

## WHAT'S AHEAD

- 23.1 ► The Transition Metals
- 23.2 ► Transition-Metal Complexes
- 23.3 ► Common Ligands in Coordination Chemistry
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- 23.6 ► Crystal-Field Theory

# 23

# TRANSITION METALS AND COORDINATION CHEMISTRY

## 23.1 | The Transition Metals



Humans, like all vertebrates, have red blood. The red color is due to an iron-containing protein called hemoglobin found in red blood cells. Hemoglobin is responsible for binding oxygen in the lungs and transporting it to cells throughout the body.

However, not all animals have red blood. Some marine animals, including octopuses, squids, and lobsters, have blue blood because they rely on a copper-containing protein called hemocyanine for transporting oxygen. In the deoxygenated state, hemocyanine contains two  $\text{Cu}^+$  ions separated from each other by over 400 pm, a distance too long to form a bond. When an oxygen molecule encounters this site in the protein, an electron transfer reaction takes place in which the  $\text{O}_2$  molecule is reduced to the peroxide ion,  $\text{O}_2^{2-}$ , while both copper ions are oxidized to  $\text{Cu}^{2+}$ , as shown in **Figure 23.1**. The presence of  $\text{Cu}^{2+}$  ions in oxygenated hemocyanine is responsible for the blue color of the blood.

Among the blue bloods of the animal kingdom, the blood of the horseshoe crab (as shown in the image at the beginning of this section) is the most valuable. That's because the primitive immune system of the horseshoe crab contains a substance called limulus amoebocyte lysate (LAL), which protects the crabs from infection by binding to potentially harmful viruses and bacterial endotoxins. It was discovered in the early 1960s that LAL could be used to detect trace amounts of toxic substances in drugs and medical devices.

The importance of transition metals such as iron and copper is not limited to biology and medicine. Transition metals and their alloys are used as structural materials as well as in numerous other applications such as coins and jewelry and as electronic conductors in wires and electronic devices. The presence of partially filled *d*-orbitals allows transition-metal compounds to act as catalysts, magnets, and pigments.

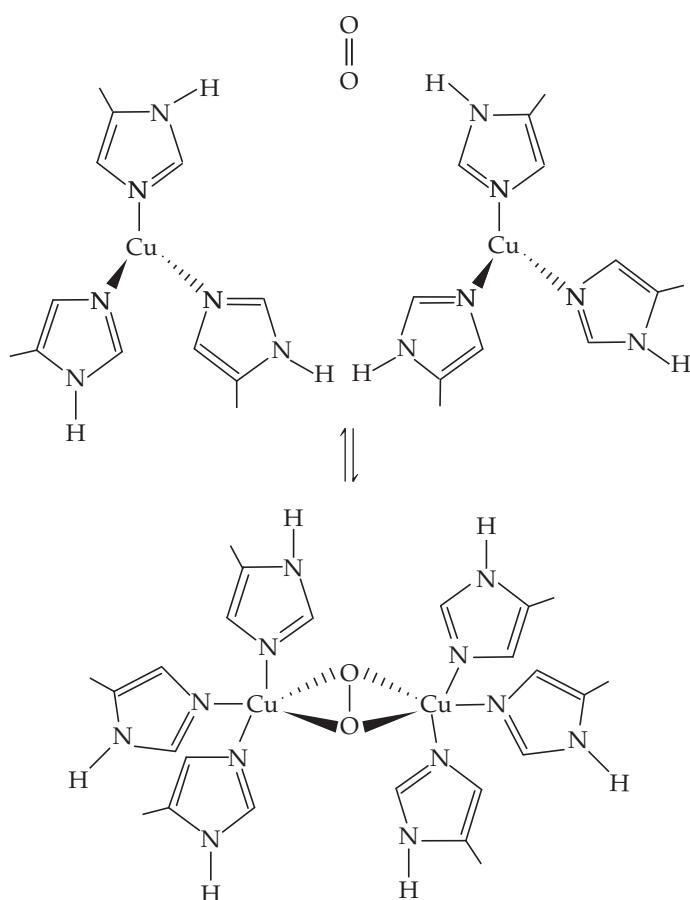
In earlier chapters, we saw that metal ions can function as Lewis acids, forming covalent bonds with molecules and ions that act as Lewis bases. (Section 16.8) We have encountered many ions and compounds that result from such interactions, such as  $[\text{Ag}(\text{NH}_3)_2]^+$  in Section 17.5 and hemoglobin in Section 13.6. In this chapter, we focus on the rich and important chemistry associated with such complex assemblies of metal ions surrounded by molecules and ions. Metal compounds of this kind are called *coordination compounds*, and the branch of chemistry that focuses on them is called *coordination chemistry*. We start by reviewing the general physical properties of the transition metals. By the end of this section, you should be able to

- Understand the physical properties of transition metals including metallic radius and magnetic properties.

The part of the periodic table in which the *d* orbitals are being filled as we move left to right across a row is the home of the transition metals (**Figure 23.2**).

With some exceptions (e.g., platinum, gold), metallic elements are found in nature as solid inorganic compounds called **minerals**. Notice from **Table 23.1** that minerals are identified by common names rather than chemical names.

Most transition metals in minerals have oxidation states ranging from +1 to +4. To obtain a pure metal from its mineral, various chemical processes must be performed to reduce the metal to its elemental form. **Metallurgy** is the science and technology of extracting metals from their natural sources and preparing them for practical use. It usually involves several steps: (1) mining, that is, removing the relevant *ore* (a mixture of minerals)



**▲ Figure 23.1** Hemocyanine binds oxygen. The  $\text{Cu}^+$  ions are each bound by three nitrogen atoms from the hemocyanine protein in the deoxygenated state (left). As the  $\text{O}_2$  molecule binds between the  $\text{Cu}^+$  ions, it is reduced to  $\text{O}_2^{2-}$  while the  $\text{Cu}^+$  ions are oxidized to  $\text{Cu}^{2+}$  ions.

3	4	5	6	7	8	9	10	11	12
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

**▲ Figure 23.2** The position of the transition metals in the periodic table. They are Groups 3–12 in Periods 4, 5, and 6. The short-lived, radioactive transition metals from Period 7 are not shown.

**TABLE 23.1 Principal Mineral Sources of Some Transition Metals**

Metal	Mineral	Mineral Composition
Chromium	Chromite	$\text{FeCr}_2\text{O}_4$
Cobalt	Cobaltite	$\text{CoAsS}$
Copper	Chalcocite	$\text{Cu}_2\text{S}$
	Chalcopyrite	$\text{CuFeS}_2$
	Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Iron	Hematite	$\text{Fe}_2\text{O}_3$
	Magnetite	$\text{Fe}_3\text{O}_4$
Manganese	Pyrolusite	$\text{MnO}_2$
Mercury	Cinnabar	$\text{HgS}$
Molybdenum	Molybdenite	$\text{MoS}_2$
Titanium	Rutile	$\text{TiO}_2$
	Ilmenite	$\text{FeTiO}_3$
Zinc	Sphalerite	$\text{ZnS}$

from the ground, (2) concentrating the ore or otherwise preparing it for further treatment, (3) reducing the ore to obtain the free metal, (4) purifying the metal, and (5) mixing it with other elements to modify its properties. This last process produces an *alloy*, a metallic material composed of two or more elements.

### Physical Properties

Some physical properties of the Period 4 (also known as “first-row”) transition metals are listed in **Table 23.2**. The properties of the heavier transition metals vary similarly across Periods 5 and 6.

**Figure 23.3** shows the atomic radius observed in close-packed metallic structures as a function of group number.\* The trends seen in the graph are a result of two competing forces. On the one hand, increasing effective nuclear charge favors a decrease in radius as we move left to right across each period. On the other hand, the metallic bonding strength increases until we reach the middle of each period and then decreases as we fill antibonding orbitals. As a general rule, a bond shortens as it becomes stronger. For Groups 3 through 6, these two effects work cooperatively and the result is a marked decrease in radius. In elements to the right of Group 6, the two effects counteract each other, reducing the decrease and eventually leading to an increase in radius.

**TABLE 23.2 Properties of the Period 4 Transition Metals**

Group	3	4	5	6	7	8	9	10	11	12
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ground-state electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Metallic radius (pm)	164	147	135	129	137	126	125	125	128	137
Density (g/cm <sup>3</sup> )	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420
Crystal structure*	hcp	hcp	bcc	bcc	**	bcc	hcp	fcc	fcc	hcp

\*Abbreviations for crystal structures are hcp = hexagonal close packed, fcc = face-centered cubic, bcc = body-centered cubic.

\*\*Manganese has a more complex crystal structure.

\*Note that the radii defined in this way, often referred to as metallic radii, differ somewhat from the bonding atomic radii defined in Section 7.3.

In general, atomic radii increase as we move down in a given group in the periodic table because of the increasing principal quantum number of the outer-shell electrons. However, Figure 23.2 shows that once we move beyond the Group 3 elements, the Period 5 and Period 6 transition elements in a given group have virtually the same radii. In Group 5, for example, tantalum in Period 6 has virtually the same radius as niobium in Period 5. This interesting and important effect has its origin in the lanthanide series, elements 57 through 70. The filling of 4f orbitals through the lanthanide elements causes a steady increase in the effective nuclear charge, producing a size decrease, called the **lanthanide contraction**, that just offsets the increase we expect as we go from Period 5 transition metals to Period 6. Thus, the Period 5 and Period 6 transition metals in each group have very similar radii and chemical properties. For example, the Group 4 metals zirconium (Period 5) and hafnium (Period 6) always occur together in nature and are very difficult to separate.

## Electron Configurations and Oxidation States

Transition metals owe their location in the periodic table to the filling of the *d* subshells, as you saw in Figure 6.28. Many of the chemical and physical properties of transition metals result from the unique characteristics of the *d* orbitals. For a given transition-metal atom, the valence  $(n - 1)d$  orbitals are smaller than the corresponding valence *ns* and *np* orbitals. In quantum mechanical terms, the  $(n - 1)d$  orbital wave functions drop off more rapidly as we move away from the nucleus than do the *ns* and *np* orbital wave functions. This characteristic feature of the *d* orbitals limits their interaction with orbitals on neighboring atoms, but not so much that they are insensitive to surrounding atoms. As a result, electrons in these orbitals behave sometimes like valence electrons and sometimes like core electrons. The details depend on location in the periodic table and the atom's environment.

When transition metals are oxidized, *they lose their outer s electrons before they lose electrons from the d subshell*. The electron configuration of Fe is  $[Ar]3d^64s^2$ , for example, whereas that of  $Fe^{2+}$  is  $[Ar]3d^6$ . Formation of  $Fe^{3+}$  requires loss of one *3d* electron, giving  $[Ar]3d^5$ . Most transition-metal ions contain partially occupied *d* subshells, which are responsible in large part for three characteristics:

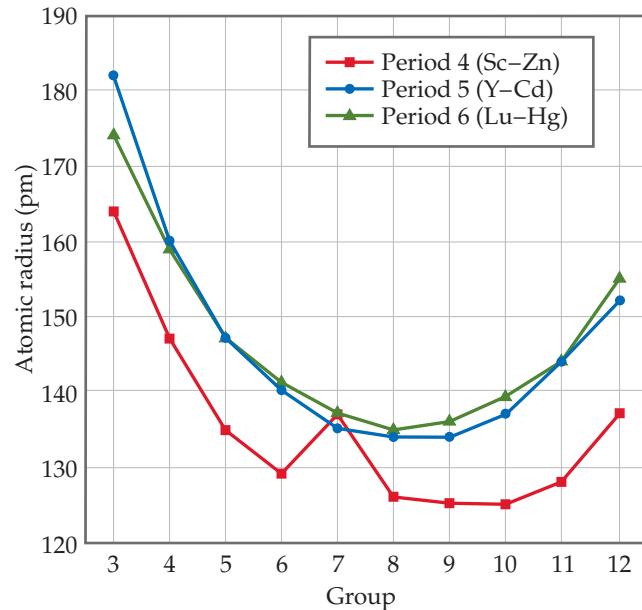
1. Transition metals often have more than one stable oxidation state.
2. Many transition-metal compounds are colored, as shown in **Figure 23.4**.
3. Transition metals and their compounds often exhibit magnetic properties.

**Figure 23.5** shows the common nonzero oxidation states for the Period 4 transition metals. The +2 oxidation state, which is common for most transition metals, is due to the loss of the two outer 4s electrons. This oxidation state is found for all these elements except Sc, where the 3+ ion with an [Ar] configuration is particularly stable.

Oxidation states above +2 are due to successive losses of *3d* electrons. From Sc through Mn the maximum oxidation state increases from +3 to +7, equaling in each case the total number of 4s plus *3d* electrons in the atom. Thus, manganese has a maximum oxidation state of  $2 + 5 = +7$ . As we move to the right beyond Mn in Figure 23.5, the maximum oxidation state decreases. This decrease is due to the attraction of *d* orbital electrons to the nucleus, which increases faster than the attraction of the *s* orbital electrons to the nucleus as we move left to right across the periodic table. In other words, in each period the *d* electrons become more corelike as the atomic number increases. By the time we get to zinc, it is not possible to remove electrons from the *3d* orbitals through chemical oxidation.

## Go Figure

Does the variation in radius of the transition metals follow the same trend as the effective nuclear charge on moving from left to right across the periodic table?



▲ **Figure 23.3** Radii of transition metals as a function of group number.

**Go Figure**

In which transition-metal ion of this group are the  $3d$  orbitals completely filled?

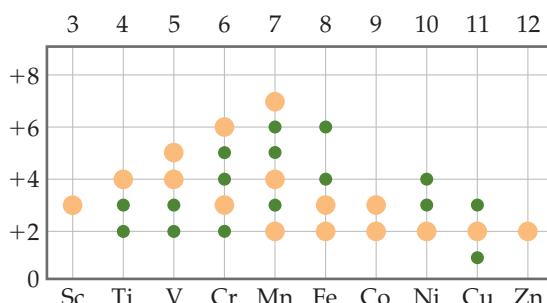


▲ **Figure 23.4** Aqueous solutions of transition metal ions. Left to right:  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ . The counterion is nitrate in all cases.

**Go Figure**

Are there any ions in this figure for which the  $4s$  orbitals are not empty? For which ions are the  $3d$  orbitals empty?

- Most frequently seen
- Less common



▲ **Figure 23.5** Nonzero oxidation states of the Period 4 transition metals.

In the transition metals of Periods 5 and 6, the increased size of the  $4d$  and  $5d$  orbitals makes it possible to attain maximum oxidation states as high as +8, which is achieved in  $\text{RuO}_4$  and  $\text{OsO}_4$ . In general, the maximum oxidation states are found only when the metals are combined with the most electronegative elements, especially O, F, and in some cases Cl.

**Magnetism**

The spin that an electron possesses gives the electron a *magnetic moment*, a property that causes the electron to behave like a tiny magnet. In a *diamagnetic* solid, defined as one in which all the electrons in the solid are paired, the spin-up and spin-down electrons cancel one another. Diamagnetic substances are generally described as being nonmagnetic, but when a diamagnetic substance is placed in a magnetic field, the motions of the electrons cause the substance to be very weakly repelled by the magnet. In other words, these supposedly nonmagnetic substances do show some very faint magnetic character in the presence of a magnetic field.

A substance in which the atoms or ions have one or more unpaired electrons is *paramagnetic*. In a paramagnetic solid, the electrons on one atom or ion do not influence the unpaired electrons on neighboring atoms or ions. As a result, the magnetic moments on the atoms or ions

are randomly oriented and constantly changing direction, as shown in **Figure 23.6(a)**. When a paramagnetic substance is placed in a magnetic field, however, the magnetic moments tend to align parallel to one another, producing a net attractive interaction with the magnet. Thus, unlike a diamagnetic substance, which is weakly repelled by a magnetic field, a paramagnetic substance is attracted to a magnetic field.

When you think of a magnet, you probably picture a simple iron magnet. Iron exhibits **ferromagnetism**, a form of magnetism much stronger than paramagnetism. Ferromagnetism arises when the unpaired electrons of the atoms or ions in a solid are influenced by the orientations of the electrons in neighboring atoms or ions. The most stable (lowest-energy) arrangement is when the spins of electrons on adjacent atoms or ions are aligned in the same direction, as in Figure 23.6(b). When a ferromagnetic solid is placed in a magnetic field, the electrons tend to align strongly in a direction parallel to the magnetic field. The attraction to the magnetic field that results may be as much as a million times stronger than that for a paramagnetic substance.

When a ferromagnet is removed from an external magnetic field, the interactions between the electrons cause the ferromagnetic substance to maintain a magnetic moment. We then refer to it as a *permanent magnet* (Figure 23.7).

The only ferromagnetic transition metals are Fe, Co, and Ni, but many alloys also exhibit ferromagnetism, which is in some cases stronger than the ferromagnetism of the pure metals. Particularly powerful ferromagnetism is found in compounds containing both transition metals and lanthanide metals. Two of the most important examples are SmCo<sub>5</sub> and Nd<sub>2</sub>Fe<sub>14</sub>B.

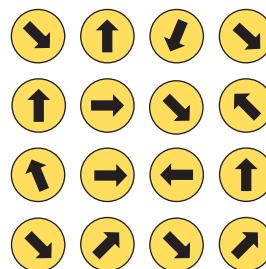
Two additional types of magnetism involving ordered arrangements of unpaired electrons are depicted in Figure 23.6. In materials that exhibit **antiferromagnetism** [Figure 23.6(c)], the unpaired electrons on a given atom or ion align so that their spins are oriented in the direction opposite the spin direction on neighboring atoms. This means that the spin-up and spin-down electrons cancel each other. Examples of antiferromagnetic substances are chromium metal, FeMn alloys, and such transition-metal oxides as Fe<sub>2</sub>O<sub>3</sub>, LaFeO<sub>3</sub>, and MnO.

A substance that exhibits **ferrimagnetism** [Figure 23.6(d)] has both ferromagnetic and antiferromagnetic characteristics. Like an antiferromagnet, the unpaired electrons align so that the spins in adjacent atoms or ions point in opposite directions. However, unlike an antiferromagnet, the net magnetic moments of the spin-up electrons are not fully canceled by the spin-down electrons. This can happen because the magnetic centers have different numbers of unpaired electrons (NiMnO<sub>3</sub>), because the number of magnetic sites aligned in one direction is larger than the number aligned in the other direction (Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>), or because both of these conditions apply (Fe<sub>3</sub>O<sub>4</sub>). Because the magnetic moments do not cancel, the properties of ferrimagnetic materials are similar to the properties of ferromagnetic materials.

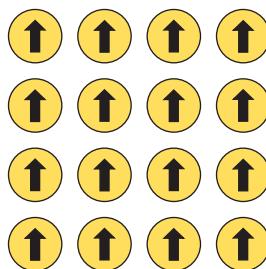
Ferromagnets, ferrimagnets, and antiferromagnets all become paramagnetic when heated above a critical temperature. This happens when the thermal energy is sufficient to overcome the forces determining the spin directions of the electrons. This temperature is called the *Curie temperature*,  $T_C$ , for ferromagnets and ferrimagnets and the *Néel temperature*,  $T_N$ , for antiferromagnets.

### Go Figure

Describe how the representation shown for the paramagnetic material would change if the material were placed in a magnetic field.



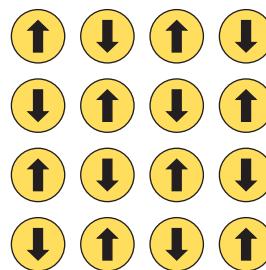
Paramagnetic; spin direction is constantly changing and random in the absence of an external magnetic field



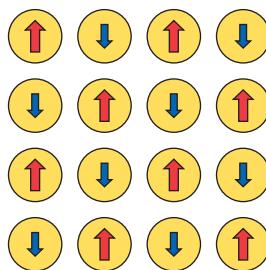
Ferromagnetic; spins align parallel to each other

(a)

(b)



Antiferromagnetic; spins align in opposite directions and cancel each other



Ferrimagnetic; unequal spins align in opposite directions but do not completely cancel each other

(c)

(d)

▲ Figure 23.6 The relative orientation of electron spins in various types of magnetic substances.



▲ Figure 23.7 A permanent magnet. Permanent magnets are made from ferromagnetic and ferrimagnetic materials.

## Self-Assessment Exercise

- 23.1** Do you expect TiCl<sub>4</sub> to exhibit any of the magnetic properties shown in figure 23.6?

- (a) Yes  
(b) No

## Exercises

**23.2** Which periodic trend is partially responsible for the observation that the maximum oxidation state of the transition-metal elements peaks near Groups 7 and 8? (a) The number of valence electrons reaches a maximum at Group 8. (b) The effective nuclear charge increases on moving left across each period. (c) The radii of the transition-metal elements reach a minimum for Group 8, and as the size of the atoms decreases it becomes easier to remove electrons.

- 23.3** For each of the following compounds, determine the electron configuration of the transition-metal ion. (a) CuO, (b) Cu<sub>2</sub>O, (c) V<sub>2</sub>O<sub>5</sub>, (d) MnO.
- 23.4** How many electrons are in the valence *d* orbitals in these transition-metal ions? (a) Ru<sup>3+</sup>, (b) Pd<sup>2+</sup>, (c) Ti<sup>2+</sup>, (d) W<sup>6+</sup>.
- 23.5** Which type of magnetic material cannot be used to make permanent magnets, a ferromagnetic substance, an anti-ferromagnetic substance, or a ferrimagnetic substance?

23.1 (b)

Answers to Self-Assessment Exercise

## 23.2 | Transition-Metal Complexes



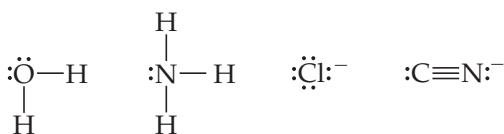
Gold has been highly valued for thousands of years. It is one of the few metals to occur naturally as an element. Its distribution is widespread but almost always in extremely low concentrations. In the few places where it has been concentrated into alluvial deposits, nuggets may be extracted by panning or using a separation table. The high density of gold means that it drops to the bottom of the pan and the slurry of unwanted material above it can be decanted. Panning for gold is still performed by artisan prospectors but requires nuggets to be visible to the eye. Commercial gold mines use an extraction process to recover fine grained gold. Here, the gold-bearing rock is crushed and leached with a sodium cyanide solution in the presence of air. This forms the soluble gold ion, [Au(CN)<sub>2</sub>]<sup>-</sup>, which is concentrated in by absorption onto fine carbon particles and recovered electrolytically. The hazards associated with using large quantities of cyanide have stimulated research into an alternate leaching material but the inertness of gold—one of the properties that makes it so desirable—means the choices are limited.

In this section, we start our discussion of coordination chemistry, and by the end, you should be able to

- Understand the component parts of a coordination compound
- Determine the charge on the metal in a complex ion

The transition metals occur in many interesting and important molecular forms. Species that are assemblies of a central transition-metal ion bonded to a group of surrounding molecules or ions, such as  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , are called **metal complexes**, or merely *complexes*.<sup>\*</sup> If the complex carries a net charge, it is generally called a *complex ion*. Compounds that contain complexes are known as **coordination compounds**.

The molecules or ions that bond to the metal ion in a complex are known as **ligands** (from the Latin word *ligare*, “to bind”). There are two  $\text{NH}_3$  ligands bonded to  $\text{Ag}^+$  in the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$ , for instance, and six  $\text{H}_2\text{O}$  ligands bonded to  $\text{Fe}^{3+}$  in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Each ligand functions as a Lewis base and so donates a pair of electrons to form the ligand–metal bond. Thus, every ligand has at least one unshared pair of valence electrons. Four of the most frequently encountered ligands,



illustrate that most ligands are either polar molecules or anions. In forming a complex, the ligands are said to *coordinate* to the metal.

## The Development of Coordination Chemistry: Werner's Theory

Because compounds of the transition metals are beautifully colored, the chemistry of these elements fascinated chemists even before the periodic table was introduced. During the late 1700s through the 1800s, the many coordination compounds that were isolated and studied had properties that were puzzling in light of the bonding theories prevailing at the time. **Table 23.3**, for example, lists a series of  $\text{CoCl}_3 \cdot \text{NH}_3$  compounds that have strikingly different colors. Note that the third and fourth species have different colors, even though the originally assigned formula was the same for both,  $\text{CoCl}_3 \cdot 4 \text{ NH}_3$ .

The modern formulations of the compounds in Table 23.3 are based on various lines of experimental evidence. For example, all four compounds are strong electrolytes but yield different numbers of ions when dissolved in water. Dissolving  $\text{CoCl}_3 \cdot 6 \text{ NH}_3$  in water yields four ions per formula unit ( $[\text{Co}(\text{NH}_3)_6]^{3+}$  plus three  $\text{Cl}^-$  ions), whereas  $\text{CoCl}_3 \cdot 5 \text{ NH}_3$  yields only three ions per formula unit ( $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and two  $\text{Cl}^-$  ions). Furthermore, the reaction of the compounds with excess aqueous silver nitrate leads to the precipitation of different amounts of  $\text{AgCl}(s)$ . When  $\text{CoCl}_3 \cdot 6 \text{ NH}_3$  is treated with excess  $\text{AgNO}_3(aq)$ , 3 mol of  $\text{AgCl}(s)$  precipitate per mole of complex, which means all three  $\text{Cl}^-$  ions in the complex can react to form  $\text{AgCl}(s)$ . By contrast, when  $\text{CoCl}_3 \cdot 5 \text{ NH}_3$  is treated with excess  $\text{AgNO}_3(aq)$ , only 2 mol of  $\text{AgCl}(s)$  precipitate per mole of complex,

**TABLE 23.3 Properties of Some Ammonia Complexes of Cobalt(III)**

Original Formulation	Color	Ions per Formula Unit	“Free” $\text{Cl}^-$ Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{ NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{ NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{ NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{ NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

\*Most of the coordination compounds we examine in this chapter contain transition-metal ions, although ions of other metals can also form complexes.

telling us that one of the  $\text{Cl}^-$  ions in the complex does not react. These results are summarized in Table 23.3.

