized light

One way that chiral isomers differ is in the way they affect polarized light. Light is *electromagnetic radiation* that possesses both electric and magnetic components that behave like vectors. These vectors oscillate in directions perpendicular to the direction in which the light wave is traveling (Figure 21.22a). In ordinary light, the oscillations of the electric and magnetic fields of the photons are oriented randomly around the direction of the light beam. In **plane-polarized light**, all the oscillations occur in the same plane (Figure 21.22b). Ordinary light can be polarized in several ways. One is to pass it through a special film of plastic, as in a pair of Polaroid sunglasses. This has the effect of filtering out all the vibrations except those that are in one plane (Figure 21.22b).

Chiral isomers like those described in Figures 21.20 and 21.21 are said to be **optically active** and have the ability to rotate plane-polarized light, as illustrated in Figure 21.23. Because of this phenomenon, chiral isomers are said to be **optical isomers**.



**FIG. 21.23 Rotation of polarized light by a chiral substance.** When plane-polarized light passes through a solution of a chiral substance, the plane of polarization is rotated either to the left or to the right. In this illustration, the plane of polarization of the light is rotated to the left by a measurable angle  $\theta$  (as seen facing the light source).

### 21.9 BONDING IN TRANSITION METAL COMPLEXES INVOLVES *d* ORBITALS

Complexes of the transition metals differ from the complexes of other metals in two special ways: (1) they are usually colored, whereas complexes of the representative metals are usually (but not always) colorless, and (2) their magnetic properties are often affected by the ligands attached to the metal ion. For example, it is not unusual for a given metal ion to form complexes with different ligands to give a rainbow of colors, as illustrated in Figure 21.24 for a series of complexes of cobalt. Also, because transition metal ions often have incompletely filled *d* subshells, we expect to find many of them with unpaired *d* electrons, and compounds that contain them should be paramagnetic. But for a given metal ion, the number of unpaired electrons is not always the same from one complex to another. For example,  $\text{Fe}^{2+}$  has four of its six  $3d$  electrons unpaired in the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion, but all of its electrons are paired in the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion. As a result, the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion is paramagnetic and the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is diamagnetic.

**FIG. 21.24** Colors of complex ions depend on the nature of the ligands. Each of these brightly colored solutions contains a complex ion of  $\text{Co}^{3+}$ . The variety of colors arises because of the different ligands (molecules or anions) that are bonded to the cobalt ion in the complexes. (Michael Watson.)



#### Crystal field theory considers how *d* orbital energies are affected by the ligands

Any theory that attempts to explain the bonding in complex ions must also explain their colors and magnetic properties. One of the simplest theories that does this is the **crystal field theory**. The theory gets its name from its original use in explaining the behavior of transition metal ions in crystals. It was discovered later that the theory works well for transition metal complexes, too.

Crystal field theory ignores covalent bonding in complexes. It assumes that the primary stability comes from the electrostatic attractions between the positively charged metal ion and the negative charges of the ligand anions or dipoles. Crystal field theory's unique approach, though, is the way it examines how the negative charges on the ligands affect the energy of the complex by influencing the energies of the *d* orbitals of the metal ion, and this is what we will focus our attention on here. To understand the theory, therefore, it is essential that you know how the *d* orbitals are shaped and especially how they are oriented in space relative to each other. The *d* orbitals were described in Chapter 7, and they are illustrated again in Figure 21.25.

First, notice that four of the *d* orbitals have the same shape but point in different directions. These are the  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ . Each has four lobes of electron density. The fifth *d* orbital, labeled  $d_{z^2}$ , has two lobes that point in opposite directions along the *z* axis plus a small donut-shaped ring of electron density around the center that is concentrated in the *xy* plane.

Of prime importance to us are the *directions* in which the lobes of the *d* orbitals point. Notice that three of them— $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ —point *between* the *x*, *y*, and *z* axes. The other two—the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals—have their maximum electron densities *along* the *x*, *y*, and *z* axes.

More complete theories consider the covalent nature of metal–ligand bonding, but crystal field theory nevertheless provides a useful model for explaining the colors and magnetic properties of complexes.

The labels for the *d* orbitals come from the mathematics of quantum mechanics.

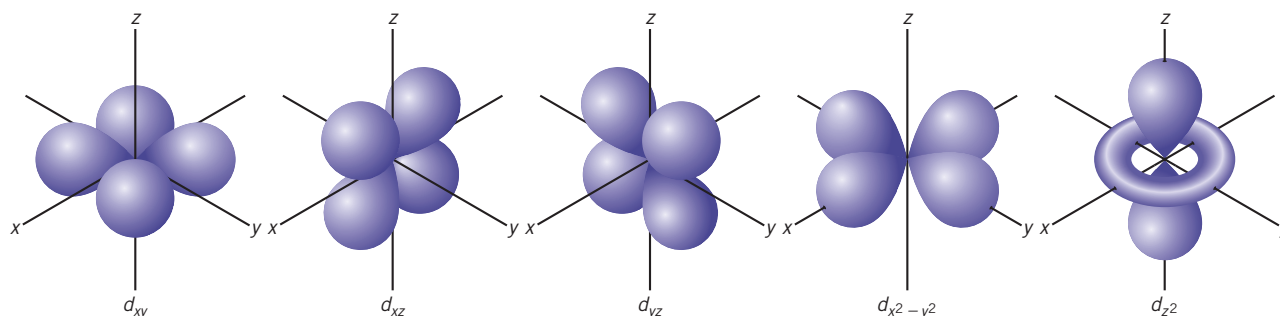
21.9 Bonding in Transition Metal Complexes Involves  $d$  Orbitals 885

FIG. 21.25 The shapes and directional properties of the five  $d$  orbitals of a  $d$  subshell.

Now let's consider constructing an octahedral complex within this coordinate system. We can do this by bringing ligands in along each of the axes as shown in Figure 21.26. The question we want to answer is, "How do these ligands affect the energies of the  $d$  orbitals?"

In an isolated atom or ion, all the  $d$  orbitals of a given  $d$  subshell have the same energy. Therefore, an electron will have the same energy regardless of which  $d$  orbital it occupies. In an octahedral complex, however, this is no longer true. If the electron is in the  $d_{x^2-y^2}$  or  $d_{z^2}$  orbital, it is forced to be nearer the negative charge of the ligands than if it is in a  $d_{xy}$ ,  $d_{xz}$ , or  $d_{yz}$  orbital. Since the electron itself is negatively charged and is repelled by the charges of the ligands, the electron's potential energy will be higher in the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals than in a  $d_{xy}$ ,  $d_{xz}$ , or  $d_{yz}$  orbital. Therefore, as the complex is formed, the  $d$  subshell actually splits into *two* new energy levels as shown in Figure 21.27. Here we see that regardless of which orbital the electron occupies, its energy increases because it is repelled by the negative charges of the approaching ligands. However, the electron is repelled *more* (and has a higher energy) if it is in an orbital that points directly at the ligands than if it occupies an orbital that points between them.

In an octahedral complex, the energy difference between the two sets of  $d$  orbital energy levels is called the **crystal field splitting**. It is usually given the symbol  $\Delta$  (delta), and its magnitude depends on the following factors:

**The nature of the ligand.** Some ligands produce a larger splitting of the energies of the  $d$  orbitals than others. For a given metal ion, for example, cyanide always gives a large value of  $\Delta$  and  $F^-$  always gives a small value. We will have more to say about this later.

**The oxidation state of the metal.** For a given metal and ligand, the size of  $\Delta$  increases with an increase in the oxidation number of the metal. As electrons are removed from a metal and the charge on the ion becomes more positive, the ion becomes smaller. This

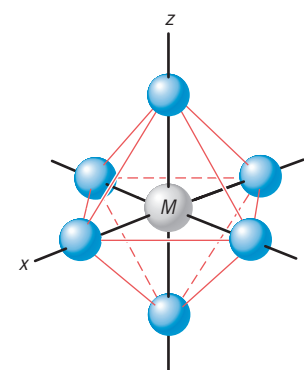
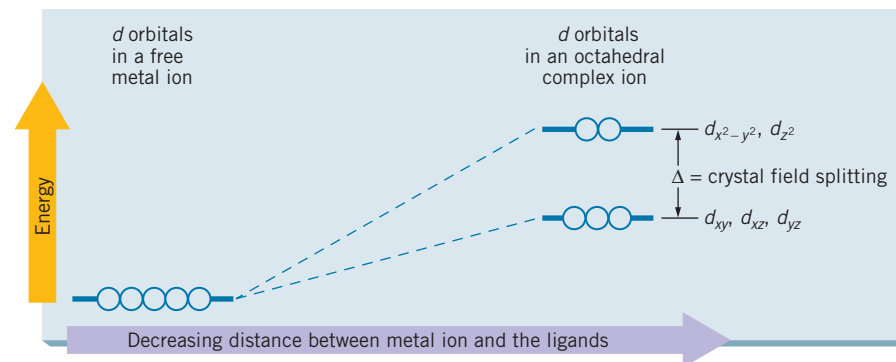


FIG. 21.26 An octahedral complex ion with ligands that lie along the  $x$ ,  $y$ , and  $z$  axes.



**TOOLS**  
Crystal field splitting pattern for octahedral complexes

FIG. 21.27 The changes in the energies of the  $d$  orbitals of a metal ion as an octahedral complex is formed. As the ligands approach the metal ion, the  $d$  orbitals split into two new energy levels.