In 1893, the Swiss chemist Alfred Werner (1866–1919) proposed a theory that successfully explained the observations in Table 23.3. In a theory that became the basis for understanding coordination chemistry, Werner proposed that any metal ion exhibits both a primary valence and a secondary valence. The *primary valence* is the oxidation state of the metal, which is +3 for the complexes in Table 23.3. The *secondary valence* is the number of atoms bonded to the metal ion, which is also called the **coordination number**. For these cobalt complexes, Werner deduced a coordination number of 6 with the ligands in an octahedral arrangement around the  $\text{Co}^{3+}$  ion.

Werner's theory provided a beautiful explanation for the results in Table 23.3. The  $\text{NH}_3$  molecules are ligands bonded to the  $\text{Co}^{3+}$  ion (through the nitrogen atom as we will see later); if there are fewer than six  $\text{NH}_3$  molecules, the remaining ligands are  $\text{Cl}^-$  ions. The central metal and the ligands bound to it constitute the **coordination sphere** of the complex.

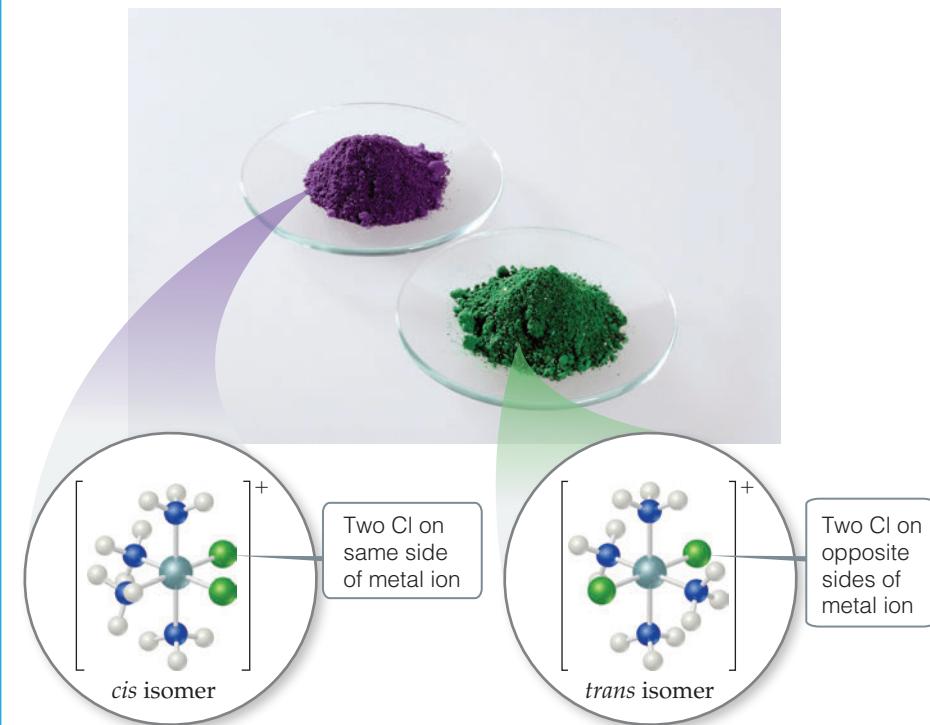
In writing the chemical formula for a coordination compound, Werner suggested using square brackets to signify the makeup of the coordination sphere in any given compound. He therefore proposed that  $\text{CoCl}_3 \cdot 6 \text{ NH}_3$  and  $\text{CoCl}_3 \cdot 5 \text{ NH}_3$  are better written as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , respectively. He further proposed that the chloride ions that are part of the coordination sphere are bound so tightly that they do not dissociate when the complex is dissolved in water. Thus, dissolving  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  in water produces a  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  ion and two  $\text{Cl}^-$  ions.

Werner's ideas also explained why there are two forms of  $\text{CoCl}_3 \cdot 4 \text{ NH}_3$ . Using Werner's postulates, we write the formula as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ . As shown in Figure 23.8, there are two ways to arrange the ligands in the  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  complex, called the *cis* and *trans* forms. In the *cis* form, the two chloride ligands occupy adjacent vertices of the octahedral arrangement. In *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  the two chlorides are opposite each other. It is this difference in positions of the Cl ligands that leads to two compounds, one violet and one green.



### Go Figure

Is there another way to arrange the chloride ions in the  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  ion besides the two shown in this figure?



▲ Figure 23.8 Isomers of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ . The *cis* isomer is violet, and the *trans* isomer is green.

The insight Werner provided into the bonding in coordination compounds is even more remarkable when we realize that his theory predated Lewis's ideas of covalent bonding by more than 20 years! Because of his tremendous contributions to coordination chemistry, Werner was awarded the 1913 Nobel Prize in Chemistry.

### Sample Exercise 23.1

#### Identifying the Coordination Sphere of a Complex

Palladium(II) tends to form complexes with coordination number 4. A compound has the composition  $\text{PdCl}_2 \cdot 3 \text{ NH}_3$ . (a) Write the formula for this compound that best shows the coordination structure. (b) When an aqueous solution of the compound is treated with excess  $\text{AgNO}_3(aq)$ , how many moles of  $\text{AgCl}(s)$  are formed per mole of  $\text{PdCl}_2 \cdot 3 \text{ NH}_3$ ?

#### SOLUTION

**Analyze** We are given the coordination number of Pd(II) and a chemical formula indicating that the complex contains  $\text{NH}_3$  and  $\text{Cl}^-$ . We are asked to determine (a) which ligands are attached to Pd(II) in the compound and (b) how the compound behaves toward  $\text{AgNO}_3$  in aqueous solution.

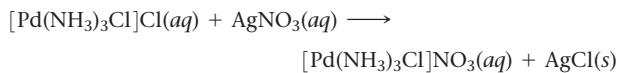
**Plan** (a) Because of their charge, the  $\text{Cl}^-$  ions can be either in the coordination sphere, where they are bonded directly to the metal, or outside the coordination sphere, where they are bonded ionically to the complex. The electrically neutral  $\text{NH}_3$  ligands must be in the coordination sphere, and we will assume that four ligands are bonded to the Pd(II) ion. (b) Any chlorides in the coordination sphere do not precipitate as  $\text{AgCl}$ .

#### Solve

(a) By analogy to the ammonia complexes of cobalt(III) shown in Figure 23.7, we predict that the three  $\text{NH}_3$  are ligands attached to the Pd(II) ion. The fourth ligand around Pd(II) is one chloride ion. The second chloride ion is not a ligand; it serves only as a *counterion* (a noncoordinating ion that balances charge)

in the compound. We conclude that the formula showing the structure best is  $[\text{Pd}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ .

(b) Because only the non-ligand  $\text{Cl}^-$  can react, we expect to produce 1 mol of  $\text{AgCl}(s)$  per mole of complex. The balanced equation is



This is a metathesis reaction in which one of the cations is the  $[\text{Pd}(\text{NH}_3)_3\text{Cl}]^+$  complex ion.

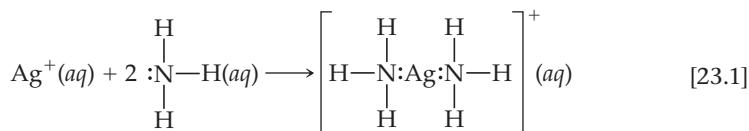
#### ► Practice Exercise

When the compound  $\text{RhCl}_3 \cdot 4 \text{ NH}_3$  is dissolved in water and treated with excess  $\text{AgNO}_3(aq)$  one mole of  $\text{AgCl}(s)$  is formed for every mole of  $\text{RhCl}_3 \cdot 4 \text{ NH}_3$ . What is the correct way to write the formula of this compound?

- (a)  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_3]$  (b)  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (c)  $[\text{Rh}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$   
 (d)  $[\text{Rh}(\text{NH}_3)_4]\text{Cl}_3$  (e)  $[\text{RhCl}_3](\text{NH}_3)_4$

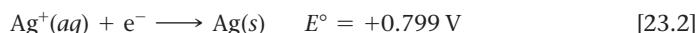
## The Metal-Ligand Bond

The bond between a ligand and a metal ion forms as a result of a Lewis acid-base interaction. Because the ligands have available pairs of electrons, they can function as Lewis bases (electron-pair donors). Metal ions (particularly transition-metal ions) have empty valence orbitals, so they can act as Lewis acids (electron-pair acceptors). We can picture the bond between the metal ion and ligand as the result of their sharing a pair of electrons initially on the ligand:



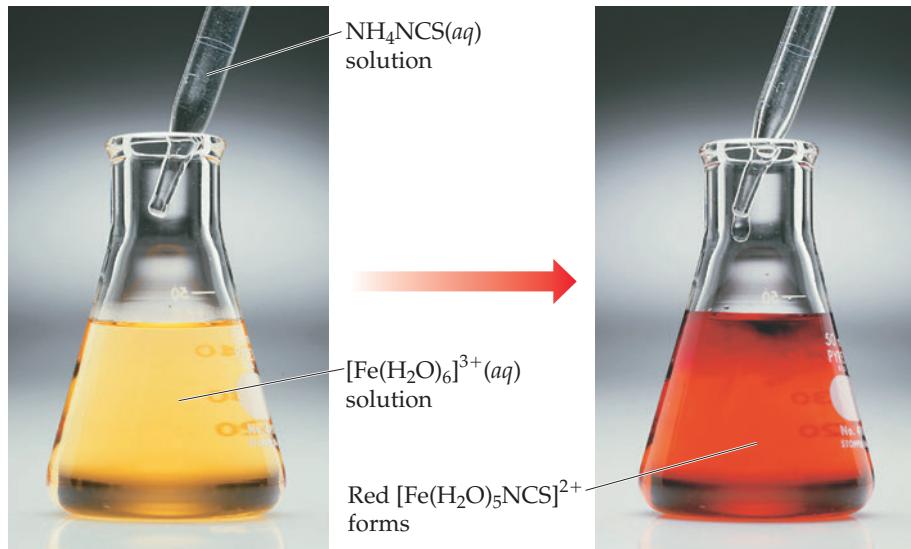
The formation of metal-ligand bonds can markedly alter the properties we observe for the metal ion. A metal complex is a distinct chemical species that has physical and chemical properties different from those of the metal ion and ligands from which it is formed. As one example, Figure 23.9 shows the color change that occurs when aqueous solutions of  $\text{NCS}^-$  (colorless) and  $\text{Fe}^{3+}$  (yellow) are mixed, forming  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$ .

Complex formation can also significantly change other properties of metal ions, such as their ease of oxidation or reduction. Silver ion, for example, is readily reduced in water,



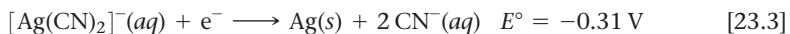
 Go Figure

Does the coordination number of iron change during this reaction? Does the oxidation number of iron change?



▲ Figure 23.9 The reaction between  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(aq)$  and  $\text{NCS}^-(aq)$ .

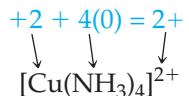
but the  $[\text{Ag}(\text{CN})_2]^-$  ion is not so easily reduced because complexation by  $\text{CN}^-$  ions stabilizes silver in the +1 oxidation state:



Hydrated metal ions are complexes in which the ligand is water. Thus,  $\text{Fe}^{3+}(aq)$  consists largely of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . It is important to realize that ligands can undergo reaction. For example, we saw in Figure 16.18 that a water molecule in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(aq)$  can be deprotonated to yield  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}(aq)$  and  $\text{H}^+(aq)$ . The iron ion retains its oxidation state; the coordinated hydroxide ligand, with a 1– charge, reduces the complex charge to 2+. Ligands can also be displaced from the coordination sphere by other ligands, if the incoming ligands bind more strongly to the metal ion than the original ones. For example, ligands such as  $\text{NH}_3$ ,  $\text{NCS}^-$ , and  $\text{CN}^-$  can replace  $\text{H}_2\text{O}$  in the coordination sphere of metal ions.

### Charges, Coordination Numbers, and Geometries

The charge of a complex is the sum of the charges on the metal and on the ligands. In  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  we can deduce the charge on the complex ion because we know that the charge of the sulfate ion is 2–. Because the compound is electrically neutral, the complex ion must have a 2+ charge,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . We can then use the charge of the complex ion to deduce the oxidation number of copper. Because the  $\text{NH}_3$  ligands are uncharged molecules, the oxidation number of copper must be +2:



Recall that the number of atoms directly bonded to the metal atom in a complex is the *coordination number* of the complex. Thus, the silver ion in  $[\text{Ag}(\text{NH}_3)_2]^+$  has a



## Sample Exercise 23.2

### Determining the Oxidation Number of a Metal in a Complex



What is the oxidation number of the metal in  $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ ?

#### SOLUTION

**Analyze** We are given the chemical formula of a coordination compound and asked to determine the oxidation number of its metal atom.

**Plan** To determine the oxidation number of Rh, we need to figure out what charges are contributed by the other groups. The overall charge is zero, so the oxidation number of the metal must balance the charge due to the rest of the compound.

**Solve** The  $\text{NO}_3$  group is the nitrate anion, which has a 1<sup>-</sup> charge. The  $\text{NH}_3$  ligands carry zero charge, and the Cl is a coordinated chloride ion, which has a 1<sup>-</sup> charge. The sum of all the charges must be zero:

$$x + 5(0) + (-1) + 2(-1) = 0$$

The oxidation number of rhodium,  $x$ , must therefore be +3.

#### ► Practice Exercise

In which of the following compounds does the transition-metal have the highest oxidation number?  
**(a)**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  **(b)**  $\text{K}_2[\text{PtCl}_6]$  **(c)**  $\text{Rb}_3[\text{MoO}_3\text{F}_3]$   
**(d)**  $\text{Na}[\text{Ag}(\text{CN})_2]$  **(e)**  $\text{K}_4[\text{Mn}(\text{CN})_6]$

coordination number of 2, and the cobalt ion has a coordination number of 6 in all four complexes in Table 23.3.

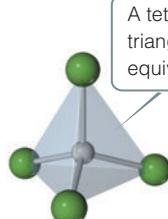
Some metal ions have only one observed coordination number. The coordination number of chromium(III) and cobalt(III) is invariably 6, for example, and that of platinum(II) is always 4. For most metals, however, the coordination number is different for different ligands. In these complexes, the most common coordination numbers are 4 and 6.

The coordination number of a metal ion is often influenced by the relative sizes of the metal ion and the ligands. As the ligand gets larger, fewer of them can coordinate to the metal ion. Thus, iron(III) is able to coordinate to six fluorides in  $[\text{FeF}_6]^{3-}$  but to only four chlorides in  $[\text{FeCl}_4]^-$ . Ligands that transfer substantial negative charge to the metal also produce reduced coordination numbers. For example, six ammonia molecules can coordinate to nickel(II), forming  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , but only four cyanide ions can coordinate to this ion, forming  $[\text{Ni}(\text{CN})_4]^{2-}$ .

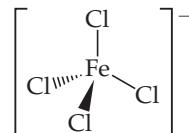
The most common coordination geometries for coordination complexes are shown in **Figure 23.10**. Complexes in which the coordination number is 4 have two geometries—tetrahedral and square planar. The tetrahedral geometry is the more common of the two and is especially prevalent among nontransition metals. The square planar geometry is characteristic of transition-metal ions with eight  $d$  electrons in the valence shell, such as platinum(II) and gold(III). Complexes with a coordination number of 6 almost always have an octahedral geometry. Even though the octahedron can be drawn as a square with one ligand above and another below the plane, all six vertices are equivalent.

#### Go Figure

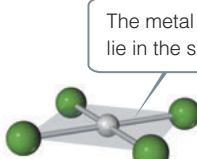
In the drawings on the right-hand side, what does the solid wedge connecting atoms represent? What does the dashed wedge connecting atoms represent?



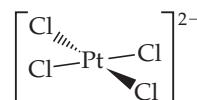
A tetrahedron has four triangular faces and four equivalent vertices.



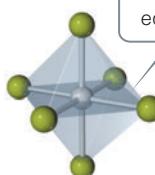
Tetrahedral geometry



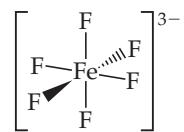
The metal and all four ligands lie in the same plane.



Square planar geometry



An octahedron has eight triangular faces and six equivalent vertices.



Octahedral geometry

▲ **Figure 23.10** Common geometries of coordination complexes.

In complexes having coordination number 4, the geometry is typically either tetrahedral or square planar. In complexes having coordination number 6, the geometry is nearly always octahedral.

## Self-Assessment Exercise

**23.6** What is the coordination number, charge on the metal, and geometry of the complex:  $[\text{Au}(\text{CN})_2]^-$ ?

- (a)  $\text{Au}^+$ , Coordination number = 2, Linear geometry
- (b)  $\text{Au}^{3+}$ , Coordination number = 3, Linear geometry
- (c)  $\text{Au}^-$ , Coordination number = 6, Octahedral geometry

## Exercises

**23.7** Which species are more likely to act as ligands? (a) Positively charged ions or negatively charged ions? (b) Neutral molecules that are polar or those that are nonpolar?

**23.8** Crystals of hydrated chromium(III) chloride are green, have an empirical formula of  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ , and are highly soluble. (a) Write the complex ion that exists in this compound. (b) If the complex is treated with excess  $\text{AgNO}_3(aq)$ , how many moles of  $\text{AgCl}$  will precipitate per mole of  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  dissolved in solution? (c) Crystals of anhydrous chromium(III) chloride are violet and insoluble in aqueous solution. The coordination geometry of chromium in these crystals is octahedral, as is almost always the

case for  $\text{Cr}^{3+}$ . How can this be the case if the ratio of Cr to Cl is not 1:6?

**23.9** Indicate the coordination number and the oxidation number of the metal for each of the following complexes:

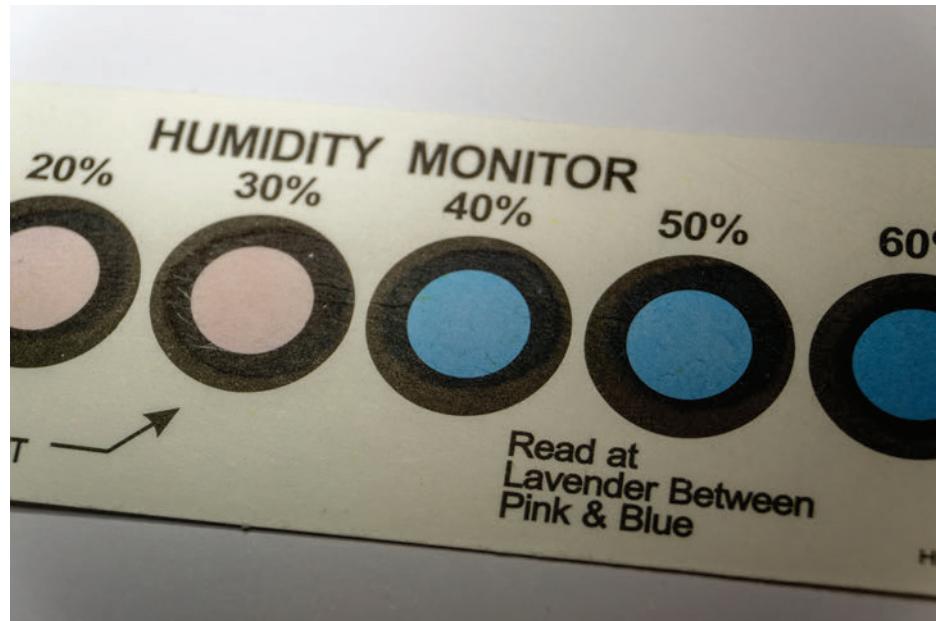
- (a)  $\text{K}_2\text{PtCl}_4$
- (b)  $[\text{Ni}(\text{CO})_4]\text{Br}_2$
- (c)  $\text{OsO}_4$
- (d)  $[\text{Mn}(\text{en})_3](\text{NO}_3)_2$
- (e)  $[\text{Cr}(\text{en})(\text{NH}_3)_4]\text{Cl}_3$
- (f)  $[\text{Zn}(\text{bipy})_2](\text{ClO}_4)_2$

23.6 (a)

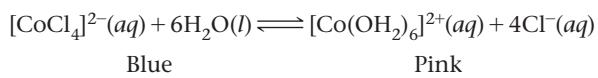
Answers to Self-Assessment Exercise



### 23.3 | Common Ligands in Coordination Chemistry



We have already seen that the color of a complex can vary greatly even when the same metal ion is involved. Cobalt provides another good example of this, having a blue  $[\text{CoCl}_4]^{2-}$  complex and pink  $[\text{Co}(\text{OH}_2)_6]^{2+}$  complex. The two complexes, when dissolved in water, are in equilibrium:



When the complexes are immobilized in a gel, the equilibrium can still operate and provides a visual guide to the degree of hydration of the gel. This is frequently used in combination with silica gel desiccants to indicate when the drying agents need regenerating.

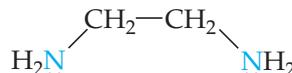
By the end of this section, you should be able to

- Identify common ligands and distinguish between chelating and nonchelating ligands.

The ligand atom that binds to the central metal ion in a coordination complex is called the **donor atom** of the ligand. Ligands having only one donor atom are called **monodentate ligands** (from the Latin, meaning “one-toothed”). These ligands are able to occupy only one site in a coordination sphere. Ligands having two donor atoms are **bidentate ligands** (“two-toothed”), and those having three or more donor atoms are **polydentate ligands** (“many-toothed”). In both bidentate and polydentate species, the multiple donor atoms can simultaneously bond to the metal ion, thereby occupying two or more sites in a coordination sphere. **Table 23.4** gives examples of all three types of ligands.

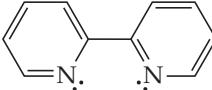
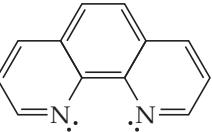
Because they appear to grasp the metal between two or more donor atoms, bidentate and polydentate ligands are also known as **chelating agents** (pronounced “KEE-laying”; from the Greek *chele*, “claw”).

One common chelating agent is the bidentate ligand *ethylenediamine*, denoted en:

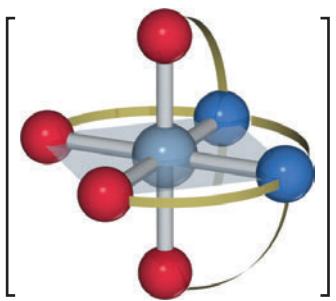
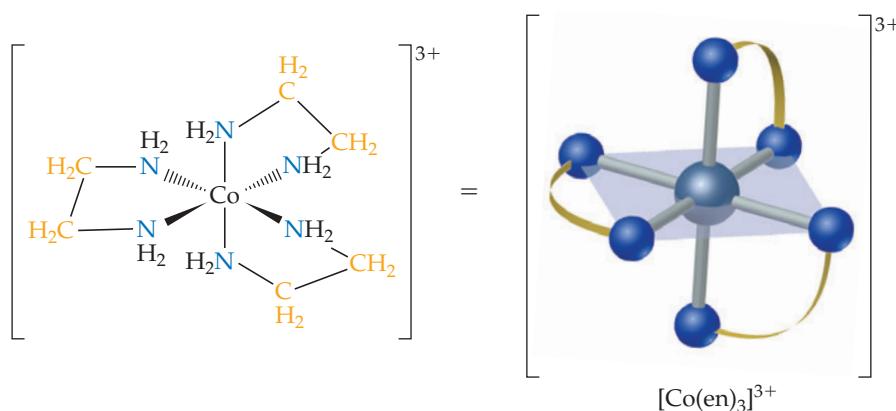


in which each donor nitrogen atom has one nonbonding electron pair. These donor atoms are sufficiently far apart to allow both of them to bond to the metal ion in

**TABLE 23.4 Some Common Ligands**

Ligand Type	Examples
Monodentate	$\text{H}_2\ddot{\text{O}}$ : Water $\text{:NH}_3$ : Ammonia
	$\text{:F}^-$ : Fluoride ion $\text{:Cl}^-$ : Chloride ion
	$[\text{:C}\equiv\text{N}:]^-$ : Cyanide ion $[\text{:S}=\text{C}=\text{:N}:]^-$ : Thiocyanate ion
	$[\text{:O}-\text{H}]^-$ : Hydroxide ion $[\text{:O}-\text{N}=\text{:O}:]^-$ : Nitrite ion
Bidentate	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\   \quad   \\ \text{H}_2\ddot{\text{N}} \quad \text{NH}_2 \end{array}$ : Ethylenediamine (en)
	 Bipyridine (bipy or bpy)
	 Ortho-phenanthroline (o-phen)
	$[\text{C}(=\text{O})\text{C}(\text{O})\text{O}]^{2-}$ : Oxalate ion
	$[\text{C}(\text{O})\text{O}]^{2-}$ : Carbonate ion
Polydentate	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \quad \text{CH}_2-\text{CH}_2 \\   \quad   \quad \quad   \quad   \\ \text{H}_2\ddot{\text{N}} \quad \text{NH} \quad \quad \text{NH}_2 \quad \quad \text{NH}_2 \end{array}$ : Diethylenetriamine
	$[\text{O}=\text{P}(\text{O})_2\text{O}]^{5-}$ : Triphosphate ion
	$[\text{O}=\text{C}(\text{CH}_2\text{CH}_2\text{N}(\text{H})(\text{CH}_2\text{CH}_2\text{N}(\text{H})(\text{CH}_2\text{CH}_2\text{O}))\text{C}(=\text{O})\text{O}]^{4-}$ : Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ )

► **Figure 23.11** The  $[\text{Co}(\text{en})_3]^{3+}$  ion. The ligand is ethylenediamine.