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means that the ligands are attracted to the metal more strongly and they can approach the center of the complex more closely. As a result, they also approach the  $d$  orbitals along the  $x$ ,  $y$ , and  $z$  axes more closely, and thereby cause a greater repulsion. This causes a greater splitting of the two  $d$  orbital energy levels and a larger value of  $\Delta$ .

**The row in which the metal occurs in the periodic table.** For a given ligand and oxidation state, the size of  $\Delta$  increases going down a group. In other words, for a given ligand, an ion of an element in the first row of transition elements has a smaller value of  $\Delta$  than the ion of a heavier member of the same group. Thus, comparing complexes of  $\text{Ni}^{2+}$  and  $\text{Pt}^{2+}$  with the same ligand, we find that the platinum complex has the larger crystal field splitting. The explanation of this is that in the larger ion (e.g.,  $\text{Pt}^{2+}$ ), the  $d$  orbitals are larger and more diffuse and extend farther from the nucleus in the direction of the ligands. This produces a larger repulsion between the ligands and the orbitals that point at them.

The magnitude of  $\Delta$  is very important in determining the properties of complexes, including the stabilities of oxidation states of the metal ions, the colors of complexes, and their magnetic properties. Let's look at some examples.

### Crystal field theory can explain the relative stabilities of oxidation states

Comparing the cations formed by chromium, it is found that the  $\text{Cr}^{2+}$  ion is very easily oxidized to  $\text{Cr}^{3+}$ . This is easily explained by crystal field theory. In water, we expect the ions to exist as the complexes  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , respectively. Let's examine the energies and electron populations of the  $d$  orbital energy levels in each complex (Figure 21.28).

The element chromium has the electron configuration

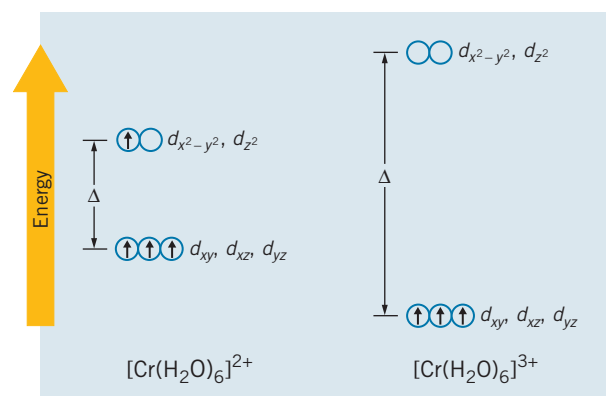


Removing two electrons gives the  $\text{Cr}^{2+}$  ion, and removing three gives  $\text{Cr}^{3+}$ .



Next, we distribute the  $d$  electrons among the various  $d$  orbitals following Hund's rule, but for  $\text{Cr}^{2+}$  we have to make a choice. Should the electrons all be forced into the lower of the two energy levels, or should they be spread out? From the diagram we see that the fourth electron does not pair with one of the others in the lower energy  $d$  orbital level. Instead, three electrons populate the lower level and the fourth is in the upper level. We will discuss *why* this happens later, but for now, let's use the two energy diagrams to explain why  $\text{Cr}^{2+}$  is so easy to oxidize.

**FIG. 21.28** Energy level diagrams for the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ions. The magnitude of  $\Delta$  is larger for the chromium(III) complex because the  $\text{Cr}^{3+}$  ion is smaller than the  $\text{Cr}^{2+}$  ion and the ligands are drawn closer to the metal ion, thereby increasing repulsions felt by the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.



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There are actually two factors that favor the oxidation of Cr(II) to Cr(III). First, the electron that is removed from  $\text{Cr}^{2+}$  to give  $\text{Cr}^{3+}$  comes from the *higher* energy level, so oxidizing the chromium(II) *removes* a high-energy electron. The second factor is the effect caused by increasing the oxidation state of the chromium. As we've pointed out, this increases the magnitude of  $\Delta$ , and as you can see, the energy of the three electrons that remain is lowered. Thus, both the removal of a high-energy electron and the lowering of the energy of the electrons that are left behind help make the oxidation occur, and the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion is very easily oxidized to  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

### Crystal field theory can explain the colors of complex ions

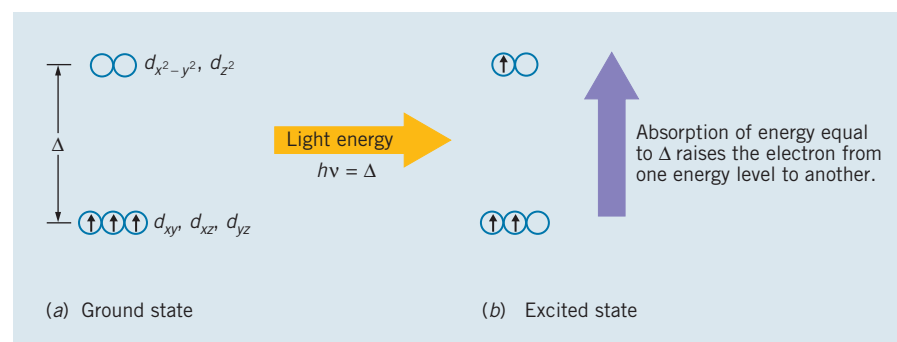
When light is absorbed by an atom, molecule, or ion, the energy of the photon raises an electron from one energy level to another. In many substances, such as sodium chloride, the energy difference between the highest energy populated level and the lowest energy unpopulated level is quite large, so the frequency of a photon that carries the necessary energy lies outside the visible region of the spectrum. The substance appears white because visible light is unaffected; it is reflected unchanged.

Remember,  $E = h\nu$ . The energy of the photon absorbed determines the frequency (and wavelength) of the absorbed light.

For complex ions of the transition metals, the energy difference between the  $d$  orbital energy levels is not very large, and photons with frequencies in the visible region of the spectrum are able to raise an electron from the lower energy set of  $d$  orbitals to the higher energy set. This is shown in Figure 21.29 for the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion.

As you know, white light contains photons of all the frequencies and colors in the visible spectrum. If we shine white light through a solution of a complex, the light that passes through has all the colors *except* those that have been absorbed. It is not difficult to determine what will be seen if we know what colors are being absorbed. All we need is a color wheel like the one shown in Figure 21.30. Across from each other on the color wheel are *complementary colors*. Green-blue is the complementary color to red, and yellow is the complementary color to violet-blue. If a substance absorbs a particular color when bathed in white light, the perceived color of the reflected or transmitted light is the complementary color. In the case of the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, the light absorbed when the electron is raised from one set of  $d$  orbitals to the other has a frequency of  $5.22 \times 10^{14}$  Hz, which is the color of yellow light. This is why a solution of the ion appears violet.<sup>7</sup>

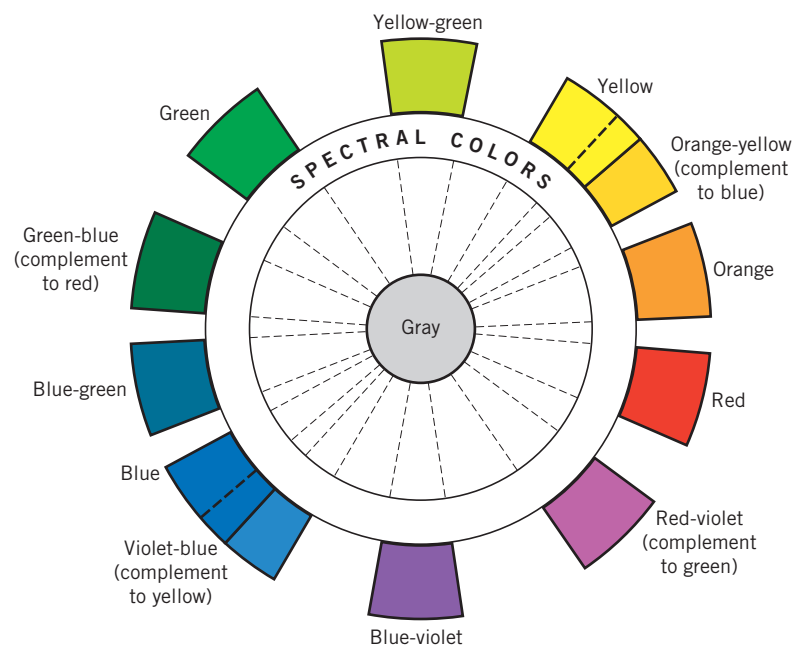
Because of the relationship between the energy and frequency of light, we see that the color of the light absorbed by a complex depends on the magnitude of  $\Delta$ ; the larger the size of  $\Delta$ , the more energy the photon must have and the higher will be the frequency of the absorbed light. For a given metal in a given oxidation state, the size of  $\Delta$  depends on the ligand. Some ligands give a large crystal field splitting, while others



**FIG. 21.29** Absorption of a photon by the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex. (a) The electron distribution in the ground state of the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion. (b) Light energy raises an electron from the lower energy set of  $d$  orbitals to the higher energy set.

<sup>7</sup>The perception of color is actually somewhat more complex than this because of the varying sensitivity of the human eye to various wavelengths. For example, the eye is much more sensitive to green than to red. If a compound reflects both of those colors with equal intensity, it will appear greenish simply because the eye sees green better than it sees red.

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**FIG. 21.30 A color wheel.** Colors that are across from each other are called complementary colors. When a substance absorbs a particular color, light that is reflected or transmitted has the color of its complement. Thus something that absorbs red light appears green-blue, and vice versa.

give a small splitting. For example, ammonia produces a larger splitting than water, so the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  absorbs light of higher energy and higher frequency than  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ . ( $[\text{Cr}(\text{NH}_3)_6]^{3+}$  absorbs blue light and appears yellow.) Because changing the ligand changes  $\Delta$ , the same metal ion is able to form a variety of complexes with a large range of colors.