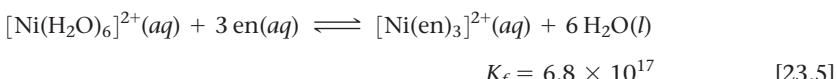
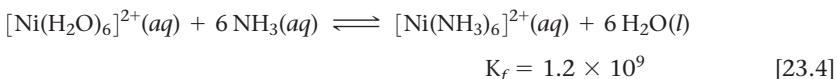
▲ **Figure 23.12** The complex ion

$[\text{Co}(\text{EDTA})]^-$ . The ligand is the polydentate ethylenediaminetetraacetate ion, whose full representation is given in Table 23.4. This representation shows how the two N and four O donor atoms coordinate to cobalt.

adjacent positions. The  $[\text{Co}(\text{en})_3]^{3+}$  complex ion, which contains three ethylenediamine ligands in the octahedral coordination sphere of cobalt(III), is shown in **Figure 23.11**. Notice that in the image on the right the en is written in a shorthand notation as two nitrogen atoms connected by an arc.

The ethylenediaminetetraacetate ion,  $[\text{EDTA}]^{4-}$ , is an important polydentate ligand that has six donor atoms. It can wrap around a metal ion using all six donor atoms, as shown in **Figure 23.12**, although it sometimes binds to a metal using only five of its donor atoms.

In general, the complexes formed by chelating ligands (that is, bidentate and polydentate ligands) are more stable than the complexes formed by related monodentate ligands. The equilibrium formation constants for  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ni}(\text{en})_3]^{2+}$  illustrate this observation:



Although the donor atom is nitrogen in both instances,  $[\text{Ni}(\text{en})_3]^{2+}$  has a formation constant that is more than  $10^8$  times larger than that of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ . This trend of generally larger formation constants for bidentate and polydentate ligands, known as the **chelate effect**, is examined in the “A Closer Look” essay on page 1118.

Chelating agents are often used to prevent one or more of the customary reactions of a metal ion without removing the ion from solution. For example, a metal ion that interferes with a chemical analysis can often be complexed and its interference thereby removed. In a sense, the chelating agent hides the metal ion. For this reason, scientists sometimes refer to these ligands as *sequestering agents*.

Phosphate ligands, such as sodium tripolyphosphate,  $\text{Na}_5[\text{OPO}_2\text{OPO}_2\text{OPO}_3]$ , are used to sequester  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in hard water so that these ions cannot interfere with the action of soap or detergents.

Chelating agents are used in many prepared foods, such as salad dressings and frozen desserts, to complex trace metal ions that catalyze decomposition reactions. Chelating agents are used in medicine to remove toxic heavy metal ions that have been ingested, such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ . One method of treating lead poisoning, for example, is to administer  $\text{Na}_2\text{Ca}(\text{EDTA})$ . The EDTA chelates the lead, allowing it to be removed from the body via urine.

## Metals and Chelates in Living Systems

Nine of the 29 elements known to be necessary for human life are transition metals. These 10 elements—V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Mo form complexes with a variety of groups present in biological systems.

Although our bodies require only small quantities of metals, deficiencies can lead to serious illness. A deficiency of manganese, for example, can lead to convulsive disorders. Some epilepsy patients have been helped by the addition of manganese to their diets.

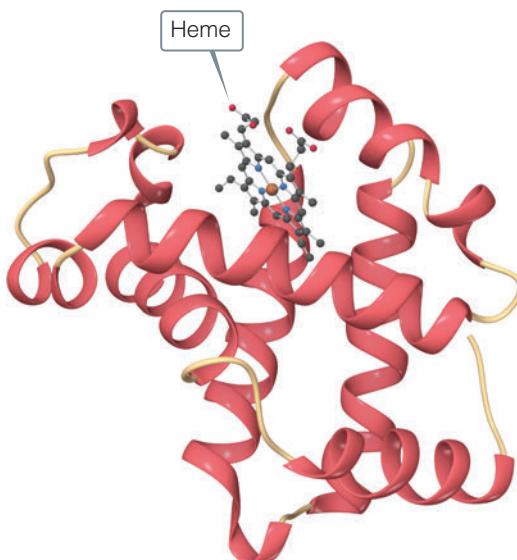
Among the most important chelating agents in nature are those derived from the *porphine* molecule (Figure 23.13). This molecule can coordinate to a metal via its four nitrogen donor atoms. Once porphine bonds to a metal ion, the two H atoms on the nitrogens are displaced to form complexes called **porphyrins**. Two important porphyrins are *heme*, in which the metal ion is Fe(II), and *chlorophyll*, with a Mg(II) central ion.

**Figure 23.14** shows a schematic structure of myoglobin, a protein that contains one heme group. Myoglobin is a *globular protein*, one that folds into a compact, roughly spherical shape. Myoglobin is found in the cells of skeletal muscle, particularly in seals, whales, and porpoises. It stores oxygen in cells, one molecule of O<sub>2</sub> per myoglobin, until it is needed for metabolic activities. Hemoglobin, the protein that transports oxygen in human blood, is made up of four heme-containing subunits, each of which is very similar to myoglobin. One hemoglobin can bind up to four O<sub>2</sub> molecules.

In both myoglobin and hemoglobin, the iron is coordinated to the four nitrogen atoms of a porphyrin and to a nitrogen atom from the protein chain (Figure 23.15). In hemoglobin, the sixth position around the iron is occupied either by O<sub>2</sub> (in oxyhemoglobin, the bright red form) or by water (in deoxyhemoglobin, the purplish red form). The oxy form is the one shown in Figure 23.15.

Carbon monoxide is poisonous because the equilibrium binding constant of human hemoglobin for CO is about 210 times greater than that for O<sub>2</sub>. As a result, a relatively small quantity of CO can inactivate a substantial fraction of the hemoglobin in the blood by displacing the O<sub>2</sub> molecule from the heme-containing subunit. For example, a person breathing air that contains only 0.1% CO takes in enough CO after a few hours to convert up to 60% of the hemoglobin (Hb) into COHb, thereby reducing the blood's normal oxygen-carrying capacity by 60%.

Under normal conditions, a nonsmoker breathing unpolluted air has about 0.3 to 0.5% COHb in her or his blood. This amount

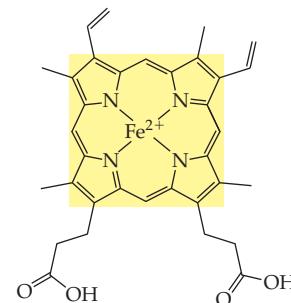


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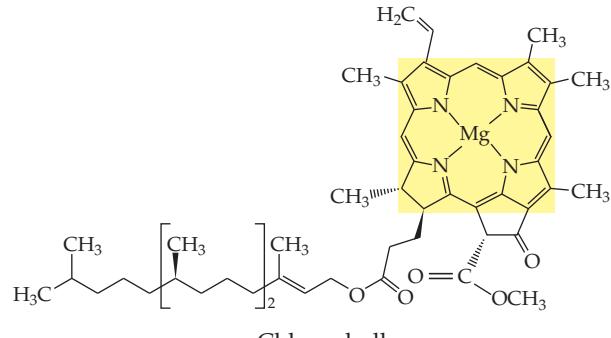
How many carbon atoms are there in porphine? How many have *sp*<sup>3</sup> hybridization? How many have *sp*<sup>2</sup> hybridization?



Porphine



Heme b



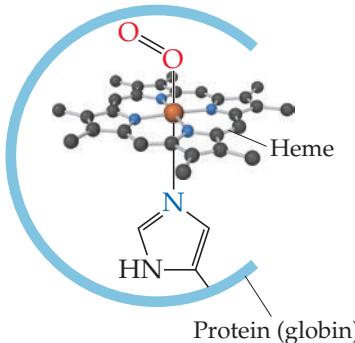
Chlorophyll a

▲ **Figure 23.13** Porphine and two porphyrins, heme b and chlorophyll a. Fe(II) and Mg(II) ions replace the two blue H atoms in porphine and bond with all four nitrogens in heme b and chlorophyll a, respectively.

◀ **Figure 23.14** Myoglobin. This ribbon diagram does not show most of the atoms.

### Go Figure

What is the coordination number of iron in the heme unit shown here? What is the identity of the blue donor atoms in the heme?



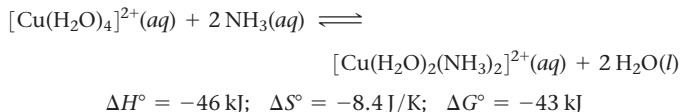
▲ Figure 23.15 Coordination sphere of the hemes in oxymyoglobin and oxyhemoglobin.

arises mainly from the production of small quantities of CO in the course of normal body chemistry and from the small amount of CO present in clean air. Exposure to higher concentrations of CO causes the COHb level to increase, which in turn leaves fewer Hb sites to which O<sub>2</sub> can bind. If the level of COHb becomes too high, oxygen transport is effectively shut down and death occurs. Because CO is colorless and odorless, CO poisoning occurs with very little warning. Improperly ventilated combustion devices, such as kerosene lanterns and stoves, thus pose a potential health hazard.

### A CLOSER LOOK Entropy and the Chelate Effect

We learned in Section 19.5 that chemical processes are favored by positive entropy changes and by negative enthalpy changes. The special stability associated with the formation of chelates, called the *chelate effect*, can be explained by comparing the entropy changes that occur with monodentate ligands with the entropy changes that occur with polydentate ligands.

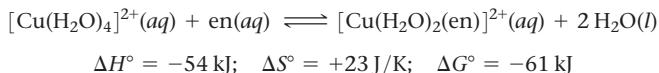
We begin with the reaction in which two H<sub>2</sub>O ligands of the square-planar Cu(II) complex [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> are replaced by monodentate NH<sub>3</sub> ligands at 27 °C:



The thermodynamic data tell us about the relative abilities of H<sub>2</sub>O and NH<sub>3</sub> to serve as ligands in this reaction. In general, NH<sub>3</sub> binds more tightly to metal ions than does H<sub>2</sub>O, so this substitution reaction is exothermic ( $\Delta H < 0$ ). The stronger bonding of the NH<sub>3</sub> ligands also causes the [Cu(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> ion to be more rigid, which is probably the reason  $\Delta S^\circ$  is slightly negative.

We can use Equation 19.20,  $\Delta G^\circ = -RT \ln K$ , to calculate the equilibrium constant of the reaction at 27 °C. The result,  $K = 3.1 \times 10^7$ , tells us that the equilibrium lies far to the right, favoring replacement of H<sub>2</sub>O by NH<sub>3</sub>. For this equilibrium, therefore, the enthalpy change,  $\Delta H^\circ = -46 \text{ kJ}$ , is large enough and negative enough to overcome the entropy change,  $\Delta S^\circ = -8.4 \text{ J/K}$ .

Now let's use a single bidentate ethylenediamine (en) ligand in our substitution reaction:

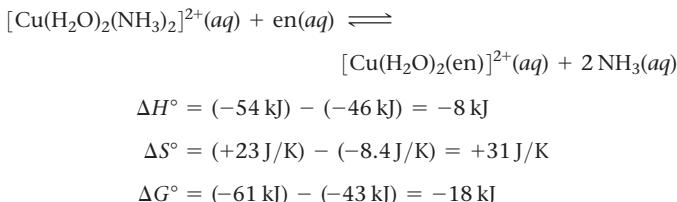


The en ligand binds slightly more strongly to the Cu<sup>2+</sup> ion than two NH<sub>3</sub> ligands, so the enthalpy change here (-54 kJ) is slightly more negative than for [Cu(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (-46 kJ). There is a big differ-

ence in the entropy change, however:  $\Delta S^\circ$  is -8.4 J/K for the NH<sub>3</sub> reaction but +23 J/K for the en reaction. We can explain the positive  $\Delta S^\circ$  value using concepts discussed in Section 19.3. Because a single en ligand occupies two coordination sites, two molecules of H<sub>2</sub>O are released when one en ligand bonds. Thus, there are three product molecules in the reaction but only two reactant molecules. The greater number of product molecules leads to the positive entropy change for the equilibrium.

The slightly more negative value of  $\Delta H^\circ$  for the en reaction (-54 kJ versus -46 kJ) coupled with the positive entropy change leads to a much more negative value of  $\Delta G^\circ$  (-61 kJ for en, -43 kJ for NH<sub>3</sub>) and thus a larger equilibrium constant:  $K = 4.2 \times 10^{10}$ .

We can combine our two equations using Hess's law to calculate the enthalpy, entropy, and free-energy changes that occur for en to replace ammonia as ligands on Cu(II):

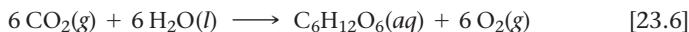


Notice that at 27 °C, the entropic contribution ( $-T\Delta S^\circ$ ) to the free-energy change,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  (Equation 19.12), is negative and greater in magnitude than the enthalpic contribution ( $\Delta H^\circ$ ). The equilibrium constant for the NH<sub>3</sub>-en reaction,  $1.4 \times 10^3$ , shows that the replacement of NH<sub>3</sub> by en is thermodynamically favorable.

The chelate effect is important in biochemistry and molecular biology. The additional thermodynamic stabilization provided by entropy effects helps stabilize biological metal-chelate complexes, such as porphyrins, and can allow changes in the oxidation state of the metal ion while retaining the structural integrity of the complex.

**Related Exercises: 23.3, 23.104**

The **chlorophylls**, which are porphyrins that contain Mg(II) (Figure 23.13), are the key components in the conversion of solar energy into forms that can be used by living organisms. This process, called **photosynthesis**, occurs in the leaves of green plants:

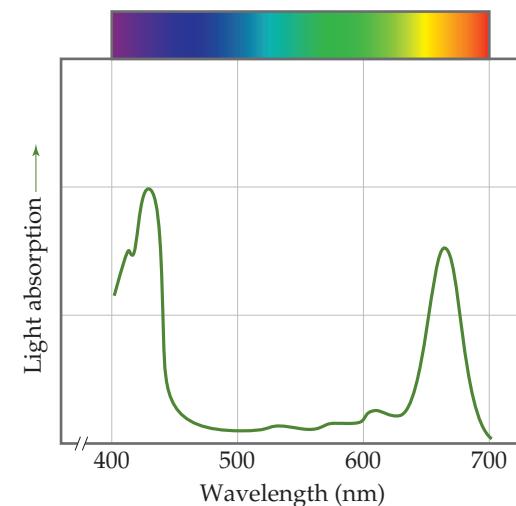


The formation of 1 mol of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , requires the absorption of 48 mol of photons from sunlight or other sources of light. Chlorophyll-containing pigments in the leaves of plants absorb the photons. Figure 23.13 shows that the chlorophyll molecule has a series of alternating, or *conjugated*, double bonds in the ring surrounding the metal ion. This system of conjugated double bonds makes it possible for chlorophyll to absorb light strongly in the visible region of the spectrum. As Figure 23.16 shows, chlorophyll is green because it absorbs red light (maximum absorption at 655 nm) and blue light (maximum absorption at 430 nm) and transmits green light.

Photosynthesis is nature's solar energy-conversion machine, and thus all living systems on Earth depend on photosynthesis for continued existence.

### Go Figure

Which peak in this curve corresponds to the lowest-energy transition by an electron in a chlorophyll molecule?

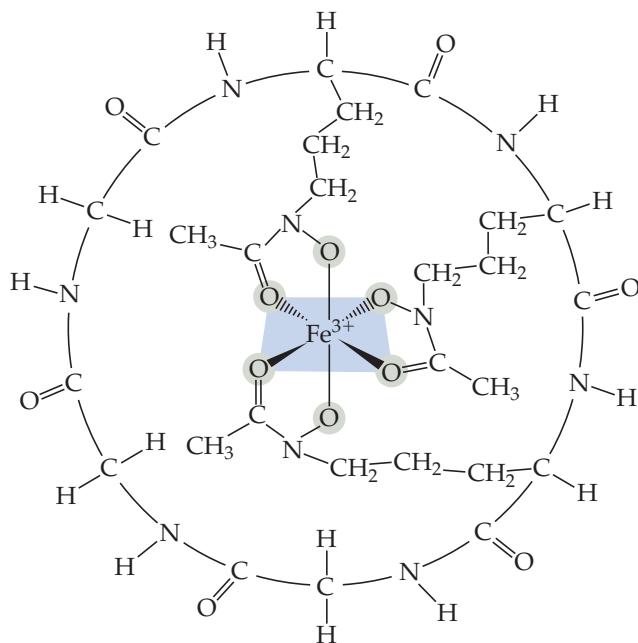


▲ Figure 23.16 The absorption of sunlight by chlorophyll.

## CHEMISTRY AND LIFE The Battle for Iron in Living Systems

Because living systems have difficulty assimilating enough iron to satisfy their nutritional needs, iron-deficiency anemia is a common problem in humans. Chlorosis, an iron deficiency in plants that makes leaves turn yellow, is also commonplace.

Living systems have difficulty assimilating iron because most iron compounds found in nature are not very soluble in water. Microorganisms have adapted to this problem by secreting an iron-binding compound, called a *siderophore*, that forms an extremely stable water-soluble complex with iron(III). One such complex is *ferrichrome* (Figure 23.17). The iron-binding strength of a siderophore is so great that it can extract iron from iron oxides.

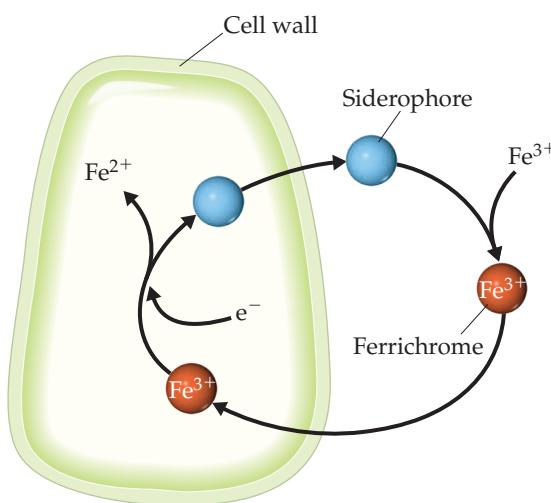


▲ Figure 23.17 Ferrichrome.

When ferrichrome enters a living cell, the iron it carries is removed through an enzyme-catalyzed reaction that reduces the strongly bonding iron(III) to iron(II), which is only weakly complexed by the siderophore (Figure 23.18). Microorganisms thus acquire iron by excreting a siderophore into their immediate environment and then taking the resulting iron complex into the cell.

In humans, iron is assimilated from food in the intestine. A protein called *transferrin* binds iron and transports it across the intestinal wall to distribute it to other tissues in the body. The normal adult body contains about 4 g of iron. At any one time, about 3 g of this iron is in the blood, mostly in the form of hemoglobin. Most of the remainder is carried by transferrin.

A bacterium that infects the blood requires a source of iron if it is to grow and reproduce. The bacterium excretes a siderophore into the blood to compete with transferrin for iron. The equilibrium constants



▲ Figure 23.18 The iron-transport system of a bacterial cell.

*Continued*

for forming the iron complex are about the same for transferrin and siderophores. The more iron available to the bacterium, the more rapidly it can reproduce and thus the more harm it can do.

Several years ago, New Zealand clinics regularly gave iron supplements to infants soon after birth. However, the incidence of certain bacterial infections was eight times higher in treated than in untreated infants. Presumably, the presence of more iron in the blood than absolutely necessary makes it easier for bacteria to obtain the iron needed for growth and reproduction.

In the United States, it is common medical practice to supplement infant formula with iron sometime during the first year of life. However, iron supplements are not necessary for infants who breast-

feed because breast milk contains two specialized proteins, lactoferrin and transferrin, which provide sufficient iron while denying its availability to bacteria. Even for infants fed with infant formulas, supplementing with iron during the first several months of life may be ill-advised.

For bacteria to continue to multiply in the blood, they must synthesize new supplies of siderophores. Synthesis of siderophores in bacteria slows, however, as the temperature is increased above the normal body temperature of 37 °C and stops completely at 40 °C. This suggests that fever in the presence of an invading microbe is a mechanism used by the body to deprive bacteria of iron.

**Related Exercise: 23.88**

## Self-Assessment Exercise

- 23.10** Cobalt(III) has a coordination number of 6 in all its complexes. Is the carbonate ion a monodentate or bidentate ligand in the  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]^+$  ion?

(a) Monodentate

(b) Bidentate

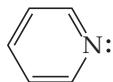
## Exercises

- 23.11** For each of the following polydentate ligands, determine (i) the maximum number of coordination sites that the ligand can occupy on a single metal ion and (ii) the number and type of donor atoms in the ligand: (a) acetylacetone ion (acac), (b) phenanthroline (phen), (c) diethylenetriamine, (d) carbonate ion, (e) triphosphate ion.

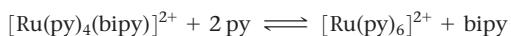
- 23.12** Indicate the likely coordination number of the metal in each of the following complexes:

- (a)  $[\text{Ru}(\text{bipy})_3](\text{NO}_3)_2$
- (b)  $\text{Re}(\text{o-phen})_2(\text{C}_2\text{O}_4)_2$
- (c)  $\text{Pd}(\text{PPh}_3)_3\text{Cl}$
- (d)  $(\text{NH}_4)_2\text{Mn}(\text{EDTA})$

- 23.13** Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ), abbreviated py, is the molecule

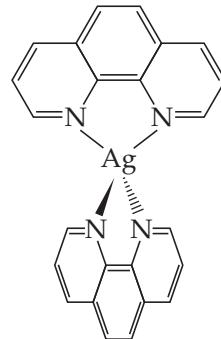


- (a) Would you expect pyridine to act as a monodentate or bidentate ligand? (b) For the equilibrium reaction



would you predict the equilibrium constant to be larger or smaller than one?

- 23.14** When silver nitrate is reacted with the molecular base *ortho*-phenanthroline, colorless crystals form that contain the transition-metal complex shown here. (a) What is the coordination geometry of silver in this complex? (b) Assuming no oxidation or reduction occurs during the reaction, what is charge of the complex shown here? (c) Do you expect any nitrate ions will be present in the crystal? (d) Write a formula for the compound that forms in this reaction.



23.10 (b)

Answers to Self-Assessment Exercise



## 23.4 | Nomenclature and Isomerism in Coordination Chemistry

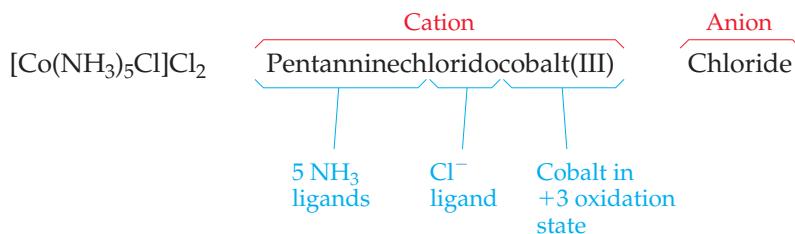


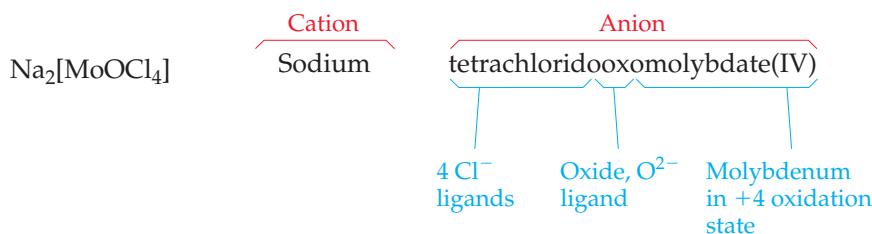
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is a simple looking coordination compound but it has a far reaching influence. It was the first of a series of platinum complexes that have been successful in the treatment of a wide range of cancers. Perhaps not surprisingly, it is on the World Health Organization's list of essential medicines. The therapeutic compound is introduced intravenously (using a medical set up similar to the one shown here) where the complex migrates to the inside of the tumour cell. Here the chloride concentration is low and one of the chloride ligands dissociates from the complex and is replaced by a water molecule. In turn, the water ligand is displaced and a nitrogen that is part of the DNA base guanine coordinates to the metal. The process is repeated with the remaining chloride ligand and the DNA-bound complex disrupts the replication of the DNA and the cell dies. There are two isomers of this complex only one of which, cisplatin, has therapeutic value. We touch on the reason for this in this shortly.

By the end of this section, you should be able to

- Systematically name simple coordination compounds and write a formula of a complex ion from its name.

When complexes were first discovered, they were named after the chemist who originally prepared them. A few of these names persist, as, for example, with the dark red substance  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ , which is still known as Reinecke's salt. Once the structures of complexes were more fully understood, it became possible to name them in a more systematic manner. Let's use two substances to illustrate how coordination compounds are named:

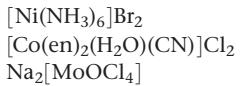




### How to Name Coordination Compounds

- In naming complexes that are salts, the name of the cation is given before the name of the anion.** Thus, in  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  we name the  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  cation and then the  $\text{Cl}^-$ .
- In naming complex ions or molecules, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of their charges. Prefixes that give the number of ligands are not considered part of the ligand name in determining alphabetical order.** Thus, the  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  ion is pentaamminechloridocobalt(III). (Be careful to note, however, that the metal is written first in the chemical formula.)
- The names of anionic ligands end in the letter *ido*, but electrically neutral ligands ordinarily bear the name of the molecules (Table 23.5).** Special names are used for  $\text{H}_2\text{O}$  (aqua),  $\text{NH}_3$  (ammine), and  $\text{CO}$  (carbonyl). For example,  $[\text{Fe}(\text{CN})_2(\text{NH}_3)_2(\text{H}_2\text{O})_2]^+$  is the diamminediaquadicyanidoiron(III) ion.
- Greek prefixes (*di-*, *tri-*, *tetra-*, *penta-*, *hexa-*) are used to indicate the number of each kind of monodentate ligand when more than one is present. If the ligand or is polydentate, the alternate prefixes *bis-*, *tris-*, *tetrakis-*, are used and the ligand name is placed in parentheses.** For example, the name for  $[\text{Co}(\text{en})_3]\text{Br}_3$  is tris(ethylenediamine)cobalt(III) bromide.
- If the complex is an anion, its name ends in *-ate*.** The compound  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is potassium hexacyanidoferate(II), for example, and the ion  $[\text{CoCl}_4]^{2-}$  is tetrachloridocobaltate(II) ion.
- The oxidation number of the metal is given in parentheses in Roman numerals following the name of the metal.**

Three examples for applying these rules are



Hexaamminenickel(II) bromide  
 Aquacyanidobis(ethylenediamine)cobalt(III) chloride  
 Sodium tetrachloridooxomolybdate(IV)

**TABLE 23.5 Some Common Ligands and Their Names**

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, $\text{N}_3^-$	Azido	Oxalate, $\text{C}_2\text{O}_4^{2-}$	Oxalato
Bromide, $\text{Br}^-$	Bromo	Oxide, $\text{O}^{2-}$	Oxo
Chloride, $\text{Cl}^-$	Chloro	Ammonia, $\text{NH}_3$	Ammine
Cyanide, $\text{CN}^-$	Cyano	Carbon monoxide, $\text{CO}$	Carbonyl
Fluoride, $\text{F}^-$	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, $\text{OH}^-$	Hydroxido	Pyridine, $\text{C}_5\text{H}_5\text{N}$	Pyridine
Carbonate, $\text{CO}_3^{2-}$	Carbonato	Water, $\text{H}_2\text{O}$	Aqua

When writing the formula of complexes, it is preferable to write the donor atom of the ligand closest to the metal. So  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  is preferred to  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .

## Sample Exercise 23.3

### Naming Coordination Compounds

Name the compounds (a)  $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}$ , (b)  $\text{K}_4[\text{Ni}(\text{CN})_4]$ .

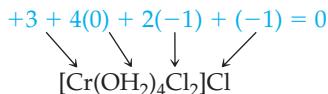
#### SOLUTION

**Analyze** We are given the chemical formulas for two coordination compounds and assigned the task of naming them.

**Plan** To name the complexes, we need to determine the ligands in the complexes, the names of the ligands, and the oxidation state of the metal ion. We then put the information together following the rules listed in the text.

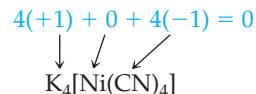
#### Solve

(a) The ligands are four water molecules—tetraqua—and two chloride ions—dichlorido. By assigning all the oxidation numbers we know for this molecule, we see that the oxidation number of Cr is +3:



Thus, we have chromium(III). Finally, the anion is chloride. The name of the compound is tetraaquadichloridochromium(III) chloride.

(b) The complex has four cyanide ion ligands,  $\text{CN}^-$ , which means tetracyanido, and the oxidation state of the nickel is zero:



Because the complex is an anion, the metal is indicated as nickelate(0). Putting these parts together and naming the cation first, we have potassium tetracyanidonickelate(0).

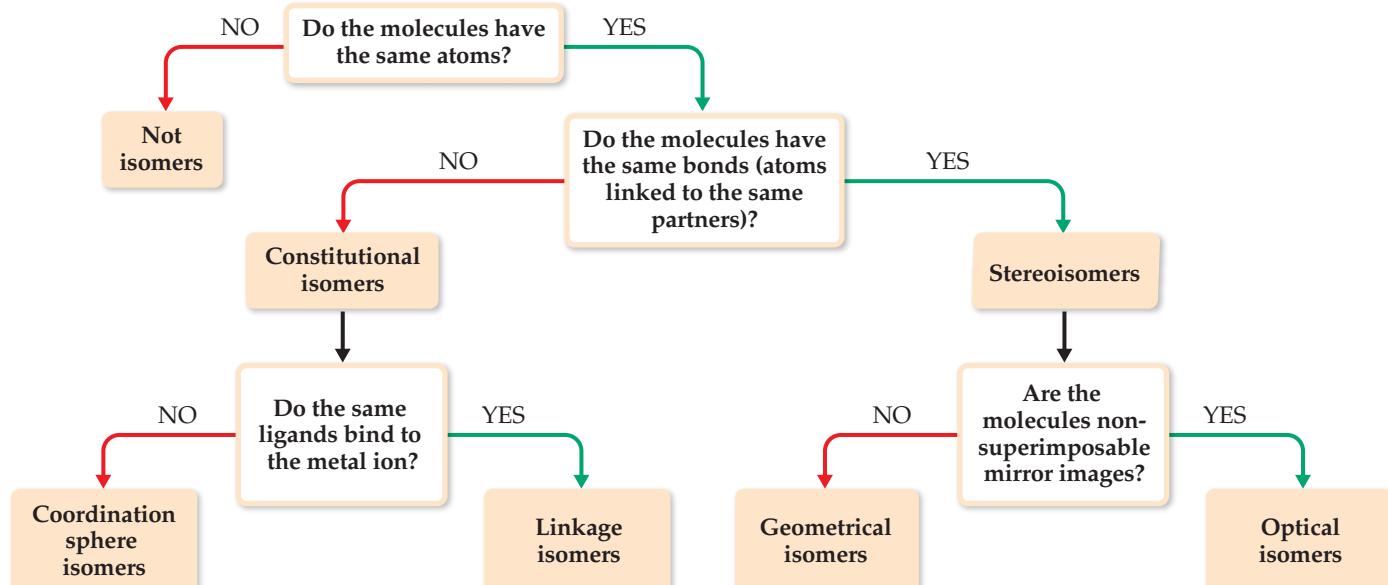
#### ► Practice Exercise

What is the name of the compound  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ?

- (a) Rhodium(III) tetraamminedichlorido chloride
- (b) Tetraammoniadichloridorhodium(III) chloride
- (c) Tetraamminedichloridorhodium(III) chloride
- (d) Tetraamminetrichlorido-rhodium(III)
- (e) Tetraamminedichloridorhodium(II) chloride

## Isomerism

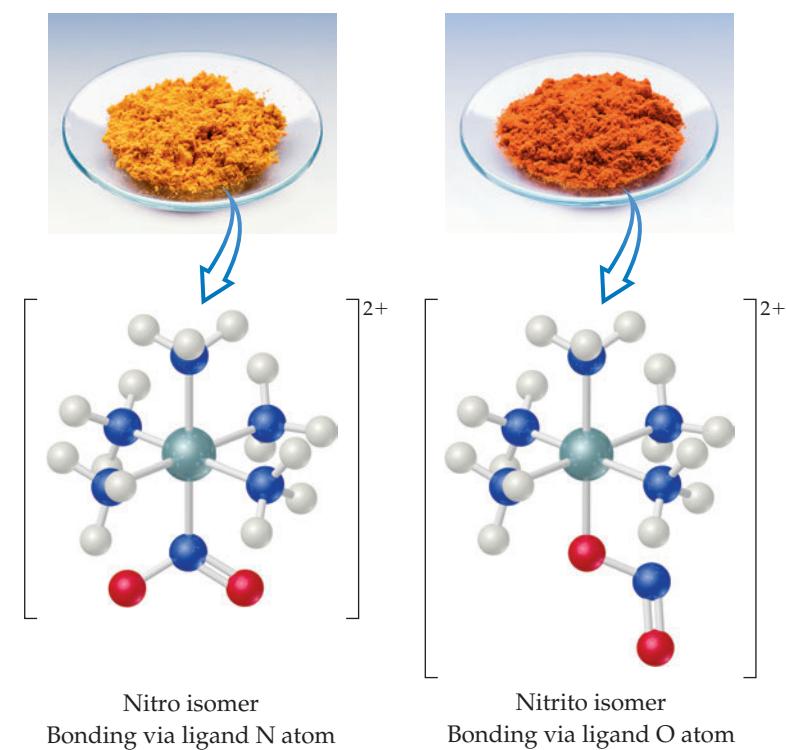
When two or more compounds have the same composition but a different arrangement of atoms, we call them **isomers**. Here we consider two main kinds of isomers in coordination compounds: **constitutional isomers** (which have different bonds) and **stereoisomers** (which have the same bonds but different ways in which the ligands occupy the space around the metal center). Each of these classes also has subclasses, as shown in **Figure 23.19**.



▲ Figure 23.19 Forms of isomerism in coordination compounds.


**Go Figure**

What are the chemical formula and name for each of the complex ions in this figure?



▲ Figure 23.20 Linkage isomerism.

## Constitutional Isomerism

Many types of constitutional isomerism are known in coordination chemistry, including the two named in Figure 23.19: linkage isomerism and coordination-sphere isomerism. **Linkage isomerism** is a relatively rare but interesting type that arises when a particular ligand is capable of coordinating to a metal in two ways. The nitrite ion,  $\text{NO}_2^-$ , for example, can coordinate to a metal ion through either its nitrogen or one of its oxygens (Figure 23.20). When it coordinates through the nitrogen atom, the  $\text{NO}_2^-$  ligand is called *nitro*; when it coordinates through the oxygen atom, it is called *nitrito* and is generally written  $\text{ONO}^-$ . The isomers shown in Figure 23.20 have different properties. The nitro isomer is yellow, for example, whereas the nitrito isomer is red.

Another ligand capable of coordinating through either of two donor atoms is thiocyanate,  $\text{SCN}^-$ , whose potential donor atoms are N and S.

**Coordination-sphere isomers** are isomers that differ in which species in the complex act as ligands, and which are outside the coordination sphere. For example, three isomers have the formula  $\text{CrCl}_3(\text{OH}_2)_6$ . When the ligands are six  $\text{H}_2\text{O}$  and the chloride ions are in the crystal lattice (as counterions), we have the violet compound  $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$ . When the ligands are five  $\text{H}_2\text{O}$  and one  $\text{Cl}^-$ , with the sixth  $\text{H}_2\text{O}$  and the two  $\text{Cl}^-$  out in the lattice, we have the green compound  $[\text{Cr}(\text{OH}_2)_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ . The third isomer,  $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ , is also a green

compound. In the two green compounds, either one or two water molecules have been displaced from the coordination sphere by chloride ions. The displaced  $\text{H}_2\text{O}$  molecules occupy a site in the crystal lattice.

## Stereoisomerism

Stereoisomers have the same chemical bonds but different spatial arrangements. In the square-planar complex  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , for example, the chlorido ligands can be either adjacent to or opposite each other (Figure 23.21). (We saw an earlier example of this type of isomerism in the cobalt complex of Figure 23.8, and we will return to that complex in a moment.) This form of stereoisomerism, in which the arrangement of the atoms is different but the same bonds are present, is called **geometric isomerism**. The isomer with like ligands in adjacent positions is the *cis* isomer, and the isomer with like ligands across from one another is the *trans* isomer.

Geometric isomers generally have different physical properties and may also have markedly different chemical reactivities. For example, *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , also called *cisplatin*, is effective in the treatment of testicular, ovarian, and certain other cancers, whereas the *trans* isomer is ineffective. This is because cisplatin forms a chelate with two nitrogens of DNA, displacing the chloride ligands. The chloride ligands of the *trans* isomer are too far apart to form the N-Pt-N chelate with the nitrogen donors in DNA.

Geometric isomerism is also possible in octahedral complexes when two or more different ligands are present, as in the *cis* and *trans* tetraamminedichloridocobalt(III) ion in Figure 23.8. Because all four corners of a tetrahedron are adjacent to one another, *cis-trans* isomerism is not observed in tetrahedral complexes.

The second type of stereoisomerism listed in Figure 23.19 is **optical isomerism**. Optical isomers, called **enantiomers**, are mirror images that cannot be superimposed on each other. They bear the same resemblance to each other that your left hand bears to

your right hand. If you look at your left hand in a mirror, the image is identical to your right hand (**Figure 23.22**). No matter how hard you try, however, you cannot superimpose your two hands on each other. An example of a complex that exhibits this type of isomerism is the  $[\text{Co}(\text{en})_3]^{3+}$  ion. Figure 23.22 shows the two enantiomers of this complex and their mirror-image relationship. Just as there is no way that we can twist or turn our right hand to make it look identical to our left, so also there is no way to rotate one of these enantiomers to make it identical to the other. Molecules or ions that are not superimposable on their mirror image are said to be **chiral** (pronounced KY-rul).

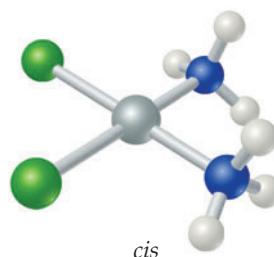
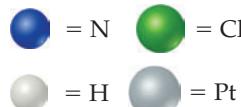
The properties of two optical isomers differ only if the isomers are in a chiral environment—that is, an environment in which there is a sense of right- and left-handedness. A chiral enzyme, for example, might catalyze the reaction of one optical isomer but not the other. Consequently, one optical isomer may produce a specific physiological effect in the body, with its mirror image producing either a different effect or none at all. Chiral reactions are also extremely important in the synthesis of pharmaceuticals and other industrially important chemicals.

Optical isomers are usually distinguished from each other by their interaction with plane-polarized light. If light is polarized—for example, by being passed through a sheet of polarizing film—the electric-field vector of the light is confined to a single plane (**Figure 23.23**). If the polarized light is then passed through a solution containing one optical isomer, the plane of polarization is rotated either to the right or to the left. The isomer that rotates the plane of polarization to the right is **dextrorotatory**; it is the dextro, or *d*, isomer (Latin *dexter*, “right”). Its mirror image rotates the plane of polarization to the left; it is **levorotatory** and is the levo, or *l*, isomer (Latin *laevus*, “left”). The  $[\text{Co}(\text{en})_3]^{3+}$  isomer on the right in Figure 23.22 is found experimentally to be the *l* isomer of this ion. Its mirror image is the *d* isomer. Because of their effect on plane-polarized light, chiral molecules are said to be **optically active**.

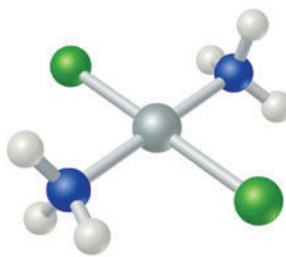
When a substance with optical isomers is prepared in the laboratory, the chemical environment during the synthesis is not usually chiral. Consequently, equal amounts of the two isomers are obtained, and the mixture is said to be **racemic**. A racemic mixture does not rotate polarized light because the rotatory effects of the two isomers cancel each other.

### Go Figure

Which of these isomers has a nonzero dipole moment?

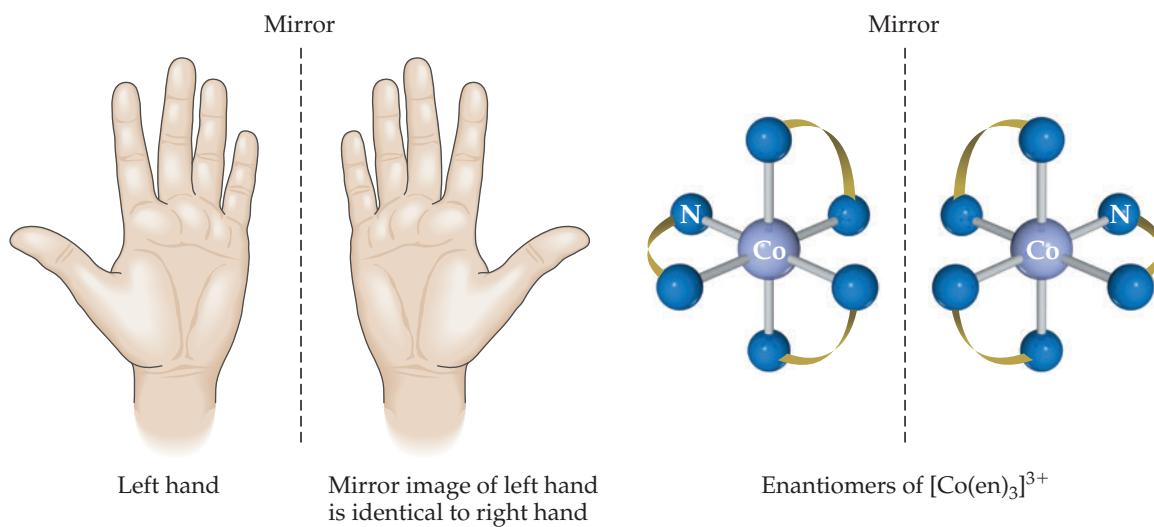


Cl ligands adjacent to each other  
NH<sub>3</sub> ligands adjacent to each other

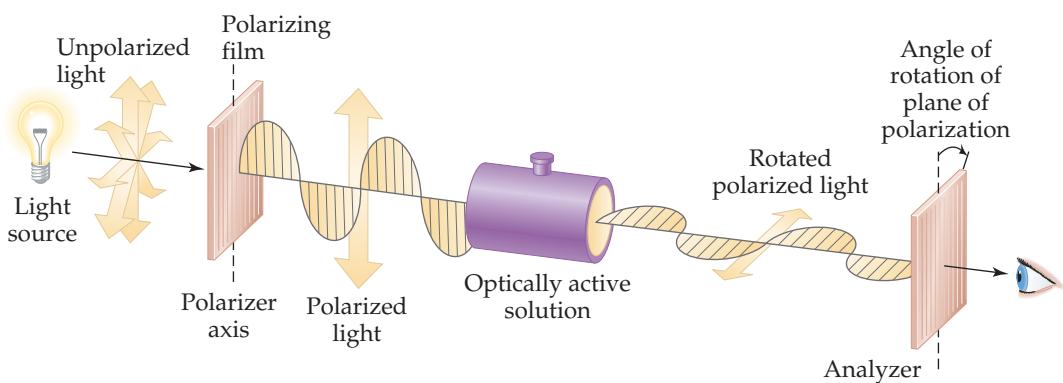


Cl ligands on opposite sides of central atom  
NH<sub>3</sub> ligands on opposite sides of central atom

▲ **Figure 23.21** Geometric isomerism.



▲ **Figure 23.22** Optical isomerism.



▲ Figure 23.23 Using polarized light to detect optical activity.

### Sample Exercise 23.4

#### Determining the Number of Geometric Isomers

The Lewis structure :C≡O: indicates that the CO molecule has two lone pairs of electrons. When CO binds to a transition-metal atom, it nearly always does so by using the C lone pair. How many geometric isomers are there for tetracarbonyldichloridoiron(II)?

#### SOLUTION

**Analyze** We are given the name of a complex containing only monodentate ligands, and we must determine the number of isomers the complex can form.

**Plan** We can count the number of ligands to determine the coordination number of the Fe and then use the coordination number to predict the geometry. We can then either make a series of drawings with ligands in different positions to determine the number of isomers or deduce the number of isomers by analogy to cases we have discussed.

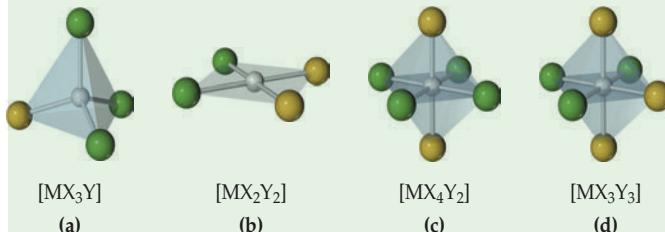
**Solve** The name indicates that the complex has four carbonyl (CO) ligands and two chloride ( $\text{Cl}^-$ ) ligands, so its formula is  $\text{Fe}(\text{CO})_4\text{Cl}_2$ . The complex therefore has a coordination number of 6, and we can assume an octahedral geometry. Like  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (Figure 23.8), it has four ligands of one type and two of another. Consequently, there are two isomers possible: one with the  $\text{Cl}^-$  ligands across the metal from each other, *trans*- $[\text{Fe}(\text{CO})_4\text{Cl}_2]$ , and one with the  $\text{Cl}^-$  ligands adjacent to each other, *cis*- $[\text{Fe}(\text{CO})_4\text{Cl}_2]$ .

**Comment** It is easy to overestimate the number of geometric isomers. Sometimes different orientations of a single isomer are

incorrectly thought to be different isomers. If two structures can be rotated so that they are equivalent, they are not isomers of each other. The problem of identifying isomers is compounded by the difficulty we often have in visualizing three-dimensional molecules from their two-dimensional representations. It is sometimes easier to determine the number of isomers if we use three-dimensional models.

#### ► Practice Exercise

Which of the following molecules does not have a geometric isomer?



### Sample Exercise 23.5

#### Predicting Whether a Complex Has Optical Isomers

Does either *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  or *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^-$  have optical isomers?

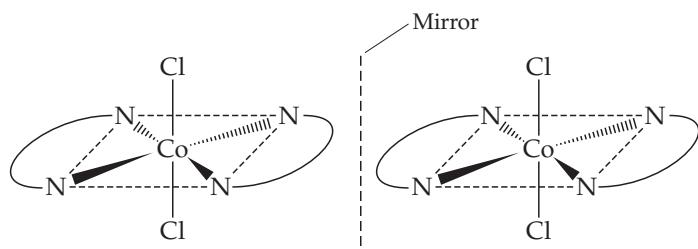
#### SOLUTION

**Analyze** We are given the chemical formula for two geometric isomers and asked to determine whether either one has optical isomers. Because en is a bidentate ligand, we know that both complexes are octahedral and both have coordination number 6.

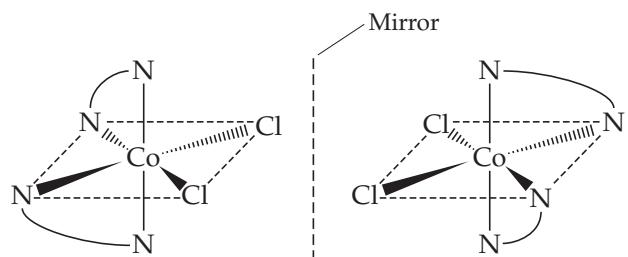
**Plan** We need to sketch the structures of the *cis* and *trans* isomers and their mirror images. We can draw the en ligand as two N atoms connected by an arc. If the mirror image cannot be superimposed on the original structure, the complex and its mirror image are optical isomers.

**Solve**

The *trans* isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  and its mirror image are shown here. Notice that the mirror image of the isomer is identical to the original. Consequently  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  does not exhibit optical isomerism.



The *cis* isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  and its mirror image are shown here. In this case the two cannot be superimposed on each other. Thus, the two *cis* structures are optical isomers (enantiomers). We say that  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is a chiral complex.

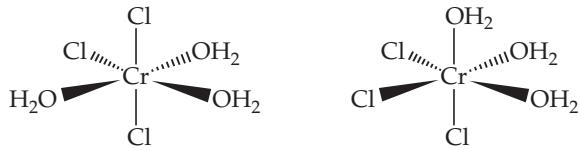
**► Practice Exercise**

Which of the following complexes has an optical isomer?

- (a) Tetrahedral  $[\text{CdBr}_2\text{Cl}_2]^{2-}$  (b) Octahedral  $[\text{CoCl}_4(\text{en})]^{2-}$  (c) Octahedral  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{2+}$  (d) Tetrahedral  $[\text{Co}(\text{NH}_3)\text{BrCl}]^{-}$

## Self-Assessment Exercise

- 23.15** How many isomers are possible for the complex:  $[\text{Cr}(\text{OH}_2)_3\text{Cl}_3]^+$ ?  
 (a) 1  
 (b) 2  
 (c) 3  
 (d) 4



## Exercises

- 23.16** Write the formula for each of the following compounds, being sure to use brackets to indicate the coordination sphere:  
 (a) hexaammineiron(II) nitrate  
 (b) tetraaquadibromidochromium(III) perchlorate  
 (c) ammonium hexachloridopalladate(IV)  
 (d) diammineoxolatonickel(II)  
 (e) Hexaamminemolybdenum(III) tetrachloridocuprate(II)
- 23.17** Write names for the following coordination compounds:  
 (a)  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$   
 (b)  $[\text{CoO}(\text{NH}_3)_5]\text{Br}$   
 (c)  $\text{Na}_2[\text{NiBr}_4]$   
 (d)  $[\text{Rh}(\text{OH}_2)_6][\text{Ag}(\text{CN})_2]_3$

- 23.18** Consider the following three complexes:  
 (Complex 1)  $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$   
 (Complex 2)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^{2+}$   
 (Complex 3)  $\text{CoClBr} \cdot 5\text{NH}_3$

Which of the three complexes can have (a) geometric isomers, (b) linkage isomers, (c) optical isomers, (d) coordination-sphere isomers?

- 23.19** Consider an octahedral complex,  $\text{MA}_2\text{B}_4$ . How many geometric isomers are expected for this compound? Will any of the isomers be optically active? If so, which ones?  
**23.20** Determine if each of the following complexes exhibits geometric isomerism. If geometric isomers exist, determine how many there are. (a)  $[\text{Rh}(\text{bipy})(o\text{-phen})_2]^{3+}$ , (b)  $[\text{Co}(\text{NH}_3)_3(\text{bipy})\text{Br}]^{2+}$ , (c) square-planar  $[\text{Pd}(\text{en})(\text{CN})_2]$ .  
**23.21** Determine if each of the following metal complexes is chiral and therefore has an optical isomer: (a) square planar  $[\text{Pd}(\text{en})(\text{CN})_2]$ , (b) octahedral  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$ , (c) octahedral  $cis-[\text{V}(\text{en})_2\text{ClBr}]$ .