■ The order of the ligands can be determined by measuring the frequencies of the light absorbed by complexes.

A ligand that produces a large crystal field splitting with one metal ion also produces a large  $\Delta$  in complexes with other metals. For example, cyanide ion is a very effective ligand and always gives a very large  $\Delta$ , regardless of the metal to which it is bound. Ammonia is less effective than cyanide ion but more effective than water. Thus, ligands can be arranged in order of their effectiveness at producing a large crystal field splitting. This sequence is called the **spectrochemical series**. Such a series containing some common ligands arranged in order of their decreasing strength is



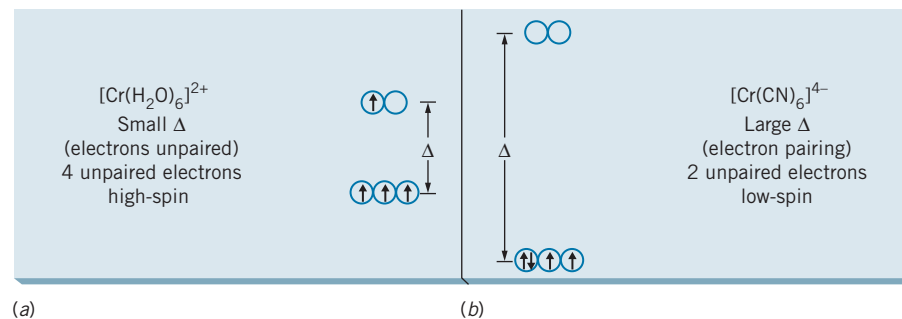
For a given metal ion, cyanide ion produces the largest  $\Delta$  and iodide produces the smallest.

### Crystal field theory can explain the magnetic properties of complexes

Let's return to the question of the electron distribution among the  $d$  orbitals in  $\text{Cr}^{2+}$  complexes. As you saw above, this ion has four  $d$  electrons, and we noted that in placing these electrons in the  $d$  orbitals we had to make a decision about where to place the fourth electron. There's no question about the fate of the first three, of course. They just spread out across the three  $d$  orbitals in the lower level with their spins unpaired. In other words, we just follow Hund's rule, which we learned to apply in Chapter 7. But when we come to the fourth electron we have to decide whether to pair it with one of the electrons already in a  $d$  orbital of the lower set or to place it in one of the  $d$  orbitals of the higher set.<sup>8</sup> If we place it in the lower energy level, we give it extra stability (lower energy), but some of this stability is lost because it requires energy, called the **pairing energy**,  $P$ , to force the electron into an orbital that's already occupied by an electron. On the other hand, if we place it in the higher level, we are relieved of the burden of pairing the electron, but it also tends to give the electron a higher energy. Thus, for the

<sup>8</sup> We've never had to make this kind of decision before because the energy levels in atoms were always widely spaced. In complex ions, however, the spacing between the two  $d$  orbital energy levels is fairly small.

**TOOLS**  
Spectrochemical series

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**FIG. 21.31** The effect of  $\Delta$  on the electron distribution in a complex with four  $d$  electrons. (a) When  $\Delta$  is small, the electrons remain unpaired. (b) When  $\Delta$  is large, the lower energy level accepts all four electrons and two electrons become paired.

fourth electron, “pairing” and “placing” work in opposite directions in the way they affect the energy of the complex.

The critical factor in determining whether the fourth electron enters the lower level and becomes paired, or whether it enters the higher level with the same spin as the other  $d$  electrons, is the magnitude of  $\Delta$ . If  $\Delta$  is larger than the pairing energy  $P$ , then greater stability is achieved if the fourth electron is paired with one in the lower level. If  $\Delta$  is small compared to  $P$ , then greater stability is obtained by spreading the electrons out as much as possible. The complexes  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{CN})_6]^{4-}$  illustrate this well.

Water is a ligand that does not produce a large  $\Delta$ , so  $P > \Delta$ , and minimum pairing of electrons takes place. This explains the energy level diagram for the  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  complex in Figure 21.31a. When cyanide is the ligand, however, a very large  $\Delta$  is obtained, and this leads to pairing of the fourth electron with one in the lower set of  $d$  orbitals. This is shown in Figure 21.31b. It is interesting to note that by measuring the degree of paramagnetism of the two complexes, it can be demonstrated experimentally that  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  has four unpaired electrons and the  $[\text{Cr}(\text{CN})_6]^{4-}$  ion has just two.

For octahedral chromium(II) complexes, there are two possibilities in terms of the number of unpaired electrons. They contain either four or two, depending on the magnitude of  $\Delta$ . When there is the maximum number of unpaired electrons, the complex is described as being **high-spin**; when there is the minimum number of unpaired electrons it is described as being **low-spin**. High- and low-spin octahedral complexes are possible when the metal has a  $d^4$ ,  $d^5$ ,  $d^6$ , or  $d^7$  electron configuration. Let's look at another example—one containing the  $\text{Fe}^{2+}$  ion, which has the electron configuration



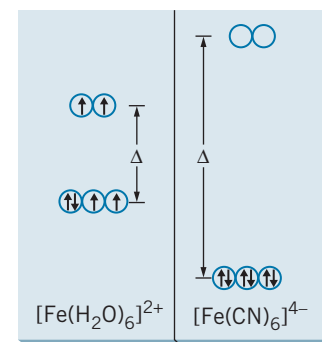
At the beginning of this section we mentioned that the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion is paramagnetic and has four unpaired electrons, while the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is diamagnetic, meaning it has no unpaired electrons. Now we can see why, by referring to Figure 21.32. Water produces a weak splitting and a minimum amount of pairing of electrons. When the six  $d$  electrons in the  $\text{Fe}^{2+}$  ion are distributed, one must be paired in the lower level after filling the upper level. The result is four unpaired  $d$  electrons, and a high-spin complex. Cyanide ion, however, produces a large splitting, so  $\Delta > P$ . This means that maximum pairing of electrons in the lower level takes place, and a low-spin complex is formed. Six electrons are just the right amount to completely fill all three of these  $d$  orbitals, and since all the electrons are paired, the complex is diamagnetic.

### Crystal field theory also applies to other geometries

The crystal field theory can be extended to geometries other than octahedral. The effect that changing the structure of the complex has on the energies of the  $d$  orbitals is to change the splitting pattern.

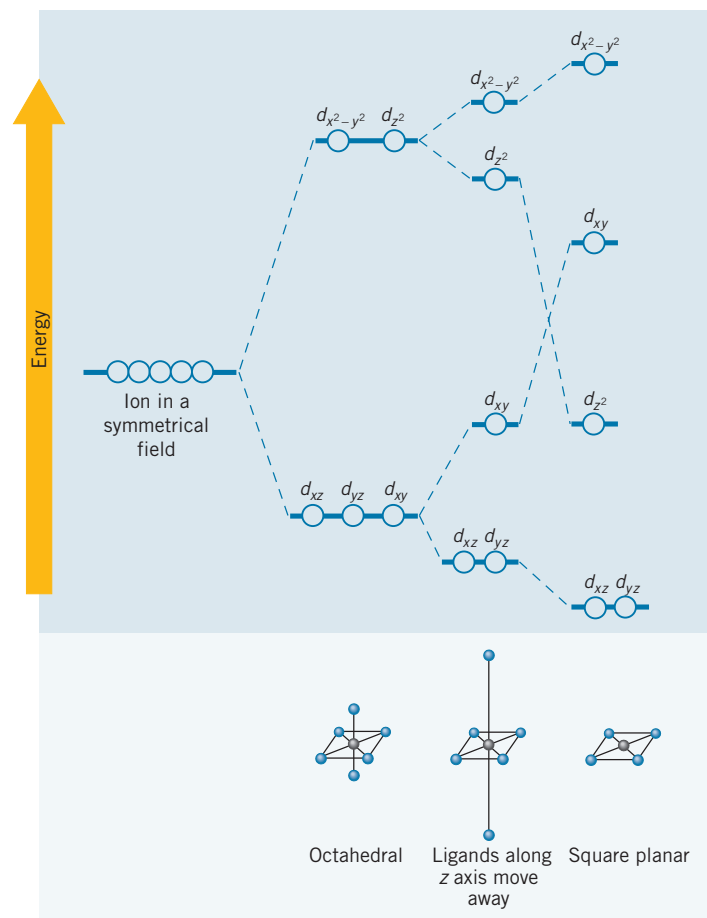
#### Square planar complexes show additional splitting of the $d$ orbital energies

We can form a square planar complex from an octahedral one by removing the ligands that lie along the  $z$  axis. As this happens, the ligands in the  $xy$  plane are able to approach the metal a little closer because they are no longer being repelled by ligands along the



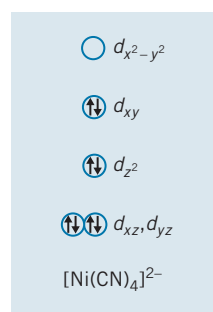
**FIG. 21.32** The distribution of  $d$  electrons in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ . The magnitude of  $\Delta$  for the cyanide complex is much larger than for the water complex. This produces a maximum pairing of electrons in the lower energy set of  $d$  orbitals in  $[\text{Fe}(\text{CN})_6]^{4-}$ .

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**FIG. 21.33** Energies of  $d$  orbitals in complexes with various structures. The splitting pattern of the  $d$  orbitals changes as the geometry of the complex changes.