23.15 (b)



## 23.5 | Color and Magnetism in Coordination Chemistry



Studies of the colors and magnetic properties of transition-metal complexes have played an important role in the development of modern models for metal-ligand bonding. We discussed the various types of magnetic behavior of the transition metals in Section 23.1, and we discussed the interaction of radiant energy with matter in Section 6.3. Let's briefly examine the significance of these two properties for transition-metal complexes before we develop a model for metal-ligand bonding.

By the end of this section, you should be able to

- Appreciate the relationship between absorbed light and perceived color.

### Color

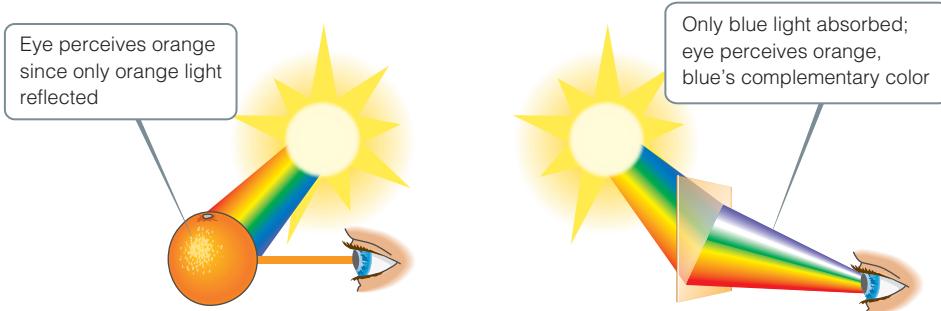
In Figure 23.4, we saw the diverse range of colors seen in salts of transition-metal ions and their aqueous solutions. In general, the color of a complex depends on the identity of the metal ion, on its oxidation state, and on the ligands bound to it. **Figure 23.24**, for

#### Go Figure

Is the equilibrium binding constant of ammonia for Cu(II) likely to be larger or smaller than that of water for Cu(II)?



▲ **Figure 23.24** The color of a coordination complex changes when the ligand changes.



**▲ Figure 23.25** Two ways of perceiving the color orange. An object appears orange either when it reflects orange light to the eye (left) or when it transmits to the eye all colors except blue, the complement of orange (middle). Complementary colors lie opposite to each other on an artist's color wheel (right).

instance, shows how the pale blue color characteristic of  $[\text{Cu}(\text{OH}_2)_4]^{2+}$  changes to deep blue-violet as  $\text{NH}_3$  ligands replace the  $\text{H}_2\text{O}$  ligands to form  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .

For a substance to have color we can see, it must absorb some portion of the spectrum of visible light. Absorption happens, however, only if the energy needed to move an electron in the substance from its ground state to an excited state corresponds to the energy of some portion of the visible spectrum. Thus, the particular energies of radiation a substance absorbs dictate the color we see for the substance.

When an object absorbs some portion of the visible spectrum, the color we perceive is the sum of the unabsorbed portions, which are either reflected or transmitted by the object and strike our eyes. (Opaque objects *reflect* light, and transparent ones *transmit* it.) If an object absorbs all wavelengths of visible light, none reaches our eyes and the object appears black. If it absorbs no visible light, it is white if opaque or colorless if transparent. If it absorbs all but orange light, the orange light is what reaches our eye and therefore is the color we see.

An interesting phenomenon of vision is that we also perceive an orange color when an object absorbs only the blue portion of the visible spectrum and all the other colors strike our eyes. This is because orange and blue are **complementary colors**, which means that the removal of blue from white light makes the light look orange (and the removal of orange makes the light look blue).

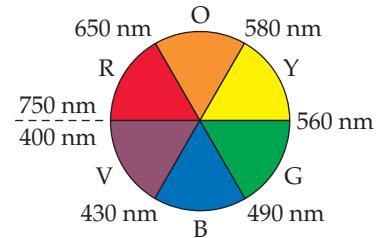
Complementary colors can be determined with an artist's color wheel, which shows complementary colors on opposite sides (**Figure 23.25**).

The amount of light absorbed by a sample as a function of wavelength is known as the sample's **absorption spectrum**. The visible absorption spectrum of a transparent sample can be determined using a spectrometer, as described in the "A Closer Look" box on page 667. The absorption spectrum of the ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is shown in **Figure 23.26**. The absorption maximum is at 500 nm, but the graph shows that much of the yellow, green, and blue light is absorbed. Because the sample absorbs all of these colors, what we see is the unabsorbed red and violet light, which we perceive as purple (the color purple is classified as a tertiary color located between red and violet on an artist's color wheel).

## Magnetism of Coordination Compounds

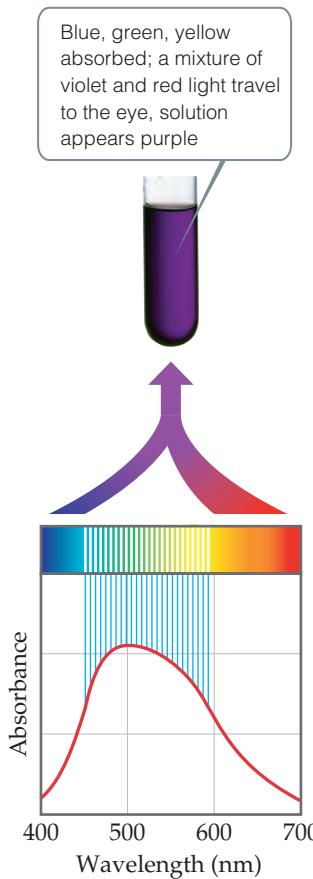
Many transition-metal complexes exhibit paramagnetism, as described in Sections 9.8 and 23.1. In such compounds, the metal ions possess some number of unpaired electrons. It is possible to experimentally determine the number of unpaired electrons per metal ion from the measured degree of paramagnetism, and experiments reveal some interesting comparisons.

Compounds of the complex ion  $[\text{Co}(\text{CN})_6]^{3-}$  have no unpaired electrons, for example, but compounds of the  $[\text{CoF}_6]^{3-}$  ion have four unpaired electrons per metal ion. Both complexes contain Co(III) with a  $3d^6$  electron configuration. Clearly, there is a major difference in the ways in which the electrons are arranged in these two cases. Any successful bonding theory must explain this difference, and we present such a theory in the next section.



### Go Figure

How would this absorbance spectrum change if you decreased the concentration of the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  in solution?



**▲ Figure 23.26** The color of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . A solution containing the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion appears purple because, as its visible absorption spectrum shows, the solution does not absorb light from the violet and red ends of the spectrum. That unabsorbed light is what reaches our eyes.



## Sample Exercise 23.6

### Relating Color Absorbed to Color Observed

The complex ion  $\text{trans}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  absorbs light primarily in the red region of the visible spectrum (the most intense absorption is at 680 nm). What is the color of the complex ion?

#### SOLUTION

**Analyze** We need to relate the color absorbed by a complex (red) to the color observed for the complex.

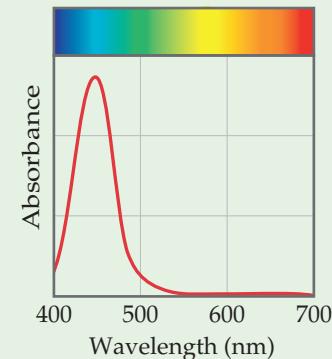
**Plan** For an object that absorbs only one color from the visible spectrum, the color we see is complementary to the color absorbed. We can use the color wheel of Figure 23.25 to determine the complementary color.

**Solve** From Figure 23.25, we see that green is complementary to red, so the complex appears green.

**Comment** As noted in Section 23.2, this green complex was one of those that helped Werner establish his theory of coordination (Table 23.3). The other geometric isomer of this complex,  $\text{cis}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , absorbs yellow light and therefore appears violet.

#### ► Practice Exercise

A solution containing a certain transition-metal complex ion has the absorption spectrum shown here.



What color would you expect a solution containing this ion to be? (a) violet (b) blue (c) green (d) orange (e) red

## Self-Assessment Exercise

**23.22** What is the electron configuration and number of unpaired electrons in a Co atom and  $\text{Co}^{3+}$  ion?

- (a) Co: [Ar]  $4s^2 3d^7$ ; 3 unpaired electrons.  $\text{Co}^{3+}$ : [Ar]  $3d^6$ ; 0 unpaired electrons.
- (b) Co: [Ar]  $4s^2 3d^7$ ; 3 unpaired electrons.  $\text{Co}^{3+}$ : [Ar]  $3d^6$ ; 4 unpaired electrons.

(c) Co: [Ar]  $4s^2 4d^7$ ; 3 unpaired electrons.  $\text{Co}^{3+}$ : [Ar]  $4d^6$ ; 4 unpaired electrons.

(d) Co: [Ar]  $4s^2 3d^7$ ; 3 unpaired electrons.  $\text{Co}^{3+}$ : [Ar]  $4s^2 3d^4$ ; 4 unpaired electrons.

## Exercises

**23.23** (a) A complex absorbs photons with an energy of  $4.51 \times 10^{-19}\text{ J}$ . What is the wavelength of these photons? (b) If this is the only place in the visible spectrum where the complex absorbs light, what color would you expect the complex to be?

**23.24** Identify each of the following coordination complexes as either diamagnetic or paramagnetic:

- (a)  $[\text{ZnBr}_4]^{2-}$
- (b)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
- (c)  $\text{OsO}_4$
- (d)  $[\text{PtCl}_4]^{2-}$

23.22 (b)

Answers to Self-Assessment Exercise



## 23.6 | Crystal-Field Theory



Ruby and emerald are allochromatic minerals. This means that their color arises from a trace impurity rather than from the bulk of the material. In these two cases it is the substitution of  $\sim 1\%$  of the  $\text{Al}^{3+}$  in the crystal lattice by  $\text{Cr}^{3+}$  that gives the red color of a ruby and the green of an emerald. Why such different colors if they both arise from the same transition metal ion? The answer lies, in part, with the nature of the crystal lattice around the chromium ion. Ruby is composed of  $\text{Al}_2\text{O}_3$ , which is colorless when pure. The lattice is compact and the distance between O and a  $\text{Cr}^{3+}$  ion is relatively short, resulting in a strong interaction and absorption of green light (giving the red appearance). In emerald, which is composed of  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , the lattice is expanded and there is a longer O— $\text{Cr}^{3+}$  distance. This means less interaction with the  $\text{Cr}^{3+}$  ion and lower-energy red light is absorbed giving a green appearance to the mineral.

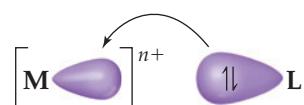
In this section, we discuss a model that explains the wide variety of colors observed in transition metal compounds. By the end of this section, you should be able to

- Predict the number of unpaired electrons in a transition metal complex.
- Use the spectrochemical series to qualitatively predict the crystal-field splitting in a complex.

Scientists have long recognized that many of the magnetic properties and colors of transition-metal complexes are related to the presence of  $d$  electrons in the metal cation. In this section, we consider a model for bonding in transition-metal complexes, **crystal-field theory**, that accounts for many of the observed properties of these substances.\* Because many predictions of crystal-field theory are qualitatively the same as those obtained with more advanced molecular-orbital theories, crystal-field theory is an excellent place to start in considering the electronic structure of coordination compounds.

The attraction of a ligand to a metal ion is essentially a Lewis acid–base interaction in which the base—that is, the ligand—donates a pair of electrons to an empty orbital on the metal ion (Figure 23.27). Much of the attractive interaction between the metal ion and the ligands is due, however, to the electrostatic forces between the positive charge on the metal ion and negative charges on the ligands. An ionic ligand, such as  $\text{Cl}^-$  or  $\text{SCN}^-$ , experiences the usual cation–anion attraction. When the ligand is a neutral molecule, as in the case of  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the negative ends of these polar molecules, which contain an unshared electron pair, are directed toward the metal ion. In this case, the attractive interaction is of

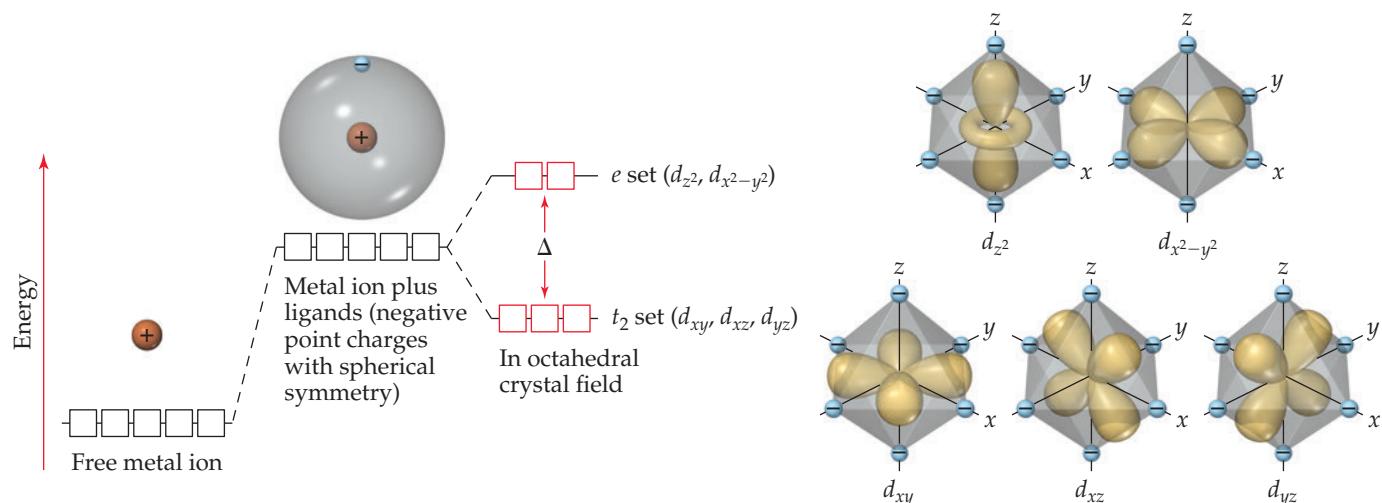
\*The name *crystal-field* arose because the theory was first developed to explain the properties of solid crystalline materials. The theory applies equally well to complexes in solution, however.



**▲ Figure 23.27** Metal–ligand bond formation. The ligand acts as a Lewis base by donating its nonbonding electron pair to an empty orbital on the metal ion. The bond that results is strongly polar with some covalent character.

**Go Figure**

Which *d* orbitals have lobes that point directly toward the ligands in an octahedral crystal-field?



▲ **Figure 23.28** Energies of *d* orbitals in a free metal ion, a spherically symmetric crystal-field, and an octahedral crystal-field.

the ion-dipole type. In either case, the ligands are attracted strongly toward the metal ion. Because of the metal-ligand electrostatic attraction, the energy of the complex is lower than the combined energy of the separated metal ion and ligands.

Although the metal ion is attracted to the ligand electrons, the metal ion's *d* electrons are repulsed by the ligands. Let's examine this effect more closely, specifically the case in which the ligands form an octahedral array around a metal ion that has coordination number 6.

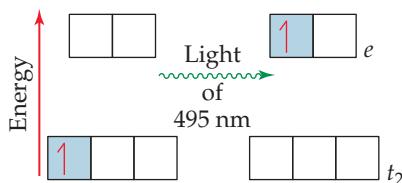
In crystal-field theory, we consider the ligands to be negative points of charge that repel the negatively charged electrons in the *d* orbitals of the metal ion. The energy diagram in Figure 23.28 shows how these ligand point charges affect the energies of the *d* orbitals. First, we imagine the complex as having all the ligand point charges uniformly distributed on the surface of a sphere centered on the metal ion. The *average* energy of the metal ion's *d* orbitals is raised by the presence of this uniformly charged sphere. Hence, the energies of all five *d* orbitals are raised by the same amount.

This energy picture is only a first approximation, however, because the ligands are not distributed uniformly on a spherical surface and, therefore, do not approach the metal ion equally from every direction. Instead, we envision the six ligands approaching along *x*-, *y*-, and *z*-axes, as shown on the right in Figure 23.28. This arrangement of ligands is called an *octahedral crystal-field*. Because the metal ion's *d* orbitals have different orientations and shapes, they do not all experience the same repulsion from the ligands and, therefore, do not all have the same energy under the influence of the octahedral crystal-field. To see why, we must consider the shapes of the *d* orbitals and how their lobes are oriented relative to the ligands.

Figure 23.28 shows that the lobes of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are directed *along* the *x*-, *y*-, and *z*-axes and so point directly toward the ligand point charges. The lobes of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, however, are directed *between* the axes and so do not point directly toward the charges. The result of this difference in orientation— $d_{x^2-y^2}$  and  $d_{z^2}$  lobes point directly toward the ligand charges;  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  lobes do not—is that an electron residing in either the  $d_{x^2-y^2}$  or  $d_{z^2}$  orbitals feels more repulsion from the negatively charged ligands. Hence the energy of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals is higher than the energy of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals. This difference in energy is represented by the red boxes in the energy diagram of Figure 23.28.


**Go Figure**

How would you calculate the energy gap between the  $t_2$  and  $e$  orbitals from this diagram?



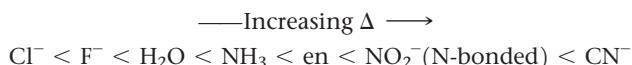
◀ **Figure 23.29** The  $d$ - $d$  transition in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is produced by the absorption of 495-nm light.

The three lower-energy  $d$  orbitals are called the  $t_2$  set of orbitals, and the two higher-energy ones are called the  $e$  set.\* The energy gap  $\Delta$  between the two sets is called the *crystal-field splitting energy*.

It might seem like the energy of the  $d_{x^2-y^2}$  orbital should be different from that of the  $d_{z^2}$  orbital because the  $d_{x^2-y^2}$  has four lobes pointing at ligands and the  $d_{z^2}$  has only two lobes pointing at ligands. However, the  $d_{z^2}$  orbital does have electron density in the  $xy$  plane, represented by the ring encircling the point where the two lobes meet. More advanced calculations show that two orbitals do indeed have the same energy in the presence of the octahedral crystal-field.

Crystal-field theory helps us account for the colors observed in transition-metal complexes. The energy gap  $\Delta$  between the  $e$  and  $t_2$  sets of  $d$  orbitals is of the same order of magnitude as the energy of a photon of visible light. It is therefore possible for a transition-metal complex to absorb visible light that excites an electron from a lower-energy ( $t_2$ )  $d$  orbital into a higher-energy ( $e$ )  $d$  orbital. In  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ , for example, the Ti(III) ion has an  $[\text{Ar}]3d^1$  electron configuration. (Recall from Section 7.4 that when determining the electron configurations of transition-metal ions, we remove the s electrons first.) Ti(III) is thus called a  $d^1$  ion. In the ground state of  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ , the single  $3d$  electron resides in an orbital in the  $t_2$  set (Figure 23.29). Absorption of 495 nm light excites this electron up to an orbital in the  $e$  set, generating the absorption spectrum shown in Figure 23.26. Because this transition involves exciting an electron from one set of  $d$  orbitals to the other, we call it a  **$d$ - $d$  transition**. As noted earlier, the absorption of visible radiation that produces this  $d$ - $d$  transition causes the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion to appear purple.

The magnitude of the crystal-field splitting energy and, consequently, the color of a complex depend on both the metal and the ligands. For example, we saw in Figure 23.4 that the color of  $[\text{M}(\text{OH}_2)_6]^{2+}$  complexes changes from reddish-pink when the metal ion is  $\text{Co}^{2+}$ , to green for  $\text{Ni}^{2+}$ , to pale blue for  $\text{Cu}^{2+}$ . If we change the ligands in the  $[\text{Ni}(\text{OH}_2)_6]^{2+}$  ion, the color also changes.  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  has a blue-violet color, while  $[\text{Ni}(\text{en})_3]^{2+}$  is purple (Figure 23.30). In a ranking called the **spectrochemical series**, ligands are arranged in order of their abilities to increase the crystal-field splitting energy, as in this abbreviated list:



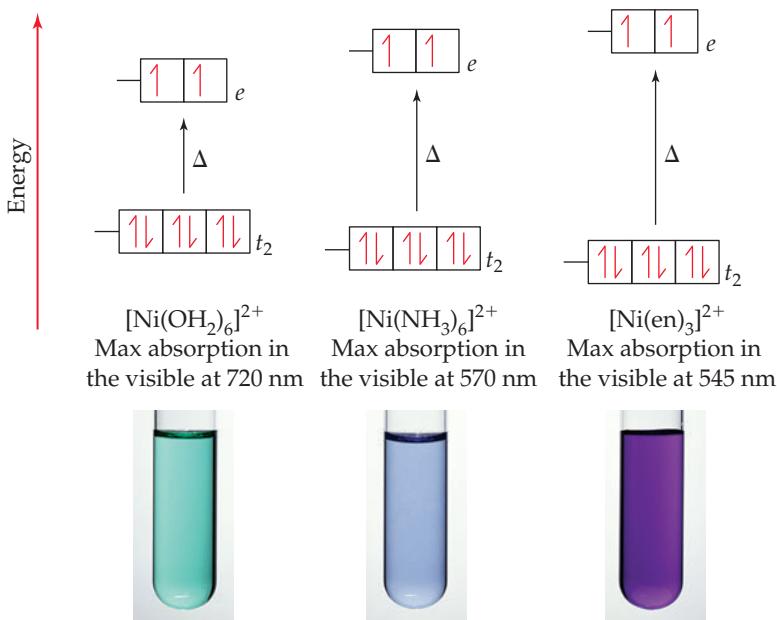
The magnitude of  $\Delta$  increases by roughly a factor of 2 from the far left to the far right of the spectrochemical series. Ligands at the low- $\Delta$  end of the spectrochemical series are termed *weak-field ligands*; those at the high- $\Delta$  end are termed *strong-field ligands*.

Let's take a closer look at the colors and crystal-field splitting as we vary the ligands for the series of  $\text{Ni}^{2+}$  complexes discussed earlier. Because the Ni atom has an  $[\text{Ar}]3d^84s^2$  electron configuration,  $\text{Ni}^{2+}$  has the configuration  $[\text{Ar}]3d^8$  and therefore is a  $d^8$  ion. The  $t_2$  set of orbitals holds six electrons, two in each orbital, while the last two electrons go into the  $e$  set of orbitals. Consistent with Hund's rule, each  $e$  orbital holds one electron and both electrons have the same spin.

\*The labels  $t_2$  for the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals and  $e$  for the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals come from the application of a branch of mathematics called *group theory* to crystal-field theory. Group theory can be used to analyze the effects of symmetry on molecular properties.

 Go Figure

If you were to use a ligand L that was a stronger field ligand than ethylenediamine, what color would you expect the  $[\text{NiL}_6]^{2+}$  complex ion to have?



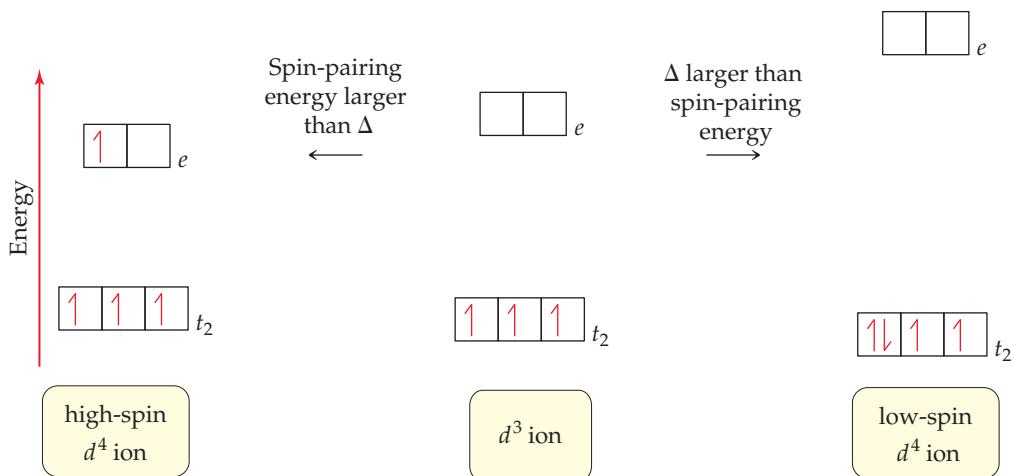
▲ **Figure 23.30** Effect of ligand on crystal-field splitting. The greater the crystal-field strength of the ligand, the greater the energy gap  $\Delta$  it causes between the  $t_2$  and  $e$  sets of the metal ion's orbitals. This shifts the wavelength of the absorption maximum to shorter values.

As the ligand changes from  $\text{H}_2\text{O}$  to  $\text{NH}_3$  to ethylenediamine, the spectrochemical series tells us that the crystal-field,  $\Delta$ , exerted by the six ligands should increase. When there is more than one electron in the  $d$  orbitals, interactions between the electrons make the absorption spectra more complicated than the spectrum shown for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  in Figure 23.26, which complicates the task of relating changes in  $\Delta$  with color. With  $d^8$  ions like  $\text{Ni}^{2+}$  three peaks are observed in the absorption spectra. Fortunately, for  $\text{Ni}^{2+}$  complexes we can simplify the analysis because only one of these three peaks falls in the visible region of the spectrum.\* Because the energy separation  $\Delta$  is increasing, the wavelength of the absorption peak should shift to a shorter wavelength. In the case of  $[\text{Ni}(\text{OH}_2)_6]^{2+}$  the absorption peak in the visible part of the spectrum reaches a maximum near 720 nm, in the red region of the spectrum. So the complex ion takes the complementary color—green. For  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  the absorption peak reaches its maximum at 570 nm near the boundary between orange and yellow. The resulting color of the complex ion is a mixture of the complementary colors—blue and violet. Finally, for  $[\text{Ni}(\text{en})_3]^{2+}$  the peak shifts to an even shorter wavelength, 540 nm, which lies near the boundary between green and yellow. The resulting color purple is a mixture of the complementary colors red and violet.

### Electron Configurations in Octahedral Complexes

Crystal-field theory helps us understand the magnetic properties and some important chemical properties of transition-metal ions. From Hund's rule, we expect electrons to always occupy the lowest-energy vacant orbitals first and to occupy a set of degenerate (same-energy) orbitals one at a time with their spins parallel. Thus, if we have a  $d^1$ ,  $d^2$ , or  $d^3$  octahedral complex, the electrons go into the lower-energy  $t_2$  orbitals, with their spins parallel. When a fourth electron must be added, we have the two choices shown in **Figure 23.31**: The electron can either go into an  $e$  orbital, where it will be the sole electron in the orbital or become the second electron in a  $t_2$  orbital. Because the

\*The other two peaks fall in the infrared (IR) and ultraviolet (UV) regions of the spectrum. For  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  the IR peak is found at 1176 nm and the UV peak at 388 nm.



**▲ Figure 23.31** Two possibilities for adding a fourth electron to a  $d^3$  octahedral complex. Whether the fourth electron goes into a  $t_2$  orbital or into an  $e$  orbital depends on the relative energies of the crystal-field splitting energy and the spin-pairing energy.

energy difference between the  $t_2$  and  $e$  sets is the splitting energy  $\Delta$ , the energy cost of going into an  $e$  orbital rather than a  $t_2$  orbital is also  $\Delta$ . Thus, the goal of filling lowest-energy available orbitals first is met by putting the electron in a  $t_2$  orbital.

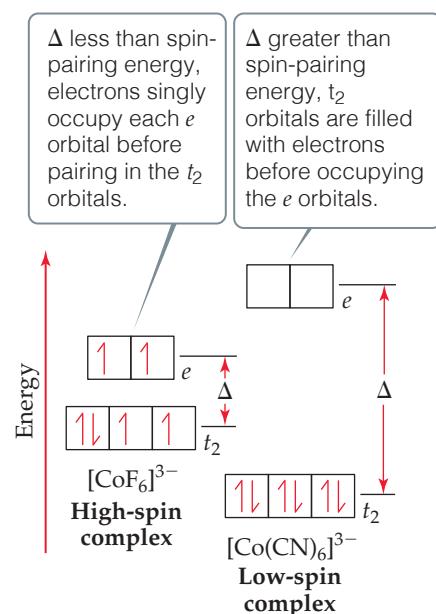
There is a penalty for doing this, however, because the electron must now be paired with the electron already occupying the orbital. The difference between the energy required to pair an electron in an occupied orbital and the energy required to place that electron in an empty orbital is called the **spin-pairing energy**. The spin-pairing energy arises from the fact that the electrostatic repulsion between two electrons that share an orbital (and so must have opposite spins) is greater than the repulsion between two electrons that are in different orbitals and have parallel spins.

In coordination complexes, the nature of the ligands and the charge on the metal ion often play major roles in determining which of the two electron arrangements shown in Figure 23.31 is used. In  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{CN})_6]^{3-}$ , both ligands have a  $1-$  charge. The  $\text{F}^-$  ion, however, is on the low end of the spectrochemical series, so it is a weak-field ligand. The  $\text{CN}^-$  ion is on the high end and so is a strong-field ligand, which means it produces a larger energy gap  $\Delta$  than the  $\text{F}^-$  ion. The splittings of the  $d$ -orbital energies in these two complexes are compared in Figure 23.32.

Cobalt(III) has an  $[\text{Ar}]3d^6$  electron configuration, so both complexes in Figure 23.32 are  $d^6$  complexes. Let's imagine that we add these six electrons one at a time to the  $d$  orbitals of the  $[\text{CoF}_6]^{3-}$  ion. The first three go into the  $t_2$  orbitals with their spins parallel. The fourth electron could pair up in one of the  $t_2$  orbitals. The  $\text{F}^-$  ion is a weak-field ligand, however, and so the energy gap  $\Delta$  between the  $t_2$  set and the  $e$  set is small. In this case, the more stable arrangement is the fourth electron in one of the  $e$  orbitals. By the same energy argument, the fifth electron goes into the other  $e$  orbital. With all five  $d$  orbitals containing one electron, the sixth must pair up, and the energy needed to place the sixth electron in a  $t_2$  orbital is less than that needed to place it in an  $e$  orbital. We end up with four  $t_2$  electrons and two  $e$  electrons.

Figure 23.32 shows that the crystal-field splitting energy  $\Delta$  is much larger in the  $[\text{Co}(\text{CN})_6]^{3-}$  complex. In this case, the spin-pairing energy is smaller than  $\Delta$ , so the lowest-energy arrangement is to place all six electrons in the  $t_2$  orbitals.

The  $[\text{CoF}_6]^{3-}$  complex is a **high-spin complex**; that is, the electrons are arranged so that they remain unpaired as much as possible. The  $[\text{Co}(\text{CN})_6]^{3-}$  ion is a **low-spin complex**; that is, the electrons are arranged so that they remain paired as much as possible while still following Hund's rule. These two electronic arrangements can be readily distinguished by measuring the magnetic properties of the complex. Experiments show that  $[\text{CoF}_6]^{3-}$  has four unpaired electrons and is paramagnetic, while  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and is diamagnetic. The absorption spectrum also shows peaks corresponding to the different values of  $\Delta$  in these two complexes.



**▲ Figure 23.32** High-spin and low-spin complexes. The high-spin  $[\text{CoF}_6]^{3-}$  ion has a weak-field ligand and so a small  $\Delta$  value. The low-spin  $[\text{Co}(\text{CN})_6]^{3-}$  ion has a strong-field ligand and so a large  $\Delta$  value. Because  $[\text{CoF}_6]^{3-}$  has unpaired electrons it is paramagnetic, while  $[\text{Co}(\text{CN})_6]^{3-}$  is diamagnetic.

In the transition metal ions of Periods 5 and 6 (which have  $4d$  and  $5d$  valence electrons), the  $d$  orbitals are larger than in the Period 4 ions (which have only  $3d$  electrons). Thus, ions from Periods 5 and 6 interact more strongly with ligands, resulting in a larger crystal-field splitting. *Consequently, metal ions in Periods 5 and 6 are invariably low spin in an octahedral crystal-field.*

## Sample Exercise 23.7

### The Spectrochemical Series, Crystal-Field Splitting, Color, and Magnetism

The compound hexaamminecobalt(III) chloride is diamagnetic and orange in color with a single absorption peak in its visible absorption spectrum. (a) What is the electron configuration of the cobalt(III) ion? (b) Is  $[\text{Co}(\text{NH}_3)_6]^{3+}$  a high-spin complex or a low-spin complex? (c) Estimate the wavelength where you expect the absorption of light to reach a maximum? (d) What color and magnetic behavior would you predict for the complex ion  $[\text{Co}(\text{en})_3]^{3+}$ ?

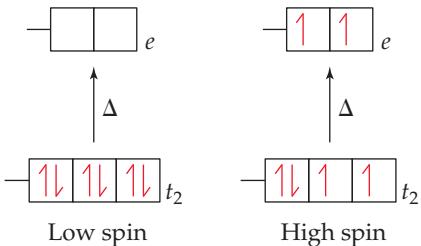
### SOLUTION

**Analyze** We are given the color and magnetic behavior of an octahedral complex containing Co with a +3 oxidation number. We need to use this information to determine its electron configuration, its spin state (low-spin or high-spin), and the color of light it absorbs. In part (d), we must use the spectrochemical series to predict how its properties will change if  $\text{NH}_3$  is replaced by ethylenediamine (en).

**Plan** (a) From the oxidation number and the periodic table we can determine the number of valence electrons for Co(III), and from that we can determine the electron configuration. (b) The magnetic behavior can be used to determine whether this compound is a low-spin or high-spin complex. (c) Since there is a single peak in the visible absorption spectrum, the color of the compound should be complementary to the color of light that is absorbed most strongly. (d) Ethylenediamine is a stronger field ligand than  $\text{NH}_3$ , so we expect a larger  $\Delta$  for  $[\text{Co}(\text{en})_3]^{3+}$  than for  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

### Solve

- (a) Co has an electron configuration of  $[\text{Ar}]4s^23d^7$ , and  $\text{Co}^{3+}$  has three fewer electrons than Co. Because transition-metal ions always lose their valence shell s electrons, the electron configuration of  $\text{Co}^{3+}$  is  $[\text{Ar}]3d^6$ .  
 (b) There are six valence electrons in the  $d$  orbitals. The filling of the  $t_2$  and  $e$  orbitals for both high-spin and low-spin complexes is shown here. Because the compound is diamagnetic, we know all of the electrons must be paired up, which allows us to determine that  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is a low-spin complex.



- (c) We are told that the compound is orange and has a single absorption peak in the visible region of the spectrum. The compound must therefore absorb the complementary color of orange, which is blue. The blue region of the spectrum ranges from approximately 430 nm to 490 nm. As an estimate we assume that the complex ion absorbs somewhere in the middle of the blue region, near 460 nm.  
 (d) Ethylenediamine is higher in the spectrochemical series than ammonia. Therefore, we expect a larger  $\Delta$  for  $[\text{Co}(\text{en})_3]^{3+}$ . Because  $\Delta$  was already greater than the spin-pairing energy for  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , we expect  $[\text{Co}(\text{en})_3]^{3+}$  to be a low-spin complex as well, with a  $d^6$  configuration, so it will also be diamagnetic. The wavelength at which the complex absorbs light will shift to higher energy. If we assume a shift in the absorption maximum from blue to violet, the color of the complex will become yellow.

**Comment** The compound  $[\text{Co}(\text{en})_3]\text{Cl}_3$ , which contains the  $[\text{Co}(\text{en})_3]^{3+}$  ion, was made and studied by Alfred Werner. This compound forms diamagnetic, golden-yellow crystals.

### ► Practice Exercise

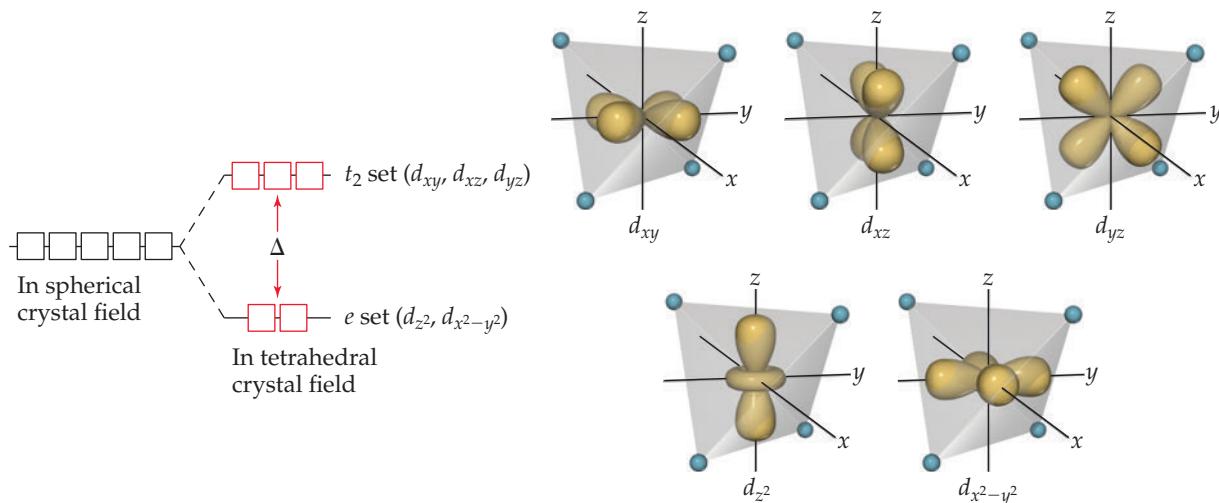
Which of the following octahedral complex ions will have the fewest number of unpaired electrons?

- (a)  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  (b)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  (c)  $[\text{FeF}_6]^{3-}$  (d)  $[\text{RhCl}_6]^{3-}$   
 (e)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

## Tetrahedral and Square-Planar Complexes

Thus far we have considered crystal-field theory only for complexes having an octahedral geometry. When there are only four ligands in a complex, the geometry is generally tetrahedral, except for the special case of  $d^8$  metal ions, which we will discuss in a moment.

The crystal-field splitting of  $d$  orbitals in tetrahedral complexes differs from that in octahedral complexes. Four equivalent ligands can interact with a central metal ion



**▲ Figure 23.33 Energies of the  $d$  orbitals in a tetrahedral crystal-field.** The splitting of the  $e$  and  $t_2$  sets of orbitals is inverted with respect to the splitting associated with an octahedral crystal-field. The crystal-field splitting energy  $\Delta$  is smaller than it is in an octahedral crystal-field.

most effectively by approaching along the vertices of a tetrahedron. In this geometry the lobes of the two  $e$  orbitals point toward the edges of the tetrahedron, exactly in between the ligands (Figure 23.33). This orientation keeps the  $d_{x^2-y^2}$  and  $d_{z^2}$  as far from the ligand point charges as possible. Consequently, these two  $d$  orbitals experience less repulsion from the ligands and lie at lower energy than the other three  $d$  orbitals. The three  $t_2$  orbitals do not point directly at the ligand point charges, but they do come closer to the ligands than the  $e$  set, and as a result they experience more repulsion and are higher in energy. As we see in Figure 23.33, the splitting of  $d$  orbitals in a tetrahedral geometry is the opposite of what we find for the octahedral geometry, namely, the  $e$  orbitals are now *below* the  $t_2$  orbitals. The crystal-field splitting energy  $\Delta$  is much smaller for tetrahedral complexes than it is for comparable octahedral complexes, in part because there are fewer ligand point charges in the tetrahedral geometry, and in part because neither set of orbitals has lobes that point directly at the ligands. Calculations show that for the same metal ion and ligand set,  $\Delta$  for the tetrahedral complex is only four-ninths as large as for the octahedral complex. For this reason, nearly all tetrahedral complexes are high spin; the crystal-field splitting energy is never large enough to overcome the spin-pairing energies.

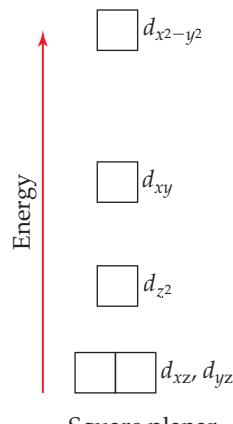
In a square-planar complex, four ligands are arranged about the metal ion such that all five species are in the  $xy$  plane. The resulting energy levels of the  $d$  orbitals are illustrated in Figure 23.34. Note in particular that the  $d_{z^2}$  orbital is considerably lower in energy than the  $d_{x^2-y^2}$  orbital. To understand why this is so, recall from Figure 23.28 that in an octahedral field the  $d_{z^2}$  orbital of the metal ion interacts with the ligands positioned above and below the  $xy$  plane. There are no ligands in these two positions in a square-planar complex, which means that the  $d_{z^2}$  orbital experiences less repulsion and so remains in a lower-energy, more stable state.

Square-planar complexes are characteristic of metal ions with a  $d^8$  electron configuration. They are nearly always low spin, with the eight  $d$  electrons spin-paired to form a diamagnetic complex. This pairing leaves the  $d_{x^2-y^2}$  orbital empty. Such an electronic arrangement is particularly common among the  $d^8$  ions of Periods 5 and 6, such as  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Ir}^+$ , and  $\text{Au}^{3+}$ .

Crystal-field theory can be used to explain many observations in addition to those we have discussed. The theory is based on electrostatic interactions between ions and atoms, which essentially means ionic bonds. Many lines of evidence show, however, that the bonding in complexes must have some covalent character. Therefore, molecular-orbital theory can also be used to describe the bonding in complexes, but the application of molecular-orbital theory to coordination compounds is beyond the scope of our discussion. Crystal-field theory, although not entirely accurate in all details, provides an adequate and useful first description of the electronic structure of complexes.

### Go Figure

For which  $d$  orbital(s) do the lobes point directly at the ligands in a square-planar crystal-field?



**▲ Figure 23.34 Energies of the  $d$  orbitals in a square-planar crystal-field.**



## Sample Exercise 23.8

### Populating *d* Orbitals in Tetrahedral and Square-Planar Complexes

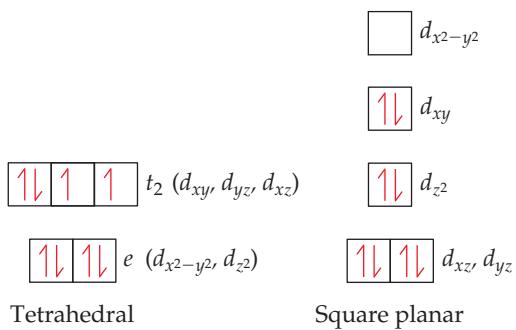
Nickel(II) complexes in which the metal coordination number is 4 can have either square-planar or tetrahedral geometry.  $[\text{NiCl}_4]^{2-}$  is paramagnetic, and  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. One of these complexes is square planar, and the other is tetrahedral. Use the relevant crystal-field splitting diagrams in the text to determine which complex has which geometry.

#### SOLUTION

**Analyze** We are given two complexes containing  $\text{Ni}^{2+}$  and their magnetic properties. We are given two molecular geometry choices and asked to use crystal-field splitting diagrams from the text to determine which complex has which geometry.

**Plan** We need to determine the number of *d* electrons in  $\text{Ni}^{2+}$  and then use Figure 23.33 for the tetrahedral complex and Figure 23.34 for the square-planar complex.

**Solve** Nickel(II) has the electron configuration  $[\text{Ar}]3d^8$ . With very few exceptions tetrahedral complexes are high spin and square-planar complexes are low spin. Therefore, the population of the *d* orbitals in the two geometries is



The tetrahedral complex has two unpaired electrons, and the square-planar complex has none. We know from Section 23.1 that the tetrahedral complex must be paramagnetic and the square planar must be diamagnetic. Therefore,  $[\text{NiCl}_4]^{2-}$  is tetrahedral, and  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar.

**Comment** Nickel(II) forms octahedral complexes more frequently than square-planar ones, whereas  $d^8$  metals from Periods 5 and 6 tend to favor square-planar coordination.

#### ► Practice Exercise

How many unpaired electrons do you predict for the tetrahedral  $[\text{MnCl}_4]^{2-}$  ion?

- (a) 1, (b) 2, (c) 3, (d) 4, (e) 5.

#### A CLOSER LOOK Charge-Transfer Color



$\text{KMnO}_4$



$\text{K}_2\text{CrO}_4$



$\text{KClO}_4$

▲ **Figure 23.35** The colors of compounds can arise from charge-transfer transitions.  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_4$  are colored due to ligand-to-metal charge-transfer transitions in their anions. Higher energy ultraviolet photons are needed to excite the charge-transfer transition in the perchlorate ion, therefore  $\text{KClO}_4$  is white.

In the laboratory portion of your course, you have probably seen many colorful transition-metal compounds, including those shown in **Figure 23.35**. Many of these compounds are colored because of *d-d* transitions. Some colored complexes, however, including the violet permanganate ion,  $\text{MnO}_4^-$ , and the yellow chromate ion,  $\text{CrO}_4^{2-}$ , derive their color from a different type of excitation involving the *d* orbitals.

The permanganate ion strongly absorbs visible light, with a maximum absorption at 565 nm. Because violet is complementary to yellow, this strong absorption in the yellow portion of the visible spectrum is responsible for the violet color of salts and solutions

of the ion. What is happening during this absorption of light? The  $\text{MnO}_4^-$  ion is a complex of Mn(VII). Because Mn(VII) has a  $[\text{Ar}]3d^0$  electron configuration, the absorption cannot be due to a *d-d* transition because there are no *d* electrons to excite! That does not mean, however, that the *d* orbitals are not involved in the transition. The excitation in the  $\text{MnO}_4^-$  ion is due to a *charge-transfer transition*, in which an electron on one oxygen ligand is excited into a vacant *d* orbital on the Mn ion (**Figure 23.36**). In essence, an electron is transferred from a ligand to the metal, so this transition is called a *ligand-to-metal charge-transfer (LMCT) transition*.

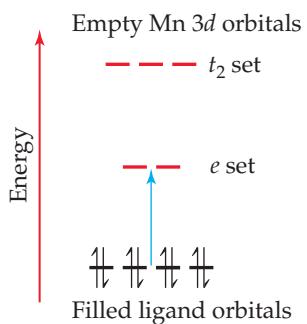
An LMCT transition is also responsible for the color of the  $\text{CrO}_4^{2-}$ , which contains the Cr(VI) ion with an [Ar]3d<sup>0</sup> electron configuration.

Also shown in Figure 23.35 is a salt of the perchlorate ion ( $\text{ClO}_4^-$ ). Like  $\text{MnO}_4^-$ ,  $\text{ClO}_4^-$  is tetrahedral and has its central atom in the +7 oxidation state. However, because the Cl atom does not have low-lying d orbitals, exciting an electron from O to Cl requires a more energetic photon than does it in  $\text{MnO}_4^-$ . The first absorption for  $\text{ClO}_4^-$  is in the ultraviolet portion of the spectrum, so no visible light is absorbed and the salt appears white.

Other complexes exhibit charge-transfer excitations in which an electron from the metal atom is excited to an empty orbital on a ligand. Such an excitation is called a *metal-to-ligand charge-transfer (MLCT) transition*.

Charge-transfer transitions are generally more intense than d-d transitions. Many metal-containing pigments used for oil painting, such as cadmium yellow ( $\text{CdS}$ ), chrome yellow ( $\text{PbCrO}_4$ ), and red ochre ( $\text{Fe}_2\text{O}_3$ ), have intense colors because of charge-transfer transitions.

**Related Exercises:** 23.96, 23.97



▲ Figure 23.36 Ligand-to-metal charge-transfer transition in  $\text{MnO}_4^-$ .

As shown by the blue arrow, an electron is excited from a nonbonding orbital on O into one of the empty d orbitals on Mn.

## Self-Assessment Exercise

- 23.25** Using the spectrochemical series as a guide, predict how many unpaired d-electrons are in the complex:  $[\text{FeBr}_6]^{3-}$ .

- (a) 1  
(b) 3  
(c) 5

## Exercises

- 23.26** The lobes of which d orbitals point directly between the ligands in (a) octahedral geometry, (b) tetrahedral geometry?
- 23.27** As shown in Figure 23.26, the d-d transition of  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  produces an absorption maximum at a wavelength of about 500 nm. (a) What is the magnitude of  $\Delta$  for  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  in kJ/mol? (b) How would the magnitude of  $\Delta$  change if the  $\text{H}_2\text{O}$  ligands in  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  were replaced with  $\text{NH}_3$  ligands?
- 23.28** The color and wavelength of the absorption maximum for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , and  $[\text{Ni}(\text{en})_3]^{2+}$  are given in Figure 23.30. The absorption maximum for the  $[\text{Ni}(\text{bipy})_3]^{2+}$  ion occurs at about 520 nm. (a) What color would you expect for the  $[\text{Ni}(\text{bipy})_3]^{2+}$  ion? (b) Based on these data, where would you put bipy in the spectrochemical series?
- 23.29** Give the number of (valence) d electrons associated with the central metal ion in each of the following complexes: (a)  $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$ , (b)  $[\text{Zr}(\text{OH}_2)_6]\text{SO}_4$ , (c)  $\text{Na}_2[\text{CuCl}_4]$ , (d)  $(\text{NH}_4)_2[\text{Ni}(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ , (e)  $\text{K}_3[\text{Fe}(\text{CN})_6]$

- 23.30** For a given metal ion and set of ligands, is the crystal-field splitting energy larger for a tetrahedral or an octahedral geometry?
- 23.31** For each of the following metals, write the electronic configuration of the atom and its 3+ ion: (a) Fe, (b) Mo, (c) Co. Draw the crystal-field energy-level diagram for the d orbitals of an octahedral complex, and show the placement of the d electrons for each 3+ ion, assuming a weak-field complex. How many unpaired electrons are there in each case?
- 23.32** Draw the crystal-field energy-level diagrams and show the placement of electrons for the following complexes: (a)  $[\text{VCl}_6]^{3-}$ , (b)  $[\text{FeF}_6]^{3-}$  (a high-spin complex), (c)  $[\text{Ru}(\text{bipy})_3]^{3+}$  (a low-spin complex), (d)  $[\text{NiCl}_4]^{2-}$  (tetrahedral), (e)  $[\text{PtBr}_6]^{2-}$ , (f)  $[\text{Ti}(\text{en})_3]^{2+}$ .
- 23.33** The ion  $[\text{Fe}(\text{CN})_6]^{3-}$  has one unpaired electron, whereas  $[\text{Fe}(\text{NCS})_6]^{3-}$  has five unpaired electrons. From these results, what can you conclude about whether each complex is high spin or low spin? What can you say about the placement of NCS<sup>-</sup> in the spectrochemical series?