For Figure 21.33, as the energies of the  $d$  orbitals change, the  $d_{z^2}$  orbital drops in energy by the same amount as the  $d_{x^2-y^2}$  rises. Similarly, the energies of the  $d_{xz}$  and  $d_{yz}$  orbitals drop only half as much as the energy of the  $d_{xy}$  rises. In this way, if all the  $d$  orbitals were filled, the changes in geometry would have no effect on the total energy of the complex.



**FIG. 21.34** Distribution of the electrons among the  $d$  orbitals of nickel in the diamagnetic  $[\text{Ni}(\text{CN})_4]^{2-}$  ion.

$z$  axis. The effect of these changes on the energies of the  $d$  orbitals is illustrated in Figure 21.33. The repulsions felt by the  $d$  orbitals that point in the  $z$  direction are reduced, so we find that the energies of the  $d_{z^2}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals drop. At the same time, the energies of the orbitals in the  $xy$  plane feel greater repulsions, so the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals rise in energy.

Nickel(II) ion (which has eight  $d$  electrons) forms a complex with cyanide ion that is square planar and diamagnetic. In this complex the strong field produced by the cyanide ions yields a large energy separation between the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals, so that a low-spin complex results. The electron distribution in this complex is illustrated in Figure 21.34.

#### Tetrahedral complexes have a $d$ orbital splitting pattern opposite that of octahedral complexes

The splitting pattern for the  $d$  orbitals in a tetrahedral complex is illustrated in Figure 21.35. Notice that the order of the energy levels is exactly opposite to that in an octahedral complex. In addition, the size of  $\Delta$  is also much smaller for a tetrahedral complex than for an octahedral one. (Actually,  $\Delta_{\text{tet}} \approx \frac{4}{9} \Delta_{\text{oct}}$  for the same metal ion with the same ligands.) This small  $\Delta$  is always less than the pairing energy, so tetrahedral complexes are always high-spin complexes.

### 21.10 METAL IONS SERVE CRITICAL FUNCTIONS IN BIOLOGICAL SYSTEMS

Most of the compounds in our bodies have structures based on carbon as the principal element, and their functions are usually related to the geometries assumed by

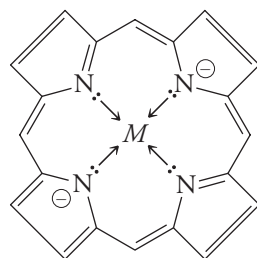
## 21.10 Metal Ions Serve Critical Functions in Biological Systems 891

carbon-containing compounds as well as the breaking and forming of carbon–carbon, carbon–oxygen, and carbon–nitrogen bonds. In Chapter 22 we will discuss some classes of biochemical molecules.

Our bodies also require certain metal ions in order to operate, and without them life cannot be sustained. For this reason, the study of metals in biological systems has become a very important branch of biochemistry, and a large number of research papers are published annually that deal with this topic. Table 21.2 lists some of the essential metals and the functions fulfilled by their ions.

A few metals, such as sodium and potassium, are found as simple monatomic ions in body fluids. Most metal ions, however, become bound by ligands and do their work as part of metal complexes. As examples, we will look briefly at two metals—iron and cobalt.

Iron is one of the essential elements required by our bodies. We obtain it in a variety of ways in our diets. Iron is involved in oxygen transport in our blood and in retaining oxygen in muscle tissue so that it's available when needed. The iron is present as  $\text{Fe}^{2+}$  held in a complex in which the basic ligand structure is



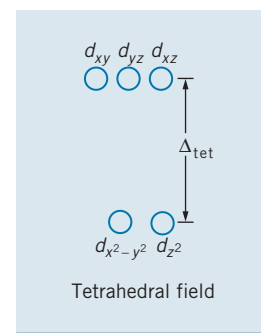
This ligand composition, with its square planar arrangement of nitrogen atoms that bind to a metal ion, is called a *porphyrin structure*. It is the ligand structure in a biologically active unit called heme. Heme is the oxygen-carrying component in the blood protein hemoglobin and in myoglobin, which is found in muscle tissue.

In the lungs,  $\text{O}_2$  molecules are absorbed by the blood and become bound to  $\text{Fe}^{2+}$  ions in the heme units of hemoglobin (Figure 21.36). Blood circulation then carries the  $\text{O}_2$  to tissues where it is needed, at which time it is released by the  $\text{Fe}^{2+}$ . One of the important functions of the porphyrin ligand in this process is to prevent the  $\text{Fe}^{2+}$  from being oxidized by the  $\text{O}_2$ . (In fact, if the iron is oxidized to  $\text{Fe}^{3+}$ , it no longer is able to carry  $\text{O}_2$ .) In muscle tissue, heme units in the protein myoglobin take  $\text{O}_2$  from hemoglobin and hold it until it's needed. In this way, muscle tissue is able to store  $\text{O}_2$  so that plenty of it is available when the muscle must work hard.

Heme units are also present in proteins called cytochromes where the iron is involved in electron transfer reactions that employ the +2 and +3 oxidation states of iron.

**TABLE 21.2** Some Biologically Important Metals and their Corresponding Human Body Functions

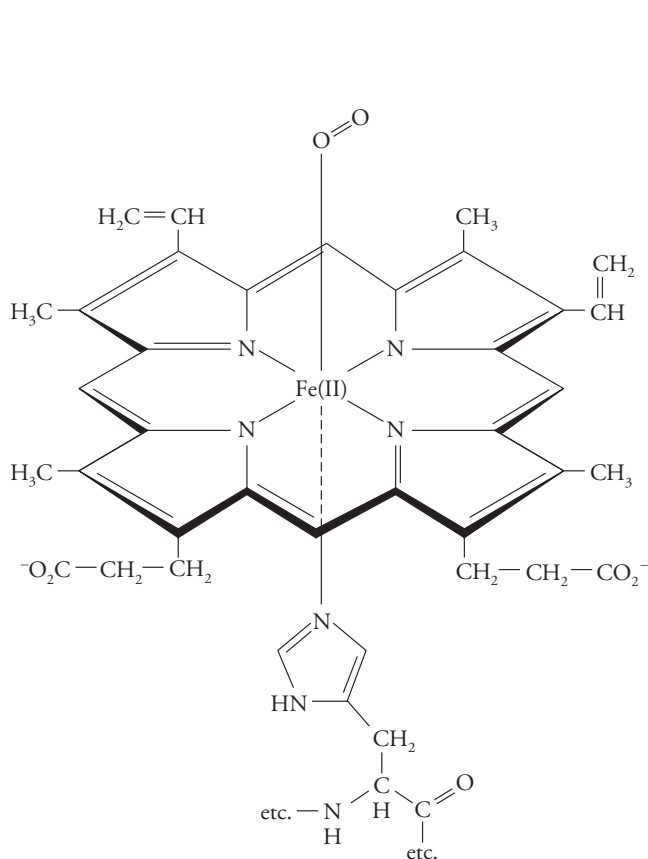
Metal	Body Function
Na, Ca	Blood pressure and blood coagulation
Fe	Oxygen transport and storage
Ca	Teeth and bone formation
Ca	Urinary stone formation
Zn	Control of pH in blood
Ca, Mg	Muscle contraction
K	Maintenance of stomach acidity
Fe, Cu	Respiration
Cu	Bone health
Ca, Fe, Co	Cell division



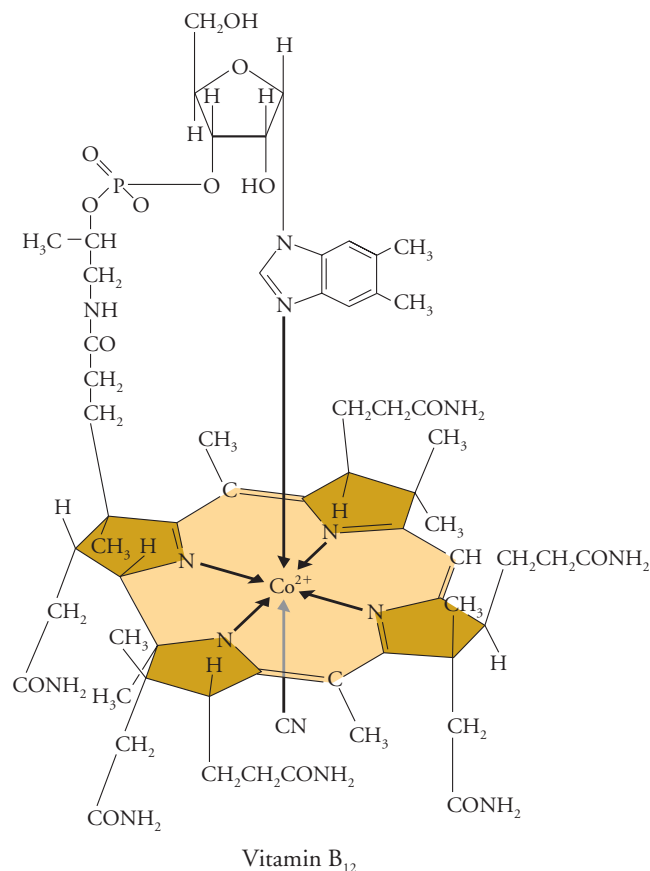
**FIG. 21.35** Splitting pattern of the  $d$  orbitals for a tetrahedral complex. The crystal field splitting for the tetrahedral structure ( $\Delta_{\text{tet}}$ ) is smaller than that for the octahedral structure ( $\Delta_{\text{oct}}$ ). For complexes with the same ligands,  $\Delta_{\text{tet}} \approx \frac{4}{9} \Delta_{\text{oct}}$ .