23.25 (c)

Answers to Self-Assessment Exercise



## Sample Integrative Exercise

### Putting Concepts Together

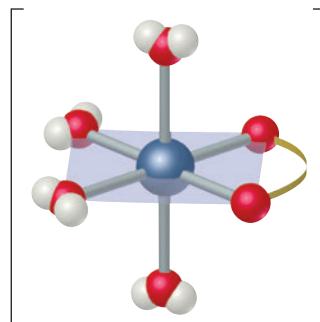
The oxalate ion has the Lewis structure shown in Table 23.4. (a) Show the geometry of the complex formed when this ion complexes with cobalt(II) to form  $[\text{Co}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]$ . (b) Write the formula for the salt formed when three oxalate ions complex with Co(II), assuming that the charge-balancing cation is  $\text{Na}^+$ . (c) Sketch all the possible geometric isomers for the cobalt complex formed in part (b). Are any of these isomers chiral? Explain. (d) The equilibrium constant for the formation of the

Continued

cobalt(II) complex produced by coordination of three oxalate anions, as in part (b), is  $5.0 \times 10^9$ , and the equilibrium constant for formation of the cobalt(II) complex with three molecules of *ortho*-phenanthroline (Table 23.4) is  $9 \times 10^{19}$ . From these results, what conclusions can you draw regarding the relative Lewis base properties of the two ligands toward cobalt(II)? (e) Using the approach described in Sample Exercise 17.14, calculate the concentration of free aqueous Co(II) ion in a solution initially containing 0.040 M oxalate (*aq*) and 0.0010 M  $\text{Co}^{2+}$ (*aq*).

## SOLUTION

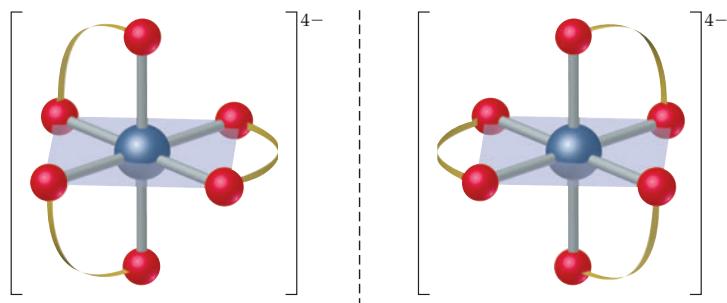
- (a) The complex formed by coordination of one oxalate ion is octahedral:



- (b) Because the oxalate ion has a charge of 2-, the net charge of a complex with three oxalate anions and one  $\text{Co}^{2+}$  ion is 4-. Therefore, the coordination compound has the formula:

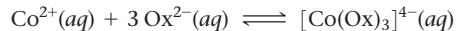


- (c) There is only one geometric isomer. The complex is chiral, however, in the same way the  $[\text{Co}(\text{en})_3]^{3+}$  complex is chiral (Figure 23.22). The two mirror images are not superimposable, so there are two enantiomers:



- (d) The *ortho*-phenanthroline ligand is bidentate, like the oxalate ligand, so they both exhibit the chelate effect. Thus, we conclude that *ortho*-phenanthroline is a stronger Lewis base toward  $\text{Co}^{2+}$  than oxalate. This conclusion is consistent with what we learned about bases in Section 16.6, that nitrogen bases are generally stronger than oxygen bases. (Recall, for example, that  $\text{NH}_3$  is a stronger base than  $\text{H}_2\text{O}$ .)

- (e) The equilibrium we must consider involves 3 mol of oxalate ion (represented as  $\text{Ox}^{2-}$ ).



The formation-constant expression is:

$$K_f = \frac{[[\text{Co}(\text{Ox})_3]^{4-}]}{[\text{Co}^{2+}][\text{Ox}^{2-}]^3}$$

Because  $K_f$  is so large, we can assume that essentially all the  $\text{Co}^{2+}$  is converted to the oxalato complex. Under that assumption, the final concentration of  $[\text{Co}(\text{Ox})_3]^{4-}$  is 0.0010 M and that of oxalate ion is  $[\text{Ox}^{2-}] = (0.040) - 3(0.0010) = 0.037 \text{ M}$  (three  $\text{Ox}^{2-}$  ions react with each  $\text{Co}^{2+}$  ion). We then have:

$$[\text{Co}^{2+}] = x \text{ M}, [\text{Ox}^{2-}] \approx 0.037 \text{ M}, [[\text{Co}(\text{Ox})_3]^{4-}] \approx 0.0010 \text{ M}$$

Inserting these values into the equilibrium-constant expression, and solving for  $x$ , we obtain  $4 \times 10^{-9} \text{ M}$ . From this, we see that the oxalate has complexed all but a tiny fraction of the  $\text{Co}^{2+}$  in solution.

$$K_f = \frac{(0.0010)}{x(0.037)^3} = 5 \times 10^9$$

$$x = 4 \times 10^{-9} \text{ M}$$

## Chapter Summary and Key Terms

**THE TRANSITION METALS (SECTION 23.1)** Metallic elements are obtained from **minerals**, which are solid inorganic compounds found in nature. **Metallurgy** is the science and technology of extracting metals from the earth and processing them for further use. Transition metals are characterized by incomplete filling of the *d* orbitals. The presence of *d* electrons in transition elements leads to multiple oxidation states. As we proceed through the transition metals in a given row of the periodic table, the attraction between the nucleus and the valence electrons increases more markedly for *d* electrons than for *s* electrons. As a result, the later transition elements in a period tend to have lower oxidation states.

The atomic and ionic radii of Period 5 transition metals are larger than those of Period 4 metals. The transition metals of Periods 5 and 6 have comparable atomic and ionic radii and are also similar in other properties. This similarity is due to the **lanthanide contraction**.

The presence of unpaired electrons in valence orbitals leads to magnetic behavior in transition metals and their compounds. In **ferromagnetic**, **ferrimagnetic**, and **antiferromagnetic** substances, the unpaired electron spins on atoms in a solid are affected by spins on neighboring atoms. In a ferromagnetic substance the spins all point in the same direction. In an antiferromagnetic substance the spins point in opposite directions and cancel one another. In a ferrimagnetic substance the spins point in opposite directions but do not fully cancel. Ferromagnetic and ferrimagnetic substances are used to make permanent magnets.

**TRANSITION-METAL COMPLEXES (SECTION 23.2)** Coordination compounds are substances that contain **metal complexes**. Metal complexes contain metal ions bonded to several surrounding anions or molecules known as **ligands**. The metal ion and its ligands make up the **coordination sphere** of the complex. The number of atoms attached to the metal ion is the **coordination number** of the metal ion. The most common coordination numbers are 4 and 6; the most common coordination geometries are tetrahedral, square planar, and octahedral.

**COMMON LIGANDS IN COORDINATION CHEMISTRY (SECTION 23.3)** Ligands that occupy only one site in a coordination sphere are called **monodentate ligands**. The atom of the ligand that bonds to the metal ion is the **donor atom**. Ligands that have two donor atoms are **bidentate ligands**. **Polydentate ligands** have three or more donor atoms. Bidentate and polydendate ligands are also called **chelating agents**. In general, chelating agents form more stable complexes than do related monodentate ligands, an observation known as the **chelate effect**. Many biologically important molecules, such as the **porphyrins**, are complexes of chelating agents. A related group of plant pigments known as **chlorophylls** are important in **photosynthesis**, the process by which plants use solar energy to convert  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into carbohydrates.

**NOMENCLATURE AND ISOMERISM IN COORDINATION CHEMISTRY (SECTION 23.4)** In naming coordination compounds, the number and type of ligands attached to the metal ion are specified, as is the oxidation state of the metal ion. **Isomers** are compounds with the same composition but different arrangements of atoms and therefore different properties. **Constitutional isomers** differ in the bonding arrangements of the ligands. **Linkage isomerism** occurs when a ligand can coordinate to a metal ion through different donor atoms. **Coordination-sphere isomers** contain different ligands in the

coordination sphere. **Stereoisomers** are isomers with the same chemical bonding arrangements but different spatial arrangements of ligands. The most common forms of stereoisomerism are **geometric isomerism** and **optical isomerism**. Geometric isomers differ from one another in the relative locations of donor atoms in the coordination sphere; the most common being *cis* and *trans* isomers. Geometric isomers differ from one another in their chemical and physical properties. Optical isomers are nonsuperimposable mirror images of each other. Optical isomers, or **enantiomers**, are **chiral**, meaning that they have a specific “handedness” and differ only in the presence of a chiral environment. Optical isomers can be distinguished from one another by their interactions with plane-polarized light; solutions of one isomer rotate the plane of polarization to the right (**dextrorotatory**), and solutions of its mirror image rotate the plane to the left (**levorotatory**). Chiral molecules, therefore, are **optically active**. A 50–50 mixture of two optical isomers does not rotate plane-polarized light and is said to be **racemic**.

**COLOR AND MAGNETISM IN COORDINATION CHEMISTRY (SECTION 23.5)** A substance has a particular color because it either reflects or transmits light of that color or absorbs light of the **complementary color**. The amount of light absorbed by a sample as a function of wavelength is known as its **absorption spectrum**. The light absorbed provides the energy to excite electrons to higher-energy states.

It is possible to determine the number of unpaired electrons in a complex from its degree of paramagnetism. Compounds with no unpaired electrons are diamagnetic.

**CRYSTAL-FIELD THEORY (SECTION 23.6)** Crystal-field theory successfully accounts for many properties of coordination compounds, including their color and magnetism. In crystal-field theory, the interaction between metal ion and ligand is viewed as electrostatic. Because some *d* orbitals point directly at the ligands whereas others point between them, the ligands split the energies of the metal *d* orbitals. For an octahedral complex, the *d* orbitals are split into a lower-energy set of three degenerate orbitals (the *t<sub>2</sub>* set) and a higher-energy set of two degenerate orbitals (the *e* set). Visible light can cause a **d-d transition**, in which an electron is excited from a lower-energy *d* orbital to a higher-energy *d* orbital. The **spectrochemical series** lists ligands in order of their ability to increase the split in *d*-orbital energies in octahedral complexes.

Strong-field ligands create a splitting of *d*-orbital energies that is large enough to overcome the **spin-pairing energy**. The *d* electrons then preferentially pair up in the lower-energy orbitals, producing a **low-spin complex**. When the ligands exert a weak crystal-field, the splitting of the *d* orbitals is small. The electrons then occupy the higher-energy *d* orbitals in preference to pairing up in the lower-energy set, producing a **high-spin complex**. Transition metal ions from Periods 5 and 6 have large crystal-field splitting energies and adopt low spin configurations in octahedral complexes.

Crystal-field theory also applies to tetrahedral and square-planar complexes, which leads to different *d*-orbital splitting patterns. In a tetrahedral crystal-field, the splitting of the *d* orbitals results in a higher-energy *t<sub>2</sub>* set and a lower-energy *e* set, the opposite of the octahedral case. The splitting in a tetrahedral crystal-field is much smaller than that in an octahedral crystal-field, so tetrahedral complexes are nearly always high-spin complexes.

## Learning Outcomes After studying this chapter, you should be able to:

- Describe the periodic trends in radii and oxidation states of the transition-metal ions, including the origin and effect of the lanthanide contraction. (Section 23.1) *Related Exercises: 23.2, 23.34, 23.44*
- Determine the oxidation number and number of *d* electrons for metal ions in complexes. (Section 23.2) *Related Exercises: 23.3, 23.4, 23.46, 23.52*

- Identify common ligands and distinguish between chelating and nonchelating ligands. (Section 23.3)  
*Related Exercises: 23.12, 23.53, 23.54, 23.56*
- Name coordination compounds given their formula and write their formula given their name. (Section 23.4)  
*Related Exercises: 23.16, 23.17, 23.57, 23.58*
- Define isomerism and differentiate between the various types of isomers. (Section 23.4) *Related Exercises: 23.18, 23.59*
- Recognize and draw the geometric isomers of a complex. (Section 23.4) *Related Exercises: 23.19, 23.20, 23.60, 23.61*

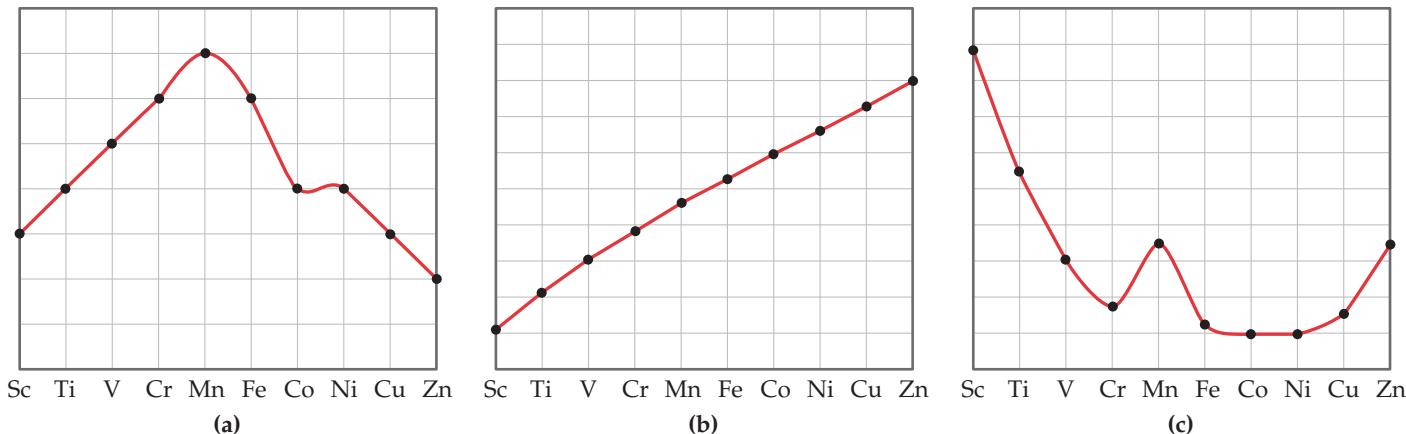
- Recognize and draw the optical isomers of a complex. (Section 23.4) *Related Exercises: 23.21, 23.62*
- Use crystal-field theory to determine the number of unpaired electrons in a complex. (Sections 23.5 and 23.6)  
*Related Exercises: 23.64, 23.70, 23.71, 23.72*
- Use the spectrochemical series to predict the relative crystal-field splitting energy and colors of metal complexes. (Sections 23.5 and 23.6) *Related Exercises: 23.28, 23.67*
- Differentiate between high-spin and low-spin ions, and identify the factors that stabilize each. (Section 23.6)  
*Related Exercises: 23.33, 23.41, 23.69, 23.72*

## Exercises

### Visualizing Concepts

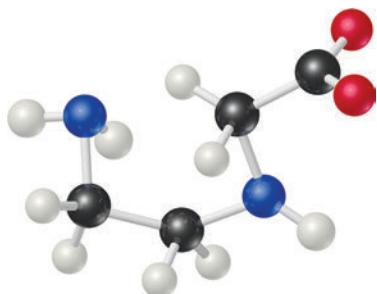
**23.34** These three graphs show the variation in radius, effective nuclear charge, and maximum oxidation state for the

transition metals of Period 4. In each part, identify which property is being plotted. [Section 23.1]



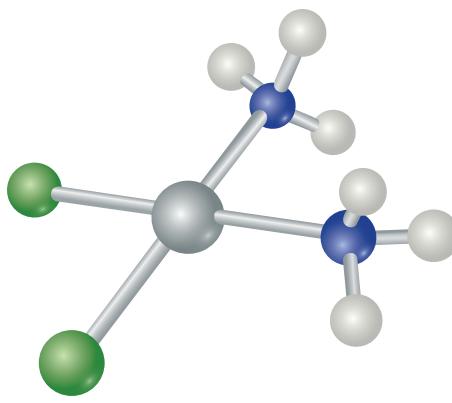
**23.35** Draw the structure for  $\text{Pt}(\text{C}_2\text{O}_4)(\text{NH}_3)_2$  and use it to answer the following questions: (a) What is the coordination number for platinum in this complex? (b) What is the coordination geometry? (c) What is the oxidation state of the platinum? (d) How many unpaired electrons are there? [Sections 23.2 and 23.6]

**23.36** Draw the Lewis structure for the ligand shown here. (a) Which atoms can serve as donor atoms? Classify this ligand as monodentate, bidentate, or polydentate. (b) How many of these ligands are needed to fill the coordination sphere in an octahedral complex? [Section 23.2]

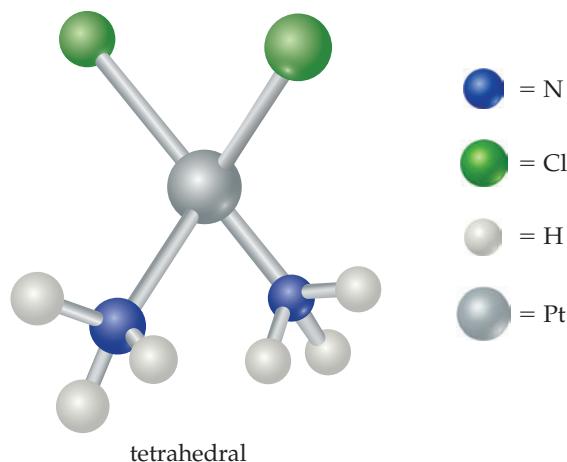


**23.37** Four-coordinate metals can have either a tetrahedral or a square-planar geometry; both possibilities are shown here

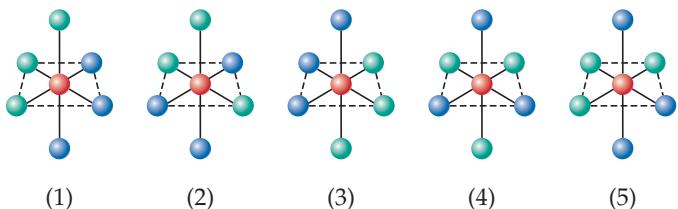
for  $[\text{PtCl}_2(\text{NH}_3)_2]$ . (a) What is the name of this molecule? (b) Would the tetrahedral molecule have a geometric isomer? (c) Would the tetrahedral molecule be diamagnetic or paramagnetic? (d) Would the square-planar molecule have a geometric isomer? (e) Would the square-planar molecule be diamagnetic or paramagnetic? (f) Would determining the number of geometric isomers help you distinguish between the tetrahedral and square-planar geometries? (g) Would measuring the molecule's response to a magnetic field help you distinguish between the two geometries? [Sections 23.4–23.6]



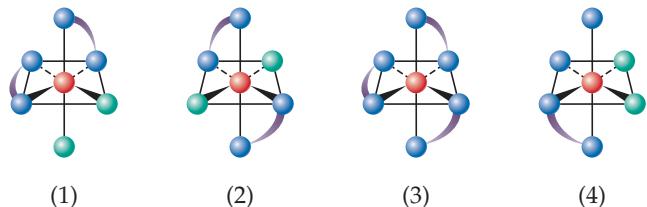
square planar



- 23.38** There are two geometric isomers of octahedral complexes of the type  $MA_3X_3$ , where M is a metal and A and X are monodentate ligands. Of the complexes shown here, which are identical to (1) and which are the geometric isomers of (1)? [Section 23.4]



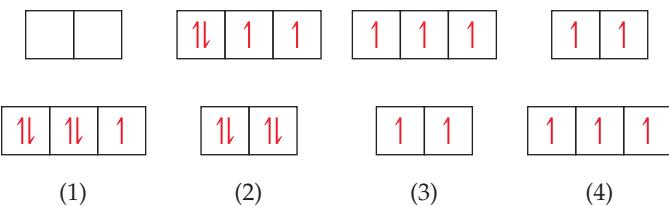
- 23.39** Which of the complexes shown here are chiral? [Section 23.4]



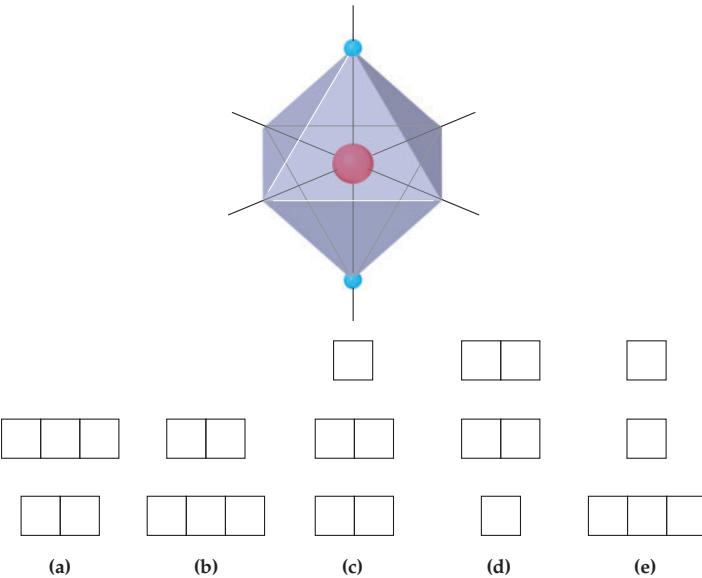
- 23.40** The solutions shown here each have an absorption spectrum with a single absorption peak like that shown in Figure 23.26. What color does each solution absorb most strongly? [Section 23.5]



- 23.41** Which of these crystal-field splitting diagrams represents: (a) a weak-field octahedral complex of  $\text{Fe}^{3+}$ , (b) a strong-field octahedral complex of  $\text{Fe}^{3+}$ , (c) a tetrahedral complex of  $\text{Fe}^{3+}$ , (d) a tetrahedral complex of  $\text{Ni}^{2+}$ ? (The diagrams do not indicate the relative magnitudes of  $\Delta$ ). [Section 23.6]



- 23.42** In the linear crystal-field shown here, the negative charges are on the z-axis. Using Figure 23.28 as a guide, predict which of the following choices most accurately describes the splitting of the d orbitals in a linear crystal-field? [Section 23.6]



- 23.43** Two  $\text{Co(III)}$  complexes are both low spin but have different ligands. A solution of one is orange and a solution of the other is yellow. Which solution is likely to contain the complex that has the stronger-field ligand? [Section 23.6]

### The Transition Metals (Section 23.1)

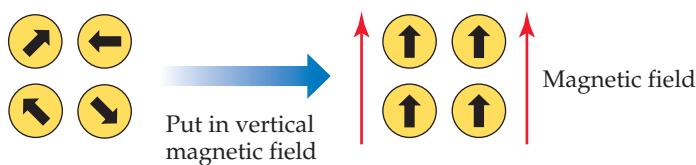
- 23.44** The lanthanide contraction explains which of the following periodic trends? (a) The atomic radii of the transition metals first decrease and then increase when moving horizontally across each period. (b) When forming ions the Period 4 transition metals lose their  $4s$  electrons before their  $3d$  electrons. (c) The radii of the Period 5 transition metals (Y–Cd) are very similar to the radii of the Period 6 transition metals (Lu–Hg).

- 23.45** Among the Period 4 transition metals (Sc–Zn), which elements do not form ions where there are partially filled  $3d$  orbitals?

- 23.46** Write out the ground-state electron configurations of (a)  $\text{Sc}^{2+}$ , (b)  $\text{Mo}^{2+}$ , (c)  $\text{Rh}^{3+}$ , (d)  $\text{Fe}^{3+}$ .

- 23.47** Which type of substance is attracted by a magnetic field, a diamagnetic substance or a paramagnetic substance?

- 23.48** What kind of magnetism is exhibited by this diagram?



- 23.49** The most important oxides of iron are magnetite,  $\text{Fe}_3\text{O}_4$ , and hematite,  $\text{Fe}_2\text{O}_3$ . (a) What are the oxidation states of iron in these compounds? (b) One of these iron oxides is ferrimagnetic, and the other is antiferromagnetic. Which iron oxide is more likely to be ferrimagnetic? Explain.

### Transition-Metal Complexes (Section 23.2)

- 23.50** (a) Using Werner's definition of valence, which property is the same as oxidation number, *primary valence* or *secondary valence*? (b) What term do we normally use for the other type of valence? (c) Why can  $\text{NH}_3$  serve as a ligand but  $\text{BH}_3$  cannot?

- 23.51** A complex is written as  $\text{NiBr}_2 \cdot 6\text{NH}_3$ . (a) What is the oxidation state of the Ni atom in this complex? (b) What is the likely coordination number for the complex? (c) If the complex is treated with excess  $\text{AgNO}_3(aq)$ , how many moles of  $\text{AgBr}$  will precipitate per mole of complex?

- 23.52** Indicate the coordination number and the oxidation number of the metal for each of the following complexes:

- (a)  $\text{Na}_2[\text{Co}(\text{EDTA})]$
- (b)  $\text{KMnO}_4$
- (c)  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
- (d)  $\text{K}_3\text{Fe}(\text{CN})_6$
- (e)  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$
- (f)  $\text{Zn}(\text{C}_2\text{O}_4)(\text{NH}_3)_2$

### Common Ligands in Coordination Chemistry (Section 23.3)

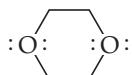
- 23.53** For each of the following molecules or polyatomic ions, draw the Lewis structure and indicate if it can act as a monodentate ligand, a bidentate ligand, or is unlikely to act as a ligand at all: (a) ethylamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ , (b) trimethylphosphine,  $\text{P}(\text{CH}_3)_3$ , (c) carbonate,  $\text{CO}_3^{2-}$ , (d) ethane,  $\text{C}_2\text{H}_6$ .

- 23.54** Polydentate ligands can vary in the number of coordination positions they occupy. In each of the following, identify the polydentate ligand present and indicate the probable number of coordination positions it occupies:

- (a)  $\text{Cr}(\text{EDTA})^-$
- (b)  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]\text{Br}_2$
- (c)  $[\text{Ru}(\text{en})(\text{NH}_3)_4]\text{Cl}_3$
- (d)  $\text{K}_2[\text{Fe}(\text{o-phen})(\text{CN})_4]$

- 23.55** For each of the following pairs, identify the molecule or ion that is more likely to act as a ligand in a metal complex: (a) carbonic acid ( $\text{H}_2\text{CO}_3$ ) or carbonate ( $\text{CO}_3^{2-}$ ), (b) water ( $\text{H}_2\text{O}$ ) or hydronium ion ( $\text{H}_3\text{O}^+$ ), (c) phosphine ( $\text{PH}_3$ ) or phosphoric acid ( $\text{H}_3\text{PO}_4$ ).

- 23.56** True or false? The following ligand can act as a bidentate ligand.



### Nomenclature and Isomerism in Coordination Chemistry (Section 23.4)

- 23.57** Write the formula for each of the following compounds, being sure to use brackets to indicate the coordination sphere:

- (a) triamminetraquachromium(III) nitrate
- (b) dichloridobis(ethylenediamine)platinum(II)
- (c) pentacarbonyliron(0)
- (d) ammonium diaquabis(oxalato)Co(II)
- (e) tris(bipyridyl)cobalt(III) sulfate

- 23.58** Write the names of the following compounds, using the standard nomenclature rules for coordination complexes:

- (a)  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$
- (b)  $\text{Hg}[\text{Co}(\text{SCN})_4]$
- (c)  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_3]$
- (d)  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{SO}_4$

- 23.59** Consider the following three complexes:

- (Complex 1)  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$
- (Complex 2)  $[\text{Pd}(\text{NH}_3)_2(\text{ONO})_2]$
- (Complex 3)  $[\text{V}(\text{en})_2\text{Cl}_2]^+$ ,

Which of the three complexes can have (a) geometric isomers, (b) linkage isomers, (c) optical isomers, (d) coordination-sphere isomers?

- 23.60** A four-coordinate complex  $\text{MA}_2\text{B}_2$  is prepared and found to have two different isomers. Is it possible to determine from this information whether the complex is square planar or tetrahedral? If so, which is it?

- 23.61** Determine if each of the following complexes exhibits geometric isomerism. If geometric isomers exist, determine how many there are. (a) tetrahedral  $[\text{Cd}(\text{H}_2\text{O})_2\text{Cl}_2]$ , (b) square-planar  $[\text{IrCl}_2(\text{PPh}_3)_2]^-$ , (c) octahedral  $[\text{Fe}(\text{o-phen})_2\text{Cl}_2]^+$ .

- 23.62** Determine if each of the following metal complexes is chiral and therefore has an optical isomer: (a) tetrahedral  $[\text{Zn}(\text{H}_2\text{O})_2\text{Cl}_2]$ , (b) octahedral *trans*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ , (c) octahedral *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ .

### Color and Magnetism in Coordination Chemistry; Crystal-Field Theory (Sections 23.5 and 23.6)

- 23.63** (a) If a complex absorbs light at 610 nm, what color would you expect the complex to be? (b) What is the energy in joules of a photon with a wavelength of 610 nm? (c) What is the energy of this absorption in kJ/mol?

- 23.64** Identify each of the following coordination complexes as either diamagnetic or paramagnetic:

- (a)  $[\text{CoBr}(\text{NH}_3)_5]^{2+}$
- (b)  $[\text{W}(\text{CN})_6]^{3-}$
- (c)  $[\text{VF}_6]^{3-}$
- (d)  $[\text{Rh}(\text{o-phen})_3]^{3+}$

- 23.65** If the lobes of a given *d*-orbital point directly at the ligands, will an electron in that orbital have a higher or lower energy than an electron in a *d*-orbital whose lobes *do not* point directly at the ligands?

- 23.66** (a) Sketch a diagram that shows the definition of the *crystal-field splitting energy* ( $\Delta$ ) for an octahedral crystal-field. (b) What is the relationship between the magnitude of  $\Delta$  and the energy of the *d-d* transition for a  $d^1$  complex? (c) Calculate  $\Delta$  in kJ/mol if a  $d^1$  complex has an absorption maximum at 545 nm.

- 23.67** The colors in the copper-containing minerals malachite, which is green and has an empirical formula of  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , and azurite, which is blue and has an empirical formula of  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ , come from a single  $d$ - $d$  transition in each compound. The compounds are sometimes found together in nature as shown here. (a) What is the electron configuration of the copper ion in each mineral? (b) Based on their colors, in which compound would you predict the crystal-field splitting  $\Delta$  is larger?



- 23.68** Give the number of (valence)  $d$  electrons associated with the central metal ion in each of the following complexes: (a)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}_2$ , (b)  $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$ , (c)  $[\text{Os}(\text{en})_3]\text{Cl}_3$ , (d)  $[\text{Cr}(\text{EDTA})]\text{SO}_4$ , (e)  $[\text{Cd}(\text{OH}_2)_6]\text{Cl}_2$ .

- 23.69** A classmate says, "A weak-field ligand usually means the complex is high spin." Is your classmate correct? Explain.

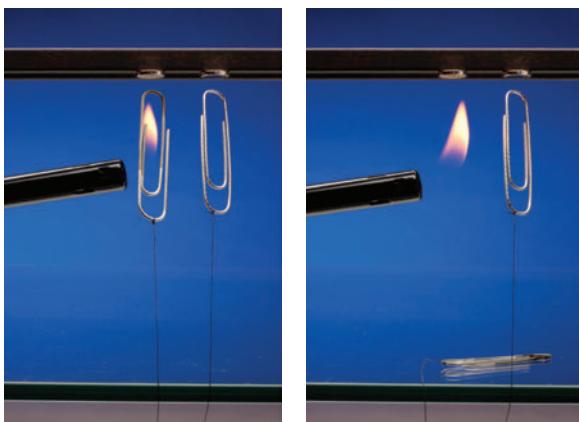
- 23.70** For each of the following metals, write the electronic configuration of the atom and its  $2+$  ion: (a) Mn, (b) Ru, (c) Rh. Draw the crystal-field energy-level diagram for the  $d$  orbitals of an octahedral complex, and show the placement of the  $d$  electrons for each  $2+$  ion, assuming a strong-field complex. How many unpaired electrons are there in each case?

- 23.71** Draw the crystal-field energy-level diagrams and show the placement of  $d$  electrons for each of the following: (a)  $[\text{Cr}(\text{OH}_2)_6]^{2+}$  (four unpaired electrons), (b)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  (a high-spin complex), (c)  $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$  (a low-spin complex), (d)  $[\text{IrCl}_6]^{2-}$  (a low-spin complex), (e)  $[\text{Cr}(\text{en})_3]^{3+}$ , (f)  $[\text{NiF}_6]^{4-}$ .

- 23.72** The complex  $[\text{Mn}(\text{NH}_3)_6]^{2+}$  contains five unpaired electrons. Sketch the energy-level diagram for the  $d$  orbitals, and indicate the placement of electrons for this complex ion. Is the ion a high-spin or a low-spin complex?

## Additional Exercises

- 23.73** The *Curie temperature* is the temperature at which a ferromagnetic solid switches from ferromagnetic to paramagnetic, and for nickel, the Curie temperature is  $354^\circ\text{C}$ . Knowing this, you tie a string to two paper clips made of nickel and hold the paper clips near a permanent magnet. The magnet attracts the paper clips, as shown in the photograph on the left. Now you heat one of the paper clips with a cigarette lighter, and the clip drops (right photograph). Explain what happened.



- 23.74** Explain why the transition metals in Periods 5 and 6 have nearly identical radii in each group.

- 23.75** Based on the molar conductance values listed here for the series of platinum(IV) complexes, write the formula for each complex so as to show which ligands are in the coordination sphere of the metal. By way of example, the molar conductances of  $0.050\text{ M NaCl}$  and  $\text{BaCl}_2$  are  $107\text{ ohm}^{-1}$  and  $197\text{ ohm}^{-1}$ , respectively.

Complex	Molar Conductance ( $\text{ohm}^{-1}$ ) of $0.050\text{ M}$ Solution
$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$	523
$\text{Pt}(\text{NH}_3)_4\text{Cl}_4$	228
$\text{Pt}(\text{NH}_3)_3\text{Cl}_4$	97
$\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	0
$\text{KPt}(\text{NH}_3)_3\text{Cl}_5$	108

\*The ohm is a unit of resistance; conductance is the inverse of resistance.

- 23.76** (a) A compound with formula  $\text{RuCl}_3 \cdot 5\text{ H}_2\text{O}$  is dissolved in water, forming a solution that is approximately the same color as the solid. Immediately after forming the solution, the addition of excess  $\text{AgNO}_3(aq)$  forms 2 mol of solid  $\text{AgCl}$  per mole of complex. Write the formula for the compound, showing which ligands are likely to be present in the coordination sphere. (b) After a solution of  $\text{RuCl}_3 \cdot 5\text{ H}_2\text{O}$  has stood for about a year, addition of  $\text{AgNO}_3(aq)$  precipitates 3 mol of  $\text{AgCl}$  per mole of complex. What has happened in the ensuing time?

- 23.77** Sketch the structure of the complex in each of the following compounds and give the full compound name:

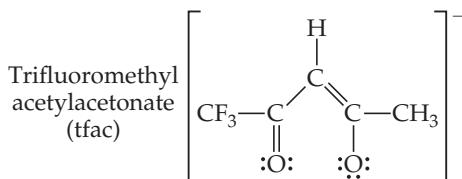
- (a)  $cis\text{-}[PtBrCl(NO_2)_2]^{2-}$
- (b)  $[Mn(CO)_3(C_6H_6)]^+$
- (c)  $cis\text{-}[CrCl_4](OH_2)_2^-$
- (d)  $trans\text{-}[Co(OH)(en)_2Cl]^+$

- 23.78** Does complex *d* in Exercise 23.77 have optical isomers?

- 23.79** The molecule *dimethylphosphinoethane*  $[(CH_3)_2PCH_2CH_2P(CH_3)_2$ , which is abbreviated dmpe] is used as a ligand for some complexes that serve as catalysts. A complex that contains this ligand is  $Mo(CO)_4(dmpe)$ . (a) Draw the Lewis structure for dmpe, and compare it with ethylenediamine as a coordinating ligand. (b) What is the oxidation state of Mo in  $Na_2[Mo(CN)_2(CO)_2(dmpe)]$ ? (c) Sketch the structure of the  $[Mo(CN)_2(CO)_2(dmpe)]^{2-}$  ion, including all the possible isomers.

- 23.80** The square-planar complex  $[Pt(en)Cl_2]$  only forms in one of two possible geometric isomers. Which isomer is not observed: *cis* or *trans*?

- 23.81** The acetylacetone ion forms very stable complexes with many metallic ions. It acts as a bidentate ligand, coordinating to the metal at two adjacent positions. Suppose that one of the  $CH_3$  groups of the ligand is replaced by a  $CF_3$  group, as shown here:



Sketch all possible isomers for the complex with three tfac ligands on cobalt(III). (You can use the symbol  $\bullet\circlearrowright$  to represent the ligand.)

- 23.82** Which transition metal atom is present in each of the following biologically important molecules: (a) hemoglobin, (b) chlorophylls, (c) siderophores, (d) hemocyanine.

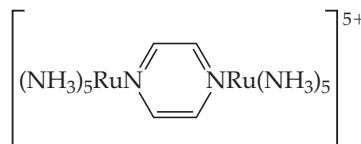
- 23.83** Carbon monoxide, CO, is an important ligand in coordination chemistry. When CO is reacted with nickel metal, the product is  $[Ni(CO)_4]$ , which is a toxic, pale yellow liquid. (a) What is the oxidation number for nickel in this compound? (b) Given that  $[Ni(CO)_4]$  is a diamagnetic molecule with a tetrahedral geometry, what is the electron configuration of nickel in this compound? (c) Write the name for  $[Ni(CO)_4]$  using the nomenclature rules for coordination compounds.

- 23.84** Some metal complexes have a coordination number of 5. One such complex is  $Fe(CO)_5$ , which adopts a *trigonal bipyramidal* geometry (see Figure 9.8). (a) Write the name for  $Fe(CO)_5$ , using the nomenclature rules for coordination compounds. (b) What is the oxidation state of Fe in this compound? (c) Suppose one of the CO ligands is replaced with a  $CN^-$  ligand, forming  $[Fe(CO)_4(CN)]^-$ . How many geometric isomers would you predict this complex could have?

- 23.85** Which of the following objects is chiral: (a) a pencil, (b) a computer keyboard, (c) a grand piano, (d) a molecular model of *cis*- $Fe(bipy)_2Cl_2$ , (e) a piece of plane A4 paper?

- 23.86** The complexes  $[CrBr_6]^{3-}$  and  $[Cr(NH_3)_6]^{3+}$  are both known. (a) Draw the *d*-orbital energy-level diagram for octahedral Cr(III) complexes. (b) What gives rise to the colors of these complexes? (c) Which of the two complexes would you expect to absorb light of higher energy?

- 23.87** One of the more famous species in coordination chemistry is the Creutz–Taube complex:



It is named for the two scientists who discovered it and initially studied its properties. The central ligand is pyrazine, a planar six-membered ring with nitrogens at opposite sides.

(a) How can you account for the fact that the complex, which has only neutral ligands, has an odd overall charge? (b) The metal is in a low-spin configuration in both cases. Assuming octahedral coordination, draw the *d*-orbital energy-level diagram for each metal. (c) In many experiments the two metal ions appear to be in exactly equivalent states. Can you think of a reason that this might appear to be so, recognizing that electrons move very rapidly compared to nuclei?

- 23.88** Solutions of  $[Co(NH_3)_6]^{2+}$ ,  $[Co(OH_2)_6]^{2+}$  (both octahedral), and  $[CoCl_4]^{2-}$  (tetrahedral) are colored. One is pink, one is blue, and one is yellow. Based on the spectrochemical series and remembering that the energy splitting in tetrahedral complexes is normally much less than that in octahedral ones, assign a color to each complex.

- 23.89** Oxyhemoglobin, with an  $O_2$  bound to iron, is a low-spin Fe(II) complex; deoxyhemoglobin, without the  $O_2$  molecule, is a high-spin complex. (a) Assuming that the coordination environment about the metal is octahedral, how many unpaired electrons are centered on the metal ion in each case? (b) What ligand is coordinated to the iron in place of  $O_2$  in deoxyhemoglobin? (c) Explain in a general way why the two forms of hemoglobin have different colors (hemoglobin is red, whereas deoxyhemoglobin has a bluish cast). (d) A 15-minute exposure to air containing 400 ppm of CO causes about 10% of the hemoglobin in the blood to be converted into the carbon monoxide complex, called carboxyhemoglobin. What does this suggest about the relative equilibrium constants for binding of carbon monoxide and  $O_2$  to hemoglobin? (e) CO is a strong-field ligand. What color might you expect carboxyhemoglobin to be?

- 23.90** Consider the tetrahedral anions  $VO_4^{3-}$  (orthovanadate ion),  $CrO_4^{2-}$  (chromate ion), and  $MnO_4^-$  (permanganate ion). (a) These anions are *isoelectronic*. What does this statement mean? (b) Would you expect these anions to exhibit *d-d* transitions? Explain. (c) As mentioned in “A Closer Look” on charge-transfer color, the violet color of  $MnO_4^-$  is due to a *ligand-to-metal charge transfer* (LMCT) transition. What is meant by this term? (d) The LMCT transition in  $MnO_4^-$  occurs at a wavelength of 565 nm. The  $CrO_4^{2-}$  ion is yellow. Is the wavelength of the LMCT transition for chromate larger or smaller than that for  $MnO_4^-$ ? Explain. (e) The  $VO_4^{3-}$  ion is colorless. Do you expect the light absorbed by the LMCT to fall in the UV or the IR region of the electromagnetic spectrum? Explain your reasoning.

- 23.91** Given the colors observed for  $VO_4^{3-}$  (orthovanadate ion),  $CrO_4^{2-}$  (chromate ion), and  $MnO_4^-$  (permanganate ion) (see Exercise 23.90), what can you say about how the energy separation between the ligand orbitals and the empty *d* orbitals changes as a function of the oxidation state of the transition metal at the center of the tetrahedral anion?

- 23.92** The blue-green color of turquoise is due to the presence of Cu(II) ions at octahedral sites which is coordinated with  $OH^-$  and  $H_2O$ . Assuming Cu(II) ions adopt an octahedral

geometry, draw the crystal-field splitting diagram for Cu(II) in this environment. Suppose that the turquoise crystal is subjected to high pressure. What do you predict for the variation in the wavelength of absorption of the turquoise as a function of pressure? Explain.

- 23.93** In 2001, chemists at State University of New York-Stony Brook succeeded in synthesizing the complex  $\text{trans}-[\text{Fe}(\text{CN})_4(\text{CO})_2]^{2-}$ , which could be a model of complexes that may have played a role in the origin of life. **(a)** Sketch the structure of the complex. **(b)** The complex is isolated as a sodium salt. Write the complete name of this salt. **(c)** What is the oxidation state of Fe in this complex? How many *d* electrons are associated with the Fe in this complex? **(d)** Would you expect this complex to be high spin or low spin? Explain.
- 23.94** When Alfred Werner was developing the field of coordination chemistry, it was argued by some that the optical activity he observed in the chiral complexes he had prepared was due to the presence of carbon atoms in the molecule. To disprove this argument, Werner synthesized a chiral complex of cobalt that had no carbon atoms in it, and he was able to resolve it into its enantiomers. Design a cobalt(III) complex that would be chiral if it could be synthesized and that contains no carbon atoms. (It may not be possible to synthesize the complex you design, but we will not worry about that for now.)

**23.95** Generally speaking, for a given metal and ligand, the stability of a coordination compound is greater for the metal in the +3 rather than in the +2 oxidation state (for metals that form stable +3 ions in the first place). Suggest an explanation, keeping in mind the Lewis acid-base nature of the metal-ligand bond.

**23.96** Many trace metal ions exist in the blood complexed with amino acids or small peptides. The anion of the amino acid glycine (gly),



can act as a bidentate ligand, coordinating to the metal through nitrogen and oxygen atoms. How many isomers are possible for **(a)**  $[\text{Zn}(\text{gly})_2]$  (tetrahedral), **(b)**  $[\text{Pt}(\text{gly})_2]$  (square planar), **(c)**  $[\text{Co}(\text{gly})_3]$  (octahedral)? Sketch all possible isomers. Use the symbol  $\bullet\circlearrowright$  to represent the ligand.

**23.97** The coordination complex  $[\text{Cr}(\text{CO})_6]$  forms colorless, diamagnetic crystals that melt at 90 °C. **(a)** What is the oxidation number of chromium in this compound? **(b)** Given that  $[\text{Cr}(\text{CO})_6]$  is diamagnetic, what is the electron configuration of chromium in this compound? **(c)** Given that  $[\text{Cr}(\text{CO})_6]$  is colorless, would you expect CO to be a weak-field or strong-field ligand? **(d)** Write the name for  $[\text{Cr}(\text{CO})_6]$  using the nomenclature rules for coordination compounds.

## Integrative Exercises

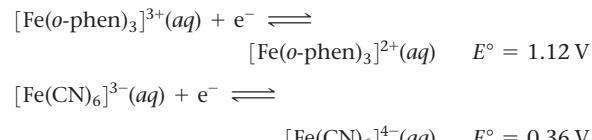
- 23.98** Metallic elements are essential components of many important enzymes operating within our bodies. *Carbonic anhydrase*, which contains  $\text{Zn}^{2+}$  in its active site, is responsible for rapidly interconverting dissolved  $\text{CO}_2$  and bicarbonate ion,  $\text{HCO}_3^-$ . The zinc in carbonic anhydrase is tetrahedrally coordinated by three neutral nitrogen-containing groups and a water molecule. The coordinated water molecule has a  $pK_a$  of 7.5, which is crucial for the enzyme's activity. **(a)** Draw the active site geometry for the Zn(II) center in carbonic anhydrase, just writing "N" for the three neutral nitrogen ligands from the protein. **(b)** Compare the  $pK_a$  of carbonic anhydrase's active site with that of pure water; which species is more acidic? **(c)** When the coordinated water to the Zn(II) center in carbonic anhydrase is deprotonated, what ligands are bound to the Zn(II) center? Assume the three nitrogen ligands are unaffected. **(d)** The  $pK_a$  of  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  is 10. Suggest an explanation for the difference between this  $pK_a$  and that of carbonic anhydrase. **(e)** Would you expect carbonic anhydrase to have a deep color, like hemoglobin and other metal-ion-containing proteins do? Explain.

- 23.99** Two different compounds have the formulation  $\text{CoBr}(\text{SO}_4) \cdot 5 \text{ NH}_3$ . Compound A is dark violet, and compound B is red-violet. When compound A is treated with  $\text{AgNO}_3(aq)$ , no reaction occurs, whereas compound B reacts with  $\text{AgNO}_3(aq)$  to form a white precipitate. When compound A is treated with  $\text{BaCl}_2(aq)$ , a white precipitate is formed, whereas compound B has no reaction with  $\text{BaCl}_2(aq)$ . **(a)** Is Co in the same oxidation state in these complexes? **(b)** Explain the reactivity of compounds A and B with  $\text{AgNO}_3(aq)$  and  $\text{BaCl}_2(aq)$ . **(c)** Are compounds A and B isomers of one another? If so, which category from Figure 23.19 best describes the isomerism observed

for these complexes? **(d)** Would compounds A and B be expected to be strong electrolytes, weak electrolytes, or nonelectrolytes?

- 23.100** An iron complex formed from a solution containing hydrochloric acid and bipyridine is purified and analyzed. It contains 9.38% Fe, 60.53% carbon, 4.06% hydrogen, and 14.12% nitrogen by mass. The remainder of the compound is chlorine. An aqueous solution of the complex has about the same electrical conductivity as an equimolar solution of  $\text{K}_2[\text{CuCl}_4]$ . Write the formula of the compound, using brackets to denote the iron and its coordination sphere.

- 23.101** The  $E^\circ$  values for two low-spin iron complexes in acidic solution are as follows:

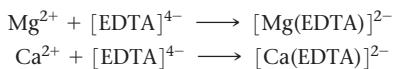


**(a)** Is it thermodynamically favorable to reduce both Fe(III) complexes to their Fe(II) analogs? Explain. **(b)** Which complex,  $[\text{Fe}(o\text{-phen})_3]^{3+}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$ , is more difficult to reduce? **(c)** Suggest an explanation for your answer to (b).

- 23.102** A platinum complex formed from a solution containing chloride ion and ammonia is found on elemental analysis to contain 23.63% chlorine, 9.34% nitrogen, 2.02% hydrogen by mass. The compound is slightly soluble in several organic solvents; its solutions in water or alcohol do not conduct electricity. It is found experimentally to have a net dipole moment. Write the chemical formula of this platinum complex, and indicate its probable structure.

- 23.103** (a) In early studies it was observed that when the complex  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Br}$  was placed in water, the electrical conductivity of a 0.05 M solution changed from an initial value of  $191 \text{ ohm}^{-1}$  to a final value of  $374 \text{ ohm}^{-1}$  over a period of an hour or so. Suggest an explanation for the observed results. (See Exercise 23.75 for relevant comparison data.) (b) Write a balanced chemical equation to describe the reaction. (c) A 500 mL solution is made up by dissolving 3.87 g of the complex. As soon as the solution is formed, and before any change in conductivity has occurred, a 25.00 mL portion of the solution is titrated with 0.0100 M  $\text{AgNO}_3$  solution. What volume of  $\text{AgNO}_3$  solution do you expect to be required to precipitate the free  $\text{Br}^-$ (aq)? (d) Based on the response you gave to part (b), what volume of  $\text{AgNO}_3$  solution would be required to titrate a fresh 25.00 mL sample of  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Br}$  after all conductivity changes have occurred?

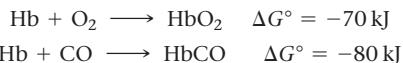
- 23.104** The total concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in a sample of hard water was determined by titrating a 0.100 L sample of the water with a solution of  $\text{EDTA}^{4-}$ . The  $\text{EDTA}^{4-}$  chelates the two cations:



It requires 31.5 mL of 0.0104 M  $[\text{EDTA}]^{4-}$  solution to reach the end point in the titration. A second 0.100 L sample was

then treated with sulfate ion to precipitate  $\text{Ca}^{2+}$  as calcium sulfate. The  $\text{Mg}^{2+}$  was then titrated with 18.7 mL of 0.0104 M  $[\text{EDTA}]^{4-}$ . Calculate the concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the hard water in mg/L.

- 23.105** Carbon monoxide is toxic because it binds more strongly to the iron in hemoglobin (Hb) than does  $\text{O}_2$ , as indicated by these approximate standard free-energy changes in blood:



Using these data, estimate the equilibrium constant at 298 K for the equilibrium



- 23.106** The value of  $\Delta$  for the  $[\text{Mn}_6]^{3-}$  complex is 198.58 kJ/mol. Calculate the expected wavelength of the absorption corresponding to promotion of an electron from the lower energy to the higher-energy  $d$ -orbital set in this complex. Should the complex absorb in the visible range?

- 23.107** A Zn electrode is immersed in a solution that is 1.00 M in  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and 1.00 M in  $\text{NH}_3$ . When the cathode is a standard hydrogen electrode, the emf of the cell is found to be +1.04 V. What is the formation constant for  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ?

## Design an Experiment

Following a procedure found in a scientific paper, you go into the lab and attempt to prepare crystals of dichlorobis(ethylenediamine) cobalt(III) chloride. The paper states that this compound can be made by reacting  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$ , an excess of ethylenediamine,  $\text{O}_2$  from the air (which acts as an oxidizing agent), water, and concentrated hydrochloric acid. At the end of the reaction, you filter off the solution and are left with a green, crystalline product. (a) What experiment(s) could you perform to confirm that you have prepared

$[\text{CoCl}_2(\text{en})_2]\text{Cl}$  and not  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ? (b) How could you verify that cobalt was present as  $\text{Co}^{3+}$  and determine the spin state of the cobalt complex in your product? (c) How many geometric isomers exist for  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ ? How could you determine if your product contains a single geometric isomer or a mixture of geometric isomers? (d) If the product does contain a single geometric isomer how would you determine which one was present? (Hint: You may find the information in Table 23.3 helpful.)