■ The porphyrin structure is present in chlorophyll, too, where the metal bound in the center is  $\text{Mg}^{2+}$ . Chlorophyll absorbs sunlight (solar energy), which is used by plants to convert carbon dioxide and water into glucose and oxygen.

■ The iron in hemoglobin also binds  $\text{CO}_2$  and helps transport it back to the lungs to be exhaled.



**FIG. 21.36 Iron(II) bound to oxygen in heme.** The porphyrin ring ligand in heme surrounds an  $\text{Fe}^{2+}$  ion that binds an  $\text{O}_2$  molecule. In its oxygenated form, the  $\text{Fe}^{2+}$  is octahedrally coordinated in the structure.



**FIG. 21.37 The structure of cyanocobalamin.** Notice the cobalt ion in the center of the square planar arrangement of nitrogen atoms that are part of the ligand structure. Overall, the cobalt is surrounded octahedrally by donor atoms.

■ The ability of transition metals to exist in different oxidation states is one reason they are used in biological systems. They can easily take part in oxidation–reduction reactions. Copper(I) and copper(II) ions constitute another pair involved in catalyzing biochemical redox reactions.

A structure similar to heme is found in cyanocobalamin, the form of vitamin  $\text{B}_{12}$  found in vitamin pills (Figure 21.37). Here, a  $\text{Co}^{2+}$  ion is held in a square planar ligand structure (called a *corrin ring*) that is slightly different from that found in heme. Certain enzymes (biological catalysts) require cobalamins to function. Vitamin  $\text{B}_{12}$  is essential in our diets and a deficiency in the vitamin leads to a disease called pernicious anemia.

We have illustrated here just a few examples of the important roles that metal ions play in living systems. They are roles that cannot be fulfilled by other carbon-based compounds, some of which will be described in Chapter 22.

## SUMMARY

### Obtaining Nonmetallic Elements in Their Free States.

Metalloids normally exist in positive oxidation states in compounds and are obtained by reduction. Common reducing agents are carbon and hydrogen. In nature, the noble gases are never found in compounds. Oxygen and nitrogen are obtained from air, and sulfur is found in natural deposits, often deep below the earth's surface. Carbon is found in coal and diamonds. Nonmetals are also found in naturally occurring compounds.

If the nonmetal is combined with a metal, oxidation is used to change it to the free element. The oxidizing strength of the halogens decreases from fluorine to iodine. In Group VIIA, a given halogen (e.g.,  $\text{F}_2$ ) is able to oxidize the halide ion below it (e.g.,  $\text{Cl}^-$ ), thereby displacing it from its compounds. Fluorine, being the most difficult element to oxidize, is obtained by electrolysis of molten mixtures of  $\text{HF}$  and  $\text{KF}$ . Elemental phosphorus is obtained from calcium phosphate by reaction with carbon and  $\text{SiO}_2$ .

**Molecular Structures of the Nonmetals.** Elements of Period 2, because of their small size, form strong  $\pi$  bonds. As a result, these elements easily participate in multiple bonding between like atoms, which accounts for diatomic molecules of  $O_2$  and  $N_2$ , and the  $\pi$ -bonded structure of graphite. Elements of Periods 3, 4, and 5 are large and their  $p$  orbitals do not overlap well to form strong  $\pi$  bonds, so these elements prefer single  $\sigma$  bonds between like atoms, which leads to more complex molecular structures.

Different forms of the same element are called **allotropes**. Oxygen exists in two allotropic forms: dioxygen ( $O_2$ ) and **ozone** ( $O_3$ ). Carbon forms several allotropes including **diamond**, **graphite**,  $C_{60}$  molecules called **buckminsterfullerene** (one member of the **fullerene** family of structures), and **carbon nanotubes**. Elemental boron consists of  $B_{12}$  clusters linked through other boron atoms to give an extremely hard solid. Sulfur forms  $S_8$  molecules that can be arranged in two different allotropic forms. Phosphorus occurs as **white phosphorus** ( $P_4$ ), **red phosphorus**, and **black phosphorus**. Silicon only forms a diamondlike structure.

**Preparation of Metals** Most metals occur in compounds where they exist in positive oxidation states and are obtained from their compounds by reduction. Ions of sodium and potassium are found in seawater, along with magnesium. Insoluble carbonate deposits of Ca and Mg arise from the shells of marine animals. Many metals are found in the earth as oxides, sulfides, and phosphates. Active metals such as sodium, magnesium, and aluminum must generally be prepared by electrolysis. Metals of intermediate activity can be obtained using chemical reducing agents such as carbon and hydrogen. Reducing a metal oxide with carbon is called **smelting**. Compounds with small heats of formation tend to be thermally unstable and can be decomposed by heat.

**Metallurgy.** Usually, when an **ore** is dug from the ground, the metal-bearing component must be enriched by a pretreatment step that removes much of the unwanted **gangue**. **Flotation** is often used with lead and copper sulfide ores. Sulfide ores are usually **roasted** to convert them to oxides, which are more easily reduced. Aluminum's amphoteric character is exploited in purifying bauxite.

Carbon, in the form of **coke** made from coal, is a common chemical reducing agent because it is plentiful and inexpensive. Metallic iron forms in a **blast furnace** where a charge of iron ore, limestone, and coke reacts in a stream of heated air. Molten iron and **slag** flow to the bottom of the furnace and are periodically tapped. **Steel** is made from this impure iron mostly by the **basic oxygen process**.

**Complex Ions of Metals.** **Coordination compounds** contain **complex ions** (also called **complexes** or **coordination complexes**), formed from a metal ion and a number of ligands. **Ligands** are Lewis bases and may be **monodentate**, **bidentate**, or, in general, **polydentate**, depending on the number of **donor atoms** that they contain. Water is the most common monodentate ligand. Polydentate ligands bind to a metal through two or more donor atoms and yield ring structures called **chelates**. Common bidentate ligands are oxalate ion and ethylenediamine (en); a common polydentate ligand is ethylenediaminetetraacetic acid (EDTA), which has six donor atoms.

In the formula of a complex, the metal is written first, followed by the formulas of the ligands (anions first in alphabetical order followed by neutral ligands in alphabetical order). Brackets are often used to enclose the set of atoms that make up the

complex, with the charge on the complex written outside the brackets. The charge on the complex is the algebraic sum of the charges on the metal ion and the charges on the ligands.

Complexes of polydentate ligands are more stable than similar complexes formed with monodentate ligands, partly because a polydentate ligand is less likely to be lost completely if one of its donor atoms becomes detached from the metal ion. The larger positive entropy change for dissociation of complexes with monodentate ligands also favors their dissociation compared with complexes of polydentate ligands. The phenomenon is called the **chelate effect**.

**Nomenclature of Complexes.** Complexes are named following a set of rules developed by the IUPAC. These are summarized on pages 876 to 878.

**Coordination Number and Structure.** The **coordination number** of a metal ion in a complex is the number of donor atoms attached to the metal ion. Polydentate ligands supply two or more donor atoms, which must be taken into account when determining the coordination number from the formula of the complex. Geometries associated with common coordination numbers are as follows: for coordination number 2, linear; for coordination number 4, tetrahedral and square planar (especially for  $Pt^{2+}$  complexes); and for coordination number 6, octahedral.

**Isomers of Coordination Compounds.** When two or more distinct compounds have the same chemical formula, they are **isomers** of each other. **Stereoisomers** have the same atoms attached to each other, but the atoms are arranged differently in space. In a **cis isomer**, attached groups of atoms are on the same side of some reference plane through the molecule. In a **trans isomer**, they are on opposite sides. Cis and trans isomerism is a form of **geometric isomerism**. **Chiral** isomers are exactly the same in every way but one—they are not **superimposable** on their mirror images. These kinds of isomers exist for complexes of the type  $M(AA)_3$ , where  $M$  is a metal ion and  $AA$  is a bidentate ligand, and also for complexes of the type  $cis-M(AA)_2a_2$ , where  $a$  is a monodentate ligand. Chiral isomers that are related as object to mirror images are said to be **enantiomers**. Because they are able to rotate **plane-polarized light**, they are called **optical isomers**.

**Crystal Field Theory.** In an octahedral complex, the ligands influence the energies of the  $d$  orbitals by splitting the  $d$  subshell into two energy sublevels. The lower energy one consists of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals; the higher energy level consists of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals. The energy difference between the two new  $d$  sublevels is the **crystal field splitting**,  $\Delta$ , and for a given ligand it increases with an increase in the oxidation state of the metal. For a given metal ion,  $\Delta$  depends on the ligand, and it depends on the period number in which the metal is found.

In the **spectrochemical series**, ligands are arranged in order of their ability to cause a large  $\Delta$ . Cyanide ion produces the largest crystal field splitting and iodide ion, the smallest. **Low-spin** complexes result when  $\Delta$  is larger than the **pairing energy**—the energy needed to cause two electrons to become paired in the same orbital. **High-spin** complexes occur when  $\Delta$  is smaller than the pairing energy. Light of energy equal to  $\Delta$  is absorbed when an electron is raised from the lower energy set of  $d$  orbitals to the higher set, and the color of the complex is determined by the colors that remain in the transmitted light. Crystal field theory can also explain the relative stabilities of oxidation states, in many cases.

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Different splitting patterns of the  $d$  orbitals occur for other geometries. The patterns for square planar and tetrahedral geometries are described in Figures 21.33 and 21.35, respectively. The value of  $\Delta$  for a tetrahedral complex is only about  $4/9$  that of  $\Delta$  for an octahedral complex.

**Metals in Living Systems.** Most metals required by living organisms perform their actions when bound as complex ions.

Heme contains  $\text{Fe}^{2+}$  held in a square planar porphyrin ligand and binds to  $\text{O}_2$  in hemoglobin and myoglobin. Heme is also found in cytochromes where it participates in redox reactions involving  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Vitamin  $\text{B}_{12}$ , required by the body to prevent the vitamin deficiency disease called pernicious anemia, contains  $\text{Co}^{2+}$  in a corrin ring structure, which is similar to the porphyrin ring.



## TOOLS FOR PROBLEM SOLVING

In this chapter you learned to apply the following concepts as tools in solving problems related to the properties of metal complexes. Study each tool carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

**Rules for writing formulas for complexes** (page 874) The following rules apply whenever you have to write the formula for a complex ion:

1. The symbol for the metal ion is always given first, followed by the ligands.
2. When more than one kind of ligand is present, anionic ligands are written first (in alphabetical order), followed by neutral ligands (also in alphabetical order).
3. The charge on the complex is the algebraic sum of the charge on the metal ion and the charges on the ligands.

**Rules for naming complexes** (pages 876 to 878) Naming complexes follows rules that are an extension of the rules you learned earlier. You have to learn them and then apply them when you have to name a complex, or write a formula given the name.

**Crystal field splitting pattern for an octahedral complex** (page 885) Figure 21.27 forms the basis for applying the principles of crystal field theory to octahedral complexes. To use it, you need the electron configuration of the metal ion. First write the electron configuration for the metal under consideration. Then remove electrons from the atom starting with the outer  $s$  subshell first, followed if necessary by electrons from the underlying  $d$  subshell. For a complex under consideration, set up the splitting diagram and place electrons into the  $d$  orbitals following Hund's rule. For  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations, you may have to decide whether a high- or low-spin configuration is preferred.

**Spectrochemical series** (page 888) Use the location of ligands in the spectrochemical series to compare their effects on the crystal field splitting. The series is



## QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at [www.wiley.com/college/brady](http://www.wiley.com/college/brady). OH = an Office Hours video is available for this problem.

### REVIEW QUESTIONS

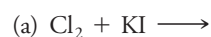
#### Recovery of Nonmetals and Metalloids from Compounds

**21.1** What is the major commercial source of  $\text{N}_2$  and  $\text{O}_2$ ?

**21.2** Why is helium found in underground deposits? Why are only small quantities of radon observed in nature?

**21.3** Chlorine,  $\text{Cl}_2$ , can be made in the lab by the reaction of  $\text{HCl}$  with  $\text{KMnO}_4$ , with  $\text{MnCl}_2$  being among the products. Write a balanced net ionic equation for the reaction, keeping in mind that  $\text{KMnO}_4$  is water soluble.

**21.4** Complete the following chemical equations. If no reaction occurs, write N.R.



**21.5** How is  $\text{Br}_2$  recovered from seawater?

**21.6** Why can't fluorine be produced by the electrolysis of aqueous  $\text{NaF}$ ? What products are formed at inert electrodes in the electrolysis of aqueous  $\text{NaF}$ ?

**21.7** Why is a molten mixture of KF and HF used in the production of  $F_2$  by electrolysis rather than molten KF by itself?

**21.8** Hydrogen fluoride is a gas that can be liquefied by cooling it to  $19.6\text{ }^\circ\text{C}$  (just slightly below room temperature). Why can't electrolysis be carried out on liquid HF to form  $F_2$  and  $H_2$ ?

**21.9** Write the chemical equation for the production of elemental phosphorus from calcium phosphate and  $SiO_2$ . What is the reducing agent in the reaction? What is the function of the  $SiO_2$ ? Why isn't  $SiO_2$  reduced to Si in the reaction?

**21.10** Under the proper conditions, iodide ion will react with  $H_2SO_4$  to generate  $I_2$  and  $H_2S$ . Write a balanced net ionic equation for the reaction.

**21.11** Why are metalloids usually recovered from their compounds by chemical reduction of their compounds rather than by oxidation?

**21.12** Write chemical equations for

- the chemical reduction of  $BCl_3$  with hydrogen.
- the production of Si from  $SiO_2$  using carbon as a reducing agent.
- the reduction of  $As_2O_3$  with hydrogen.

#### Molecular Structures of the Nonmetals and Metalloids

**21.13** Which of the nonmetals occur in nature in the form of isolated atoms?

**21.14** Why are the Period 2 elements able to form much stronger  $\pi$  bonds than the nonmetals of Period 3? Why do a Period 3 nonmetal prefer to form all  $\sigma$  bonds instead of one  $\sigma$  bond and several  $\pi$  bonds?

**21.15** Even though the nonmetals of Periods 3, 4, and 5 do not tend to form  $\pi$  bonds between like atoms, each of the halogens is able to form diatomic molecules ( $Cl_2$ ,  $Br_2$ ,  $I_2$ ). Why?

**21.16** What are *allotropes*? How do they differ from *isotopes*?

**21.17** What are the two allotropes of oxygen?

**21.18** Construct the molecular orbital diagram for  $O_2$  and explain why it has two unpaired electrons. What is the net bond order in  $O_2$ ?

**21.19** Draw the Lewis structure for  $O_3$ . Is the molecule linear, based on the VSEPR theory? Assign formal charges to the atoms in the Lewis structure. Does this suggest the molecule is polar or nonpolar?

**21.20** What beneficial function does ozone serve in the upper atmosphere?

**21.21** Describe the structure of diamond. What kind of hybrid orbitals does carbon use to form bonds in diamond? What is the geometry around carbon in this structure?

**21.22** Describe the structure of graphite. What kind of hybrid orbitals does carbon use in the formation of the molecular framework of graphite?

**21.23** Why does graphite have lubricating properties?

**21.24** Describe the  $C_{60}$  molecule. What is it called? What name is given to the series of similar substances?

**21.25** How is the structure of a carbon nanotube related to the structure of graphite?

**21.26** In elemental boron, there are clusters of boron atoms linked through other boron atoms. What is the formula for the boron clusters? What is the shape of a cluster?

**21.27** What is the molecular structure of sulfur in its most stable allotropic form?

**21.28** Make a sketch that describes the molecular structure of white phosphorus.

**21.29** What are the P—P—P bond angles in the  $P_4$  molecule? If phosphorus uses  $p$  orbitals to form the phosphorus–phosphorus bonds, what bond angle would give the best orbital overlap? On the basis of your answers to these two questions, explain why  $P_4$  is so chemically reactive.

**21.30** What structure has been proposed for red phosphorus? How do the reactivities of red and white phosphorus compare?

**21.31** What is the molecular structure of black phosphorus? In what way does the structure of black phosphorus resemble that of graphite?

**21.32** What is the molecular structure of silicon? Suggest a reason why silicon doesn't form an allotrope that's similar in structure to graphite.

#### Occurrence of Metals and Recovery of Metals from Compounds

**21.33** Which are the three most abundant metals in seawater? Why don't we find large amounts of silver ion in seawater?

**21.34** What is the origin of limestone?

**21.35** Why are many metals found as oxides and sulfides in the earth?

**21.36** Why is carbon used so often as an industrial reducing agent?

**21.37** Write equations for the reduction of copper(II) oxide with hydrogen.

**21.38** Why isn't thermal decomposition a practical method for obtaining metals such as sodium or magnesium?

**21.39** In general, why do compounds tend to decompose at high temperatures but not at low temperatures?

**21.40** In terms of thermodynamics, what must be true for us to be able to observe a substantial degree of decomposition of a compound?

**21.41** The value of  $\Delta G^\circ$  for the decomposition of a metal oxide is negative if the heat of formation of the compound is positive. Why are we able to isolate such compounds at room temperature if they are unstable toward decomposition?

**21.42** Many explosives have positive heats of formation. How does this explain why they tend to explode?

#### Metallurgy

**21.43** Use your own words to define *metallurgy*.

**21.44** What is an *ore*? What distinguishes an ore from some other potential source of a metal?

**21.45** Many rocks are composed of minerals called aluminosilicates. One such mineral is called *orthoclase* and has the formula  $KAlSi_3O_8$ . Despite their high abundance, aluminosilicates are not considered aluminum ores. What is the probable reason for this?

**21.46** What is *gangue*?

**21.47** Why can gold be separated from impurities of rock and sand by *panning*?

**21.48** Describe the *flotation process*.

**21.49** Write chemical equations for the reactions that occur when  $Cu_2S$  and  $PbS$  are roasted in air. Write a chemical equation to show how  $SO_2$  from the roasting can be kept from being released

## 896 Chapter 21 Nonmetals, Metalloids, Metals, and Metal Complexes

to the environment. Why might a sulfuric acid plant be located near a plant that roasts sulfide ores?

**21.50** Write chemical equations that show how bauxite is purified.

**21.51** Why is reduction, rather than oxidation, necessary to extract metals from their compounds?

**21.52** Sodium, magnesium, and aluminum are produced by electrolysis instead of by reduction with chemical reducing agents. Why?

**21.53** What is *coke*? How is it made?

**21.54** Write chemical equations for the reduction of PbO and CuO with carbon.

**21.55** Copper(I) sulfide can be converted to metallic copper without adding a reducing agent. Explain this using appropriate chemical equations.

**21.56** Why is a blast furnace called a *blast* furnace?

**21.57** What is the composition of the charge that's added to a blast furnace?

**21.58** Describe the chemical reactions involved in the reduction of Fe<sub>2</sub>O<sub>3</sub> that take place in a blast furnace. What is the active reducing agent in the blast furnace?

**21.59** What is slag? Write a chemical equation for its formation in a blast furnace. What are some of its uses?

**21.60** What does *refining* mean in metallurgy?

**21.61** What is the difference between pig iron and steel?

**21.62** Describe the basic oxygen process.

### Complex Ions of Metals

**21.63** The formation of the complex ion [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> is described as a Lewis acid–base reaction. Explain.

(a) What are the formulas of the Lewis acid and the Lewis base in the reaction?

(b) What is the formula of the ligand?

(c) What is the name of the species that provides the donor atom?

(d) What atom is the donor atom, and why is it so designated?

(e) What is the name of the species that is the acceptor?

**21.64** To be a ligand, a substance should also be a Lewis base. Explain.

**21.65** Why are substances that contain complex ions often called coordination compounds?

**21.66** Give the names of two molecules mentioned in the text that are electrically neutral, monodentate ligands.

**21.67** Give the formulas of four ions that have 1– charges and are monatomic, monodentate ligands.

**21.68** Use Lewis structures to diagram the formation of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> and CuCl<sub>4</sub><sup>2-</sup> ions from their respective components.

**21.69** What must be true about the structure of a ligand classified as *bidentate*?

**21.70** What is a *chelate*? Use Lewis structures to diagram the way that the oxalate ion, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, functions as a chelating agent.

**21.71** How many donor atoms does EDTA<sup>4-</sup> have?

**21.72** Explain how a salt of EDTA<sup>4-</sup> can retard the spoilage of salad dressing.

**21.73** How does a salt of EDTA<sup>4-</sup> in shampoo make the shampoo work better in hard water?

**21.74** The cobalt(III) ion, Co<sup>3+</sup>, forms a 1:1 complex with EDTA<sup>4-</sup>. What is the net charge, if any, on this complex, and what would be a suitable formula for it (using the symbol EDTA)?

**21.75** Which complex is more stable, [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> or [Cr(en)<sub>3</sub>]<sup>3+</sup>? Why?

### Coordination Number and Structure

**21.76** What is a *coordination number*? What structures are generally observed for complexes in which the central metal ion has a coordination number of 4? What is the most common structure observed for coordination number 6?

**21.77** Sketch the structure of an octahedral complex that contains only identical monodentate ligands.

**21.78** Sketch the structure of the octahedral [Co(EDTA)]<sup>-</sup> ion. Remember that donor atoms in a polydentate ligand span adjacent positions in the octahedron.

### Isomers of Coordination Compounds

**21.79** What are *isomers*?

**21.80** Define *stereoisomerism*, *geometric isomerism*, *chiral isomers*, and *enantiomers*.

**21.81** What are *cis* and *trans* isomers?

**21.82** What condition must be fulfilled in order for a molecule or ion to be chiral?

**21.83** What are *optical isomers*?

### Bonding in Complexes

**21.84** On appropriate coordinate axes, sketch and label the five *d* orbitals.

**21.85** Which *d* orbitals point *between* the *x*, *y*, and *z* axes? Which point along the coordinate axes?

**21.86** Explain why an electron in a *d*<sub>x<sup>2</sup>-y<sup>2</sup> or *d*<sub>z<sup>2</sup></sub> orbital in an octahedral complex will experience greater repulsions because of the presence of the ligands than an electron in a *d*<sub>xy</sub>, *d*<sub>xz</sub>, or *d*<sub>yz</sub> orbital.</sub>

**21.87** Sketch the *d* orbital energy level diagram for a typical octahedral complex.

**21.88** Explain why octahedral cobalt(II) complexes are easily oxidized to cobalt(III) complexes. Sketch the *d* orbital energy diagram and assume a large value of Δ when placing electrons in the *d* orbitals.

**21.89** Explain how the same metal in the same oxidation state is able to form complexes of different colors.

**21.90** If a complex appears red, what color light does it absorb? What color light is absorbed if the complex appears yellow?

**21.91** What does the term *spectrochemical series* mean? How can the order of the ligands in the series be determined?

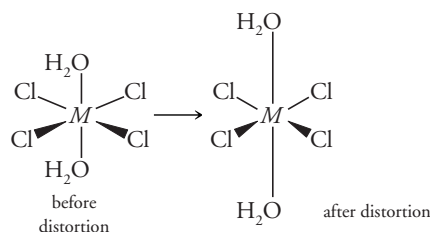
**21.92** What do the terms *low-spin complex* and *high-spin complex* mean?

**21.93** For which *d* orbital electron configurations are both high-spin and low-spin complexes possible?

**21.94** Indicate by means of a sketch what happens to the *d* orbital electron configuration of the [Fe(CN)<sub>6</sub>]<sup>4-</sup> ion when it absorbs a photon of visible light.

**21.95** The complex  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is diamagnetic. Sketch the  $d$  orbital energy level diagram for the complex and indicate the electron populations of the orbitals.

**21.96** Consider the complex  $[\text{MCl}_4(\text{H}_2\text{O})_2]^-$  illustrated below on the left. Suppose the structure of the complex is distorted to give the structure on the right, where the water molecules along the  $z$  axis have moved away from the metal somewhat and the four chloride ions along the  $x$  and  $y$  axes have moved closer. What effect will this distortion have on the energy level splitting pattern of the  $d$  orbitals? Use a sketch of the splitting pattern to illustrate your answer.



### Metals in Living Systems

**21.97** In what ways is the porphyrin structure important in biological systems?

**21.98** If a metal ion is held in the center of a porphyrin ring structure, what is its coordination number? (Assume the porphyrin is the only ligand.)

**21.99** What function does heme serve in hemoglobin? What does it do in myoglobin?

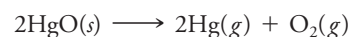
**21.100** How are the ligand ring structures similar in vitamin B<sub>12</sub> and in heme? What metal is coordinated in cobalamin?

**21.101** What are some of the roles played by calcium ion in the body?

## REVIEW PROBLEMS

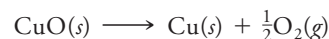
### Thermal Stability of Metal Compounds

- OH 21.102** Estimate the temperature at which  $\Delta G_f^\circ = 0$  for the decomposition of mercury(II) oxide according to the following equation.



For  $\text{HgO}$ ,  $\Delta H_f^\circ = -90.8 \text{ kJ mol}^{-1}$  and  $S^\circ = 70.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ; for  $\text{Hg}(g)$ ,  $\Delta H_f^\circ = +61.3 \text{ kJ mol}^{-1}$  and  $S^\circ = 175 \text{ J mol}^{-1} \text{ K}^{-1}$ ; for  $\text{O}_2$ ,  $S^\circ = 205 \text{ J mol}^{-1} \text{ K}^{-1}$ .

- OH 21.103** From the data below, estimate the temperature at which  $K_p = 1$  for the reaction



For  $\text{CuO}$ ,  $\Delta H_f^\circ = -155 \text{ kJ mol}^{-1}$ . Absolute entropies:  $\text{CuO}(s)$ ,  $42.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $\text{Cu}(s)$ ,  $33.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ; and  $\text{O}_2(g)$ ,  $205 \text{ J mol}^{-1} \text{ K}^{-1}$ .

### Complex Ions

**21.104** The iron(III) ion forms a complex with six cyanide ions that is often called the ferricyanide ion. What is the net charge on the complex ion, and what is its formula? What is the IUPAC name for the complex?

**21.105** The silver ion forms a complex ion with two ammonia molecules. What is the formula of the ion and what is its IUPAC name? Can the complex ion exist as a salt with the sodium ion or with the chloride ion? Write the formula of the possible salt. (Use brackets and parentheses correctly.)

**21.106** Write the formula, including its correct charge, for a complex that contains  $\text{Co}^{3+}$ , two  $\text{Cl}^-$ , and two ethylenediamine ligands.

- OH 21.107** Write the formula, including its correct charge, for a complex that contains  $\text{Cr}^{3+}$ , two  $\text{NH}_3$  ligands, and four  $\text{NO}_2^-$  ligands.

### Naming Complexes

**21.108** How would the following molecules or ions be named as ligands when writing the name of a complex ion?

- (a)  $\text{C}_2\text{O}_4^{2-}$  (c)  $\text{Cl}^-$   
(b)  $\text{S}^{2-}$  (d)  $(\text{CH}_3)_2\text{NH}$  (dimethylamine)

- OH 21.109** How would the following molecules or ions be named as ligands when writing the name of a complex ion?

- (a)  $\text{NH}_3$  (c)  $\text{SO}_4^{2-}$   
(b)  $\text{N}^{3-}$  (d)  $\text{C}_2\text{H}_3\text{O}_2^-$

**21.110** Give IUPAC names for each of the following.

- (a)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
(b)  $[\text{CrCl}_3(\text{NH}_3)_3]^-$   
(c)  $[\text{Co}(\text{NO}_2)_6]^{3-}$   
(d)  $[\text{Mn}(\text{CN})_4(\text{NH}_3)_2]^{2-}$   
(e)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

**21.111** Give IUPAC names for each of the following.

- (a)  $[\text{AgI}_2]^-$   
(b)  $[\text{SnS}_3]^{2-}$   
(c)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})_2](\text{SO}_4)_3$   
(d)  $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$   
(e)  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$

**21.112** Write chemical formulas for each of the following.

- (a) tetraaquadicyanoiron(III) ion  
(b) tetraammineoxalatonickel(II)  
(c) diaquatetracyanoferrate(III) ion  
(d) potassium hexathiocyanatomanganate(III)  
(e) tetrachlorocuprate(II) ion

**21.113** Write chemical formulas for each of the following.

- (a) tetrachloroaurate(III) ion  
(b) bis(ethylenediamine)dinitroiron(III) ion  
(c) tetraamminedicarbonatocobalt(III) nitrate  
(d) ethylenediaminetetraacetatoferrate(II) ion  
(e) diamminedichloroplatinum(II)

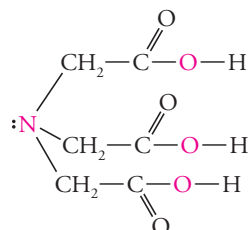
### Coordination Number and Structure

**21.114** In  $[\text{FeCl}_2(\text{H}_2\text{O})_2(\text{en})]$ , what is the coordination number of iron?

- OH 21.115** What is the coordination number of nickel in  $[\text{Ni}(\text{NO}_2)_2(\text{C}_2\text{O}_4)_2]^{4-}$ ?

## 898 Chapter 21 Nonmetals, Metalloids, Metals, and Metal Complexes

**21.116** NTA is the abbreviation for nitrilotriacetic acid, a substance that was used at one time in detergents. Its structure is



The four donor atoms of the ligand are shown in red. Sketch the structure of an octahedral complex containing the NTA ligand. Assume that two water molecules are also attached to the metal ion and that each oxygen donor atom in the NTA is bonded to a position in the octahedron that is adjacent to the nitrogen of the NTA.

**21.117** The compound shown below is called diethylenetriamine and is abbreviated “dien.”

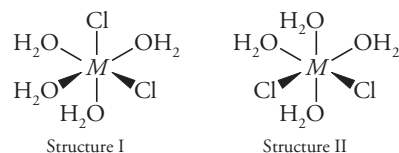


When it bonds to a metal, it is a ligand with three donor atoms.

- Which are most likely the donor atoms?
- What is the coordination number of cobalt in the complex  $[\text{Co}(\text{dien})_2]^{3+}$ ?
- Sketch the structure of the complex  $[\text{Co}(\text{dien})_2]^{3+}$ .
- Which complex would be expected to be more stable in aqueous solution,  $[\text{Co}(\text{dien})_2]^{3+}$  or  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ?
- What would be the structure of triethylenetetraamine?

## Isomers of Coordination Compounds

**21.118** Below are two structures drawn for a complex. Are they actually different isomers, or are they identical? Explain your answer.



**21.119** Below is a structure for one of the isomers of the complex  $[\text{Co}(\text{H}_2\text{O})_3(\text{dien})]^{3+}$ . Are isomers of this complex chiral? Justify your answer.



**21.120** Sketch and label the isomers of the square planar complex  $[\text{PtBrCl}(\text{NH}_3)_2]$ .

**21.121** The complex  $[\text{CoCl}_3(\text{NH}_3)_3]$  can exist in two isomeric forms. Sketch them.

**21.122** Sketch the chiral isomers of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ .

**21.123** Sketch the chiral isomers of  $[\text{CrCl}_2(\text{en})_2]^+$ . Is there a nonchiral isomer of the complex?

## Bonding in Complexes

**21.124** In which complex do we expect to find the larger  $\Delta$ ?

- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- $[\text{Cr}(\text{en})_3]^{3+}$  or  $[\text{CrCl}_6]^{3-}$

**21.125** Arrange the following complexes in order of increasing wavelength of the light absorbed by them:  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{CrCl}_6]^{3-}$ ,  $[\text{Cr}(\text{en})_3]^{3+}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{NO}_2)_6]^{3-}$ ,  $[\text{CrF}_6]^{3-}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$

**21.126** Which complex should be expected to absorb light of the highest frequency,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cr}(\text{en})_3]^{3+}$ , or  $[\text{Cr}(\text{CN})_6]^{3-}$ ?

**21.127** Which complex should absorb light at the longer wavelength?

- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Fe}(\text{CN})_6]^{4-}$
- $[\text{Mn}(\text{CN})_6]^{3-}$  or  $[\text{Mn}(\text{CN})_6]^{4-}$

**21.128** In each pair below, which complex is expected to absorb light of the shorter wavelength? Justify your answers.

- $[\text{RuCl}(\text{NH}_3)_5]^{2+}$  or  $[\text{FeCl}(\text{NH}_3)_5]^{2+}$
- $[\text{Ru}(\text{NH}_3)_6]^{2+}$  or  $[\text{Ru}(\text{NH}_3)_6]^{3+}$

**21.129** A complex  $[\text{Co}A_6]^{3+}$  is red. The complex  $[\text{Co}B_6]^{3+}$  is green. Which ligand, *A* or *B*, produces the larger crystal field splitting,  $\Delta$ ? Explain your answer.

**21.130** Referring to the two ligands, *A* and *B*, described in the preceding problem, which complex would be expected to be more easily oxidized,  $[\text{Co}A_6]^{2+}$  or  $[\text{Co}B_6]^{2+}$ ? Explain your answer.

**21.131** Referring to the complexes in the preceding two problems, would the color of  $[\text{Co}A_6]^{2+}$  more likely be red or blue?

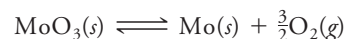
**21.132** Would the complex  $[\text{CoF}_6]^{4-}$  more likely be low-spin or high-spin? Could it be diamagnetic?

**21.133** Sketch the *d* orbital energy level diagrams for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  and predict the number of unpaired electrons in each.

## ADDITIONAL EXERCISES

**21.134** In the decomposition of  $\text{HgO}$  described in Problem 21.102, what are the equilibrium molar concentrations of  $\text{Hg}(\text{g})$  and  $\text{O}_2(\text{g})$  above solid  $\text{HgO}$  at the temperature at which  $\Delta G_T^\circ = 0$ ?

**21.135** Estimate  $K_p$  at 100, 500, and 1000 °C for the reaction



given the following data:

	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$\text{MoO}_3(\text{s})$	-754.3	78.2
$\text{Mo}(\text{s})$	0.0	28.6
$\text{O}_2(\text{g})$	0.0	205.0

**21.136** Is the complex  $[\text{Co}(\text{EDTA})]^-$  chiral? Illustrate your answer with sketches.

**21.137** The complex  $[\text{PtCl}_2(\text{NH}_3)_2]$  can be obtained as two distinct isomeric forms. Make a model of a tetrahedron and show that if the complex were tetrahedral, two isomers would be impossible.

**\*21.138** A solution was prepared by dissolving 0.500 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 100 mL of water. A silver nitrate solution was added and gave a precipitate of  $\text{AgCl}$  that was filtered from the mixture, washed, dried, and weighed. The  $\text{AgCl}$  had a mass of 0.538 g.

- What is the formula of the complex ion of chromium in the compound?
- What is the correct formula for the compound?
- Sketch the structure of the complex ion in the compound.
- How many different isomers of the complex can be drawn?

**\*21.139** The compound  $\text{Cr}_2(\text{NH}_3)_6\text{Cl}_6$  is a neutral salt in which the cation and anion are both octahedral complex ions. How many isomers (including possible structural and chiral isomers) are there that have this overall composition?

**\*21.140** The complex  $[\text{Co}(\text{CN})_6]^{4-}$  is not expected to be perfectly octahedral. Instead, the ligands in the  $xy$  plane are pulled closer to the  $\text{Co}^{2+}$  ion while those along the  $z$  axis move slightly farther away. Using information available in this chapter, explain why the distortion of the octahedral geometry leads to a net lowering of the energy of the complex.

### EXERCISES IN CRITICAL THINKING

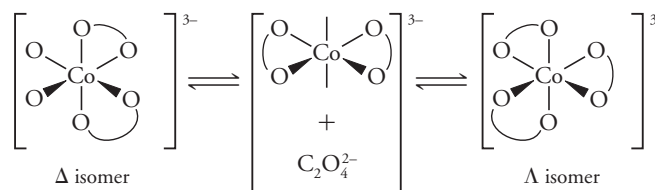
**21.141** In Section 21.2 we assumed that  $\Delta H_7^\circ \approx \Delta H_{298}^\circ$ . Why is this just an approximation? What factors would cause  $\Delta H_7^\circ$  to differ from  $\Delta H_{298}^\circ$ ?

**21.142** Graphite is a reasonably good conductor in directions parallel to the planes of the carbon atoms, but is a poor conductor in a direction perpendicular to the planes. Why is this so? Would you expect carbon nanotubes to be good conductors of electricity along their length? Explain your answer.

**21.143** Considering the fact that unshared electron pairs normally contribute to the polarity of a molecule, is the ozone molecule expected to be polar or nonpolar? How does your answer compare with the answer reached for Question 21.19?

**21.144** It was mentioned on page 858 that  $d$  orbitals are capable of participating in the formation of  $\pi$  bonds. Make a sketch that illustrates how such a bond could be formed between two  $d$  orbitals and between a  $d$  and a  $p$  orbital.

**21.145** The two chiral isomers of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (shown below) can be viewed as propellers having either a right- or left-handed twist, respectively. They are identified by the labels  $\Delta$  and  $\Lambda$ , as indicated. A 50–50 mixture of both isomers is said to be racemic and will not rotate plane-polarized light. Using various laboratory procedures the two isomers present in a racemic mixture can be separated from each other. For this complex, however, a solution of a single isomer is not stable and gradually reverts to a mixture of the two isomers by a process called racemization. Racemization involves the conversion of one isomer to the other until an equilibrium between the two isomers is achieved (i.e.,  $\Delta \rightleftharpoons \Lambda$ ). One mechanism proposed for the racemization of isomers of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  involves dissociation of an oxalate ion followed by rearrangement and then reattachment of  $\text{C}_2\text{O}_4^{2-}$ .



What experiment could you perform to test whether this is really the mechanism responsible for the racemization of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ ?