

## Covalent Network Solids, Salts, Polymers

*The transition metals are elements with partially filled  $d$  orbitals, located in the  $d$ -block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used in the isolation of the elements from their ores depends upon the concentration of the element in its ore and the difficulty of reducing ions of the elements to the metals. Metals that are more active are more difficult to reduce. Transition metals exhibit chemical behavior typical of metals. For example, they oxidize in air upon heating and react with elemental halogens to form halides. Those elements that lie above hydrogen in the activity series react with acids, producing salts and hydrogen gas. Oxides, hydroxides, and carbonates of transition metal compounds in low oxidation states are basic. Halides and other salts are generally stable in water, although oxygen must be excluded in some cases. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity. The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination number of four) and octahedral (with a coordination number of six). Cis and trans configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use. Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal  $d$  orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting ( $\Delta_{\text{oct}}$ ) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the  $t_{2g}$  orbitals are completely filled before any electrons occupy the  $e_g$  orbitals. Weak-field ligands favor formation of high-spin complexes. The  $t_{2g}$  and the  $e_g$  orbitals are singly occupied before any are doubly occupied.*

Transition metals are defined as those elements that have (or readily form) partially filled  $d$  orbitals. As shown in [Figure 40.2](#), the  $d$ -block elements in groups 3–11 are transition elements. The  $f$ -block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the  $d$  orbital is partially occupied before the  $f$  orbitals. The  $d$  orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.

**Figure 40.1**

The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

Period

Group

Periodic Table of the Elements

18

1	1	2											13	14	15	16	17	18	
1	1	2																	2
	H																		He
	1.008																		4.003
	hydrogen																		helium
2	3	4																	10
	Li	Be																	Ne
	6.94	9.012																	20.18
	lithium	beryllium																	neon
3	11	12																	18
	Na	Mg																	Ar
	22.99	24.31																	39.95
	sodium	magnesium																	argon
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
	39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38	69.72	72.63	74.92	78.97	79.90	83.80	
	potassium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
	85.47	87.62	88.91	91.22	92.91	95.95	[97]	101.1	102.9	106.4	107.9	112.4	114.8	118.7	121.8	127.6	126.9	131.3	
	rubidium	strontium	yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium	indium	tin	antimony	tellurium	iodine	xenon	
6	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
	132.9	137.3		178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	[209]	[210]	[222]	
	cesium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon	
7	87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
	Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	
	[223]	[226]		[267]	[270]	[271]	[270]	[277]	[276]	[281]	[282]	[285]	[285]	[289]	[288]	[293]	[294]	[294]	
	francium	radium		rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium	nihonium	flerovium	moscovium	livermorium	tennessine	oganesson	
				57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
				138.9	140.1	140.9	144.2	[145]	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.1	175.0	
				lanthanum	cerium	praseodymium	neodymium	promethium	samarium	europium	gadolinium	terbium	dysprosium	holmium	erbium	thulium	ytterbium	lutetium	
				89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
				[227]	232.0	231.0	238.0	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]	[262]	
				actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium	lawrencium	

Atomic number → 1

← Symbol

← Atomic mass

Name → hydrogen

Color Code

Metal

Metalloid

Nonmetal

Solid

Liquid

Gas

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

## EXAMPLE 40.0.1

### Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

(a) cerium(III)

(b) lead(II)

(c)  $\text{Ti}^{2+}$

(d)  $\text{Am}^{3+}$

(e)  $\text{Pd}^{2+}$

For the examples that are transition metals, determine to which series they belong.

### Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

(a)  $\text{Ce}^{3+}[\text{Xe}]4f^1$ ;  $\text{Ce}^{3+}$  is an inner transition element in the lanthanide series.

(b)  $\text{Pb}^{2+}[\text{Xe}]6s^25d^{10}4f^{14}$ ; the electrons are lost from the *p* orbital. This is a main group element.

(c) titanium(II)  $[\text{Ar}]3d^2$ ; first transition series

(d) americium(III)  $[\text{Rn}]5f^6$ ; actinide

(e) palladium(II)  $[\text{Kr}]4d^8$ ; second transition series

### Check Your Learning

Give an example of an ion from the first transition series with no *d* electrons.

### ✓ Answer

$\text{V}^{5+}$  is one possibility. Other examples include  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Mn}^{7+}$ .

## 40.0.2 CHEMISTRY IN EVERYDAY LIFE

### Uses of Lanthanides in Devices

Lanthanides (elements 57–71) are fairly abundant in the earth's crust, despite their historic characterization as rare earth elements. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth's crust than silver (4.5

×

$10^{-5}\%$  versus 0.79

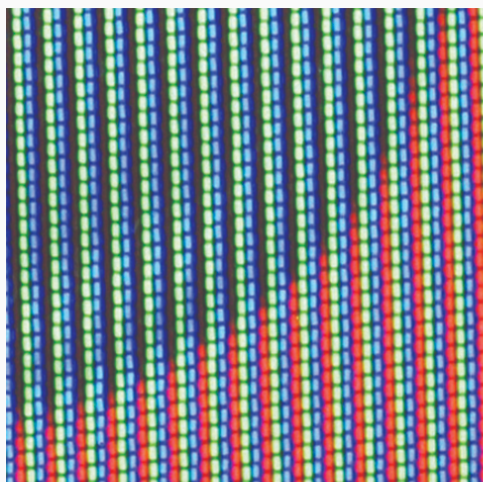


$10^{-5}\%$  by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

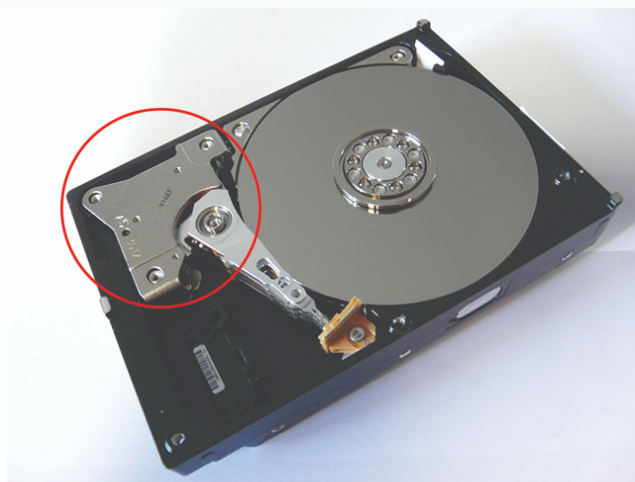
The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline ([Figure 40.3](#)). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.

**Figure 40.2**

(a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by "KUERT Datenrettung"/Flickr)



(a)



(b)

As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost \$110/kg; by 2014, the price had increased to \$470/kg. Increasing the supply of lanthanoid



elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable coordination compounds, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

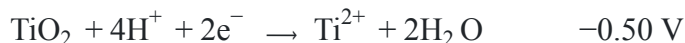
## 40.1 Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (see [Appendix H](#)), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ . On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Co}^{2+}$ , form colorful hydrated ions that are stable in water. However, ions in the period just below these ( $\text{Mo}^{3+}$ ,  $\text{Ru}^{3+}$ , and  $\text{Ir}^{2+}$ ) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as



and



Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the platinum metals. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in [Figure 40.4](#). As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

**Figure 40.3**

*Transition metals of the first transition series can form compounds with varying oxidation states.*

<sup>21</sup> <b>Sc</b>	<sup>22</sup> <b>Ti</b>	<sup>23</sup> <b>V</b>	<sup>24</sup> <b>Cr</b>	<sup>25</sup> <b>Mn</b>	<sup>26</sup> <b>Fe</b>	<sup>27</sup> <b>Co</b>	<sup>28</sup> <b>Ni</b>	<sup>29</sup> <b>Cu</b>	<sup>30</sup> <b>Zn</b>
								<b>1+</b>	
		<b>2+</b>	<b>2+</b>	<b>2+</b>	<b>2+</b>	<b>2+</b>	<b>2+</b>	<b>2+</b>	<b>2+</b>
<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	<b>3+</b>	
	<b>4+</b>	<b>4+</b>	<b>4+</b>	<b>4+</b>					
		<b>5+</b>							
			<b>6+</b>	<b>6+</b>	<b>6+</b>				
				<b>7+</b>					

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr<sup>3+</sup> ions in water and, in the absence of air, less stable Cr<sup>2+</sup> ions. The sulfide with the highest oxidation state for chromium is Cr<sub>2</sub>S<sub>3</sub>, which contains the Cr<sup>3+</sup> ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

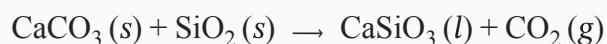
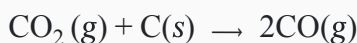
### EXAMPLE 40.1.1

#### Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

#### Solution

First, we need to look up the reduction half reactions (in [Appendix L](#)) for each oxide in the specified oxidation state:



A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

#### Check Your Learning

Predict what reaction (if any) will occur between HCl and Co(s), and between HBr and Pt(s). You will need to use the standard reduction potentials from [Appendix L](#).

#### ✓ Answer



no reaction because Pt(s) will not be oxidized by H<sup>+</sup>

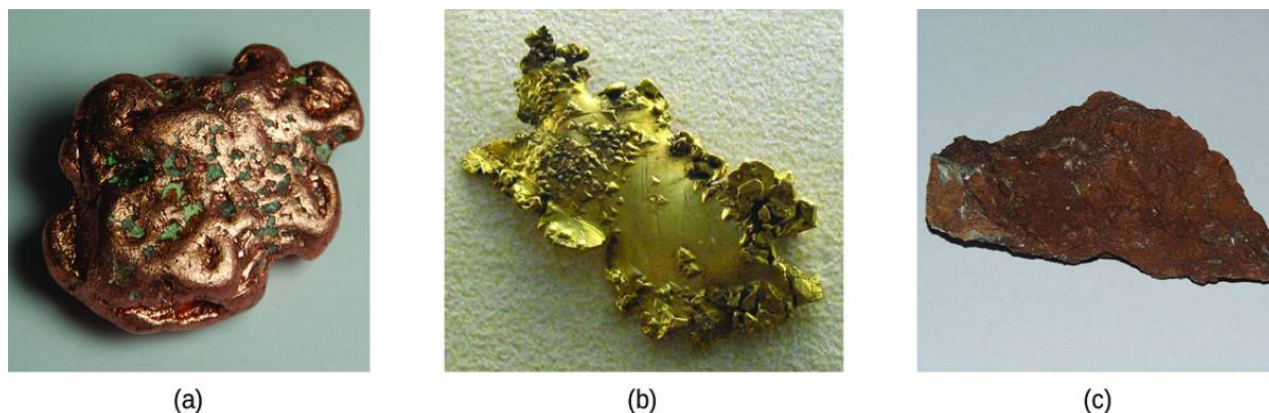
## 40.2 Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods. Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form ([Figure 40.5](#)). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe<sub>2</sub>O<sub>3</sub>). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations

developed iron smelting, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.

**Figure 40.4**

*Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by <http://images-of-elements.com/copper-2.jpg>; credit c: modification of work by <http://images-of-elements.com/iron-ore.jpg>)*



Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the  $d$ -block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the  $f$ -block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

We shall discuss the processes used for the isolation of iron, copper, and silver because these three processes illustrate the principal means of isolating most of the  $d$ -block metals. In general, each of these processes involves three principal steps: preliminary treatment, smelting, and refining.

1. Preliminary treatment. In general, there is an initial treatment of the ores to make them suitable for the extraction of the metals. This usually involves crushing or grinding the ore, concentrating the metal-bearing components, and sometimes treating these substances chemically to convert them into compounds that are easier to reduce to the metal.
2. Smelting. The next step is the extraction of the metal in the molten state, a process called smelting, which includes reduction of the metallic compound to the metal. Impurities may be removed by the addition of a compound that forms a slag—a substance with a low melting point that can be readily separated from the molten metal.
3. Refining. The final step in the recovery of a metal is refining the metal. Low boiling metals such as zinc and mercury can be refined by distillation. When fused on an inclined table, low melting metals like tin flow away from higher-melting impurities. Electrolysis is another common method for refining metals.

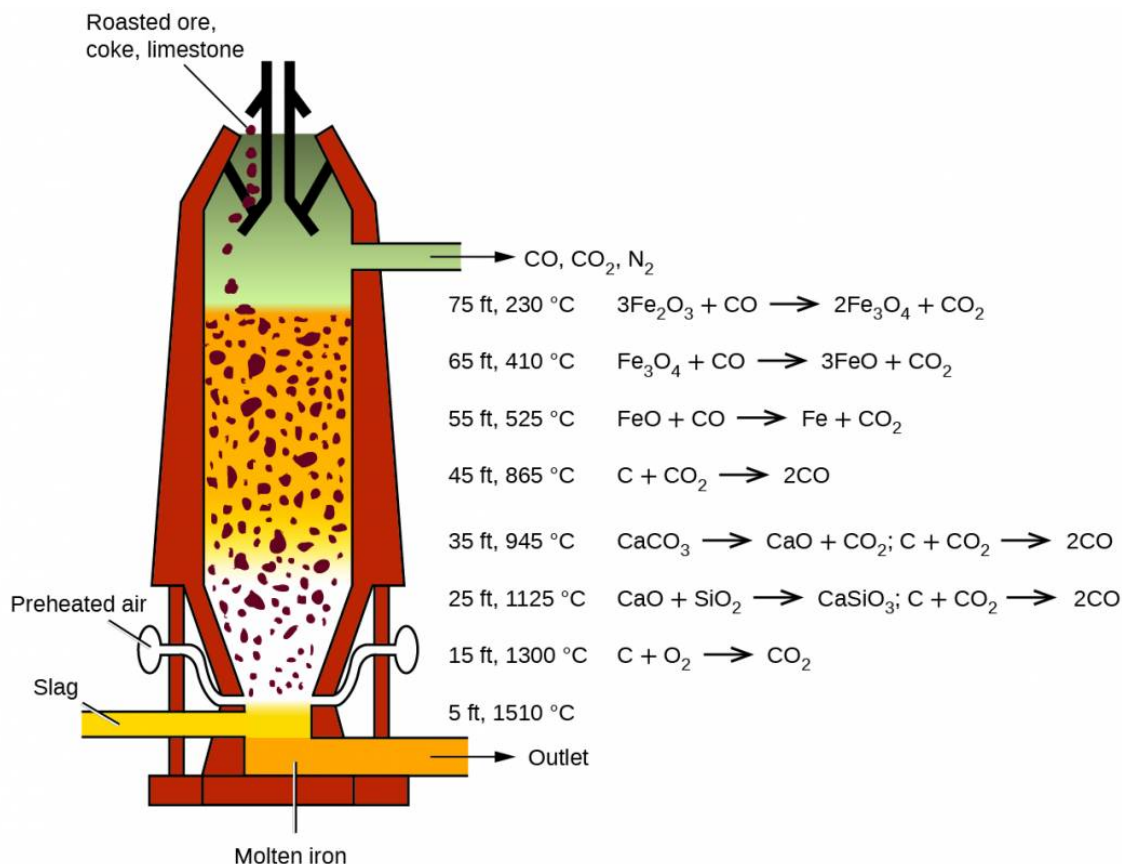
## 40.3 Isolation of Iron

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. For a long time, charcoal was the form of carbon used in the reduction process. The production and use of iron became much more widespread about 1620, when coke was introduced as the reducing agent. Coke is a form of carbon formed by heating coal in the absence of air to remove impurities.

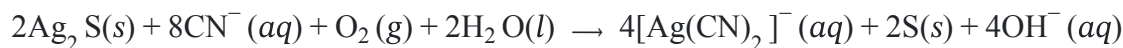
The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter ([Figure 19.6](#)) in which the roasted ore, coke, and limestone (impure  $\text{CaCO}_3$ ) are introduced continuously into the top. Molten iron and slag are withdrawn at the bottom. The entire stock in a furnace may weigh several hundred tons.

**Figure 40.5**

*Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.*



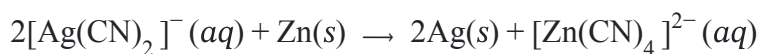
Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:



The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in [Figure 40.6](#).

The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:





Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant ([Figure 40.7](#)).

**Figure 40.6**

*Molten iron is shown being cast as steel. (credit: Clint Budd)*



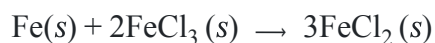
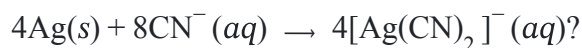
Much of the iron produced is refined and converted into steel. Steel is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle.

## LINK TO LEARNING

You can watch an animation of [steelmaking](#) that walks you through the process.

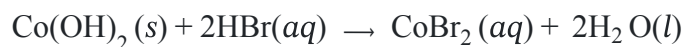
## 40.4 Isolation of Copper

The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu<sub>2</sub>S, FeS, FeO, and SiO<sub>2</sub>, is mixed with limestone, which serves as a flux (a material that aids in the removal of impurities), and heated. Molten slag forms as the iron and silica are removed by Lewis acid-base reactions:



In these reactions, the silicon dioxide behaves as a Lewis acid, which accepts a pair of electrons from the Lewis base (the oxide ion).

Reduction of the Cu<sub>2</sub>S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu<sub>2</sub>S into Cu<sub>2</sub>O. As soon as copper(I) oxide is formed, it is reduced by the remaining copper(I) sulfide to metallic copper:



The copper obtained in this way is called blister copper because of its characteristic appearance, which is due to the air blisters it contains ([Figure 40.8](#)). This impure copper is cast into large plates, which are used as anodes in the electrolytic refining of the metal (which is described in the chapter on electrochemistry).

### Figure 40.7

*Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: "Tortitude"/Wikimedia Commons)*

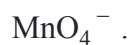
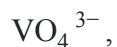
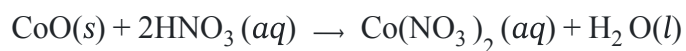


## 40.5 Isolation of Silver

Silver sometimes occurs in large nuggets ([Figure 40.9](#)) but more frequently in veins and related deposits. At one time, panning was an effective method of isolating both silver and gold nuggets. Due to their low reactivity, these metals, and a few others, occur in deposits as nuggets. The discovery of platinum was due to Spanish explorers in Central America mistaking platinum nuggets for silver. When the metal is not in the form of nuggets, it is often useful to employ a process called hydrometallurgy to separate silver from its ores. Hydrometallurgy involves the separation of a metal from a mixture by first converting it into soluble ions and then extracting and reducing them to precipitate the pure metal. In the presence of air, alkali metal cyanides readily form the soluble dicyanoargentate(I) ion,



from silver metal or silver-containing compounds such as  $\text{Ag}_2\text{S}$  and  $\text{AgCl}$ . Representative equations are:

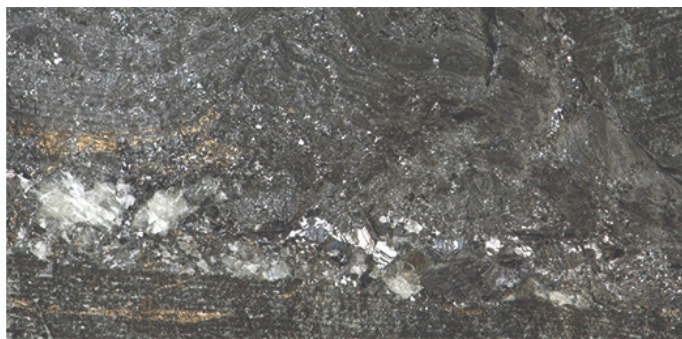


**Figure 40.8**

Naturally occurring free silver may be found as nuggets (a) or in veins (b). (credit a: modification of work by "Teravolt"/Wikimedia Commons; credit b: modification of work by James St. John)

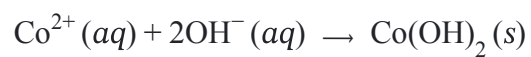


(a)



(b)

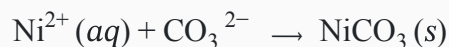
The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:



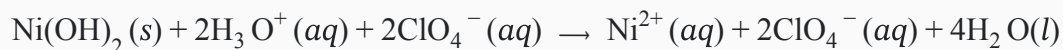
### EXAMPLE 40.5.1

#### Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargentate(I) ions:



Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:



#### Solution

The charges, as well as the atoms, must balance in reactions. The silver atom is being oxidized from the 0 oxidation state to the 1+ state. Whenever something loses electrons, something must also gain electrons (be reduced) to balance the equation. Oxygen is a good oxidizing agent for these reactions because it can gain electrons to go from the 0 oxidation state to the 2- state.

#### Check Your Learning

During the refining of iron, carbon must be present in the blast furnace. Why is carbon necessary to convert iron oxide into iron?

#### ✓ Answer

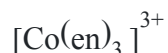
The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

## 40.6 Transition Metal Compounds

The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by the transition elements gives these compounds a metal-based, oxidation-reduction chemistry. The chemistry of several classes of compounds containing elements of the transition series follows.

### 40.6.0.1 Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:



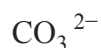


Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:



The stoichiometry of the metal halide that results from the reaction of the metal with a halogen is determined by the relative amounts of metal and halogen and by the strength of the halogen as an oxidizing agent. Generally, fluorine forms fluoride-containing metals in their highest oxidation states. The other halogens may not form analogous compounds.

In general, the preparation of stable water solutions of the halides of the metals of the first transition series is by the addition of a hydrohalic acid to carbonates, hydroxides, oxides, or other compounds that contain basic anions. Sample reactions are:

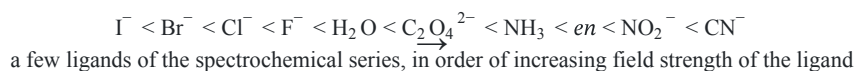


Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:



The polarity of bonds with transition metals varies based not only upon the electronegativities of the atoms involved but also upon the oxidation state of the transition metal. Remember that bond polarity is a continuous spectrum with electrons being shared evenly (covalent bonds) at one extreme and electrons being transferred completely (ionic bonds) at the other. No bond is ever 100% ionic, and the degree to which the electrons are evenly distributed determines many properties of the compound. Transition metal halides with low oxidation numbers form more ionic bonds. For example, titanium(II) chloride and titanium(III) chloride ( $\text{TiCl}_2$  and  $\text{TiCl}_3$ ) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ( $\text{TiCl}_4$ ) is a volatile liquid, consistent with having covalent titanium-chlorine bonds. All halides of the heavier *d*-block elements have significant covalent characteristics.

The covalent behavior of the transition metals with higher oxidation states is exemplified by the reaction of the metal tetrahalides with water. Like covalent silicon tetrachloride, both the titanium and vanadium tetrahalides react with water to give solutions containing the corresponding hydrohalic acids and the metal oxides:



$$\nu = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^8 \text{ m/s}}{\frac{499 \text{ nm} \times 1 \text{ m}}{10^9 \text{ nm}}} = 6.01 \times 10^{14} \text{ Hz}$$

### 40.6.0.2 Oxides

As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more

covalent. These variations in bonding are because the electronegativities of the elements are not fixed values. The electronegativity of an element increases with increasing oxidation state. Transition metals in low oxidation states have lower electronegativity values than oxygen; therefore, these metal oxides are ionic. Transition metals in very high oxidation states have electronegativity values close to that of oxygen, which leads to these oxides being covalent.

The oxides of the first transition series can be prepared by heating the metals in air. These oxides are  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ , and  $\text{CuO}$ .

Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating cobalt(II) hydroxide:

With the exception of  $\text{CrO}_3$  and  $\text{Mn}_2\text{O}_7$ , transition metal oxides are not soluble in water. They can react with acids and, in a few cases, with bases. Overall, oxides of transition metals with the lowest oxidation states are basic (and react with acids), the intermediate ones are amphoteric, and the highest oxidation states are primarily acidic. Basic metal oxides at a low oxidation state react with aqueous acids to form solutions of salts and water. Examples include the reaction of cobalt(II) oxide accepting protons from nitric acid, and scandium(III) oxide accepting protons from hydrochloric acid:

The oxides of metals with oxidation states of 4+ are amphoteric, and most are not soluble in either acids or bases. Vanadium(V) oxide, chromium(VI) oxide, and manganese(VII) oxide are acidic. They react with solutions of hydroxides to form salts of the oxyanions

and

For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids  $\text{H}_2\text{CrO}_4$  and  $\text{HMnO}_4$ , respectively.

### 40.6.0.3 Hydroxides

When a soluble hydroxide is added to an aqueous solution of a salt of a transition metal of the first transition series, a gelatinous precipitate forms. For example, adding a solution of sodium hydroxide to a solution of cobalt sulfate produces a gelatinous pink or blue precipitate of cobalt(II) hydroxide. The net ionic equation is:

In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:

These substances do not contain hydroxide ions. However, both the hydroxides and the hydrated oxides react with acids to form salts and water. When precipitating a metal from solution, it is necessary to avoid an excess of hydroxide ion, as this may lead to complex ion formation as discussed later in this chapter. The precipitated metal hydroxides can be separated for further processing or for waste disposal.

### 40.6.0.4 Carbonates

Many of the elements of the first transition series form insoluble carbonates. It is possible to prepare these carbonates by the addition of a soluble carbonate salt to a solution of a transition metal salt. For example, nickel carbonate can be prepared from solutions of nickel nitrate and sodium carbonate according to the following net ionic equation:

The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metal salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

### 40.6.0.5 Other Salts

In many respects, the chemical behavior of the elements of the first transition series is very similar to that of the main group metals. In particular, the same types of reactions that are used to prepare salts of the main group metals can be used to prepare simple ionic salts of these elements.

A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:

The common compounds that we have just discussed can also be used to prepare salts. The reactions involved include the reactions of oxides, hydroxides, or carbonates with acids. For example:

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

In our discussion of oxides in this section, we have seen that reactions of the covalent oxides of the transition elements with hydroxides form salts that contain oxyanions of the transition elements.

## 40.6.1 HOW SCIENCES INTERCONNECT

### High Temperature Superconductors

A superconductor is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb<sub>3</sub>Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

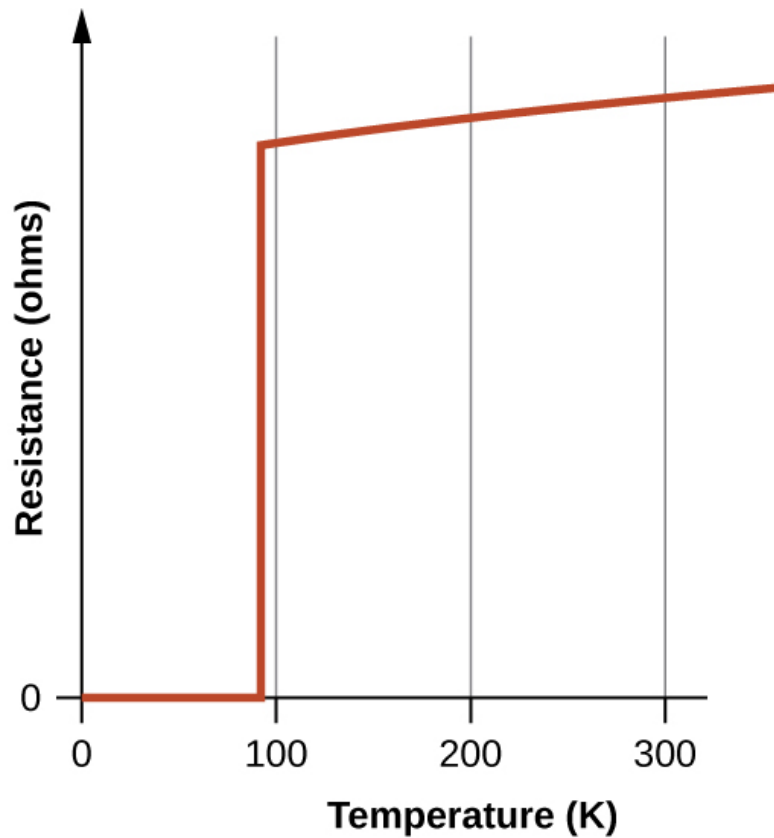
The new materials become superconducting at temperatures close to 90 K ([Figure 19.10](#)), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

Further advances during the same period included materials that became superconducting at even higher temperatures and with a wider array of materials. The DuPont team led by Uma Chowdry and Arthur Sleight identified Bismuth-Strontium-Copper-Oxides that became superconducting at temperatures as high as 110 K and, importantly, did not contain rare earth elements. Advances continued through the subsequent decades until, in 2020, a team led by Ranga Dias at University of Rochester announced the development of a room-temperature superconductor, opening doors to widespread applications. More research and development is needed to realize the potential of these materials, but the possibilities are very promising.

**Figure 40.9**

*The resistance of the high-temperature superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.*





Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.

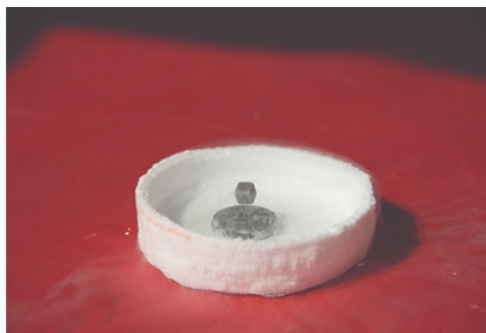
Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors ([Figure 40.11](#)).

**Figure 40.10**

*(a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)*



(a)



(b)

## LINK TO LEARNING

Watch how a [high-temperature superconductor](#) levitates around a magnetic racetrack in the video.

## Learning Objectives

By the end of this section, you will be able to:

- List the defining traits of coordination compounds
- Describe the structures of complexes containing monodentate and polydentate ligands
- Use standard nomenclature rules to name coordination compounds
- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored ([Figure 19.12](#)). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

### Figure 40.11

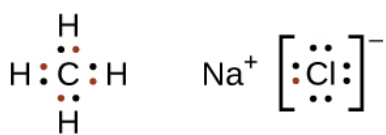
*Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell ( $d^0$ ) or with filled d subshells ( $d^{10}$ ) usually form colorless complexes. This figure shows, from left to right, solutions containing  $[M(H_2O)_6]^{n+}$  ions with  $M = Sc^{3+}(d^0)$ ,  $Cr^{3+}(d^3)$ ,  $Co^{2+}(d^7)$ ,  $Ni^{2+}(d^8)$ ,  $Cu^{2+}(d^9)$ , and  $Zn^{2+}(d^{10})$ . (credit: Sahar Atwa)*



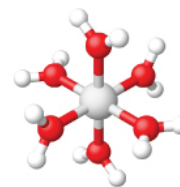
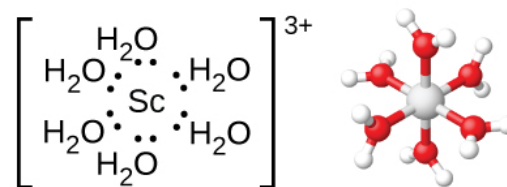
Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form  $\text{CH}_4$ . The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit  $\text{NaCl}$  (Figure 40.13). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.

**Figure 40.12**

(a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)



(a)

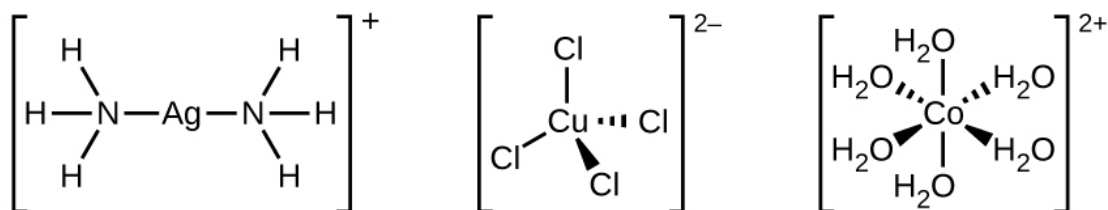


(b)

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in  $[\text{Ag}(\text{NH}_3)_2]^+$  is two ([Figure 40.14](#)). For the copper(II) ion in  $[\text{CuCl}_4]^{2-}$ , the coordination number is four, whereas for the cobalt(II) ion in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  the coordination number is six. Each of these ligands is monodentate, from the Greek for “one toothed,” meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

**Figure 40.13**

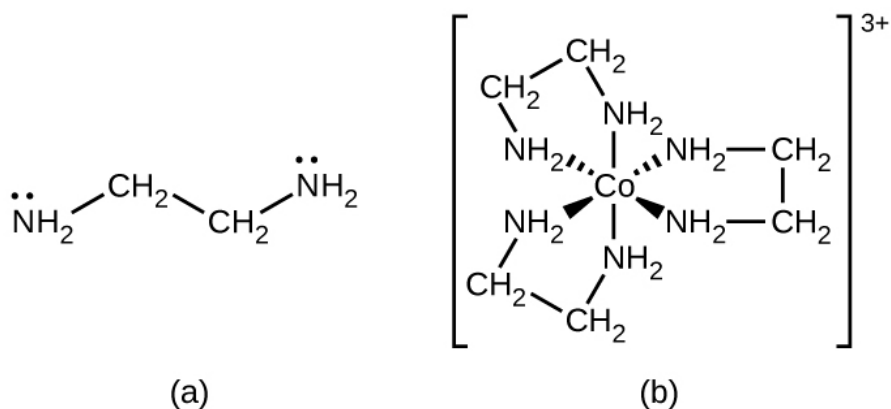
The complexes (a)  $[\text{Ag}(\text{NH}_3)_2]^+$ , (b)  $[\text{CuCl}_4]^{2-}$ , and (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.



Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base ([Figure 40.15](#)). Both of the atoms can coordinate to a single metal center. In the complex  $[\text{Co}(\text{en})_3]^{3+}$ , there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

**Figure 40.14**

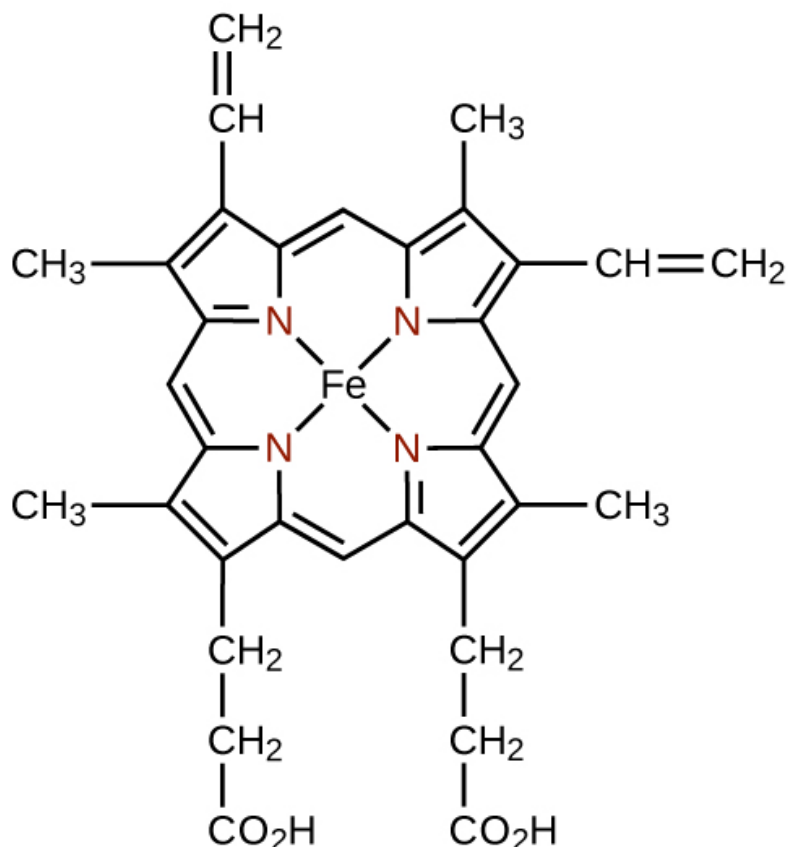
(a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex contains three of these ligands, each forming two bonds to the cobalt ion.



Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or “many teeth”) because it can bite into the metal center with more than one bond. The term chelate (pronounced “KEY-late”) from the Greek for “claw” is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab’s claw would hold a marble. [Figure 40.15](#) showed one example of a chelate. The heme complex in hemoglobin is another important example ([Figure 40.16](#)). It contains a polydentate ligand with four donor atoms that coordinate to iron.

**Figure 40.15**

The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

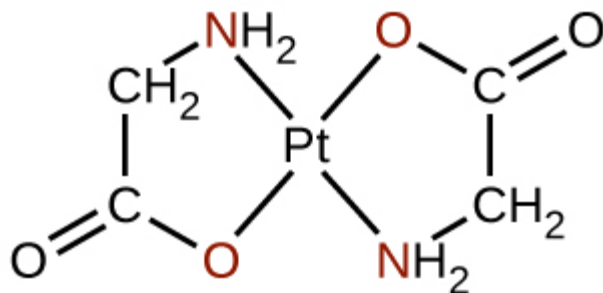


Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as  $\text{NH}_3$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$ , are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , and the anion of the acid glycine,

([Figure 40.17](#)) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme ([Figure 40.16](#)) is a tetradentate ligand.

**Figure 40.16**

Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.





## 40.7 The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding *-o* to the stem name of the group. For examples, see [Table 19.1](#). For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* ( $\text{H}_2\text{O}$ ), *ammine* ( $\text{NH}_3$ ), *carbonyl* ( $\text{CO}$ ), and *nitrosyl* ( $\text{NO}$ ). For example, name  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  as diamminetetrachloroplatinum(IV).

**Table 40.17**

*Examples of Anionic Ligands*

Anionic Ligand	Name
$\text{F}^-$	fluoro
$\text{Cl}^-$	chloro
$\text{Br}^-$	bromo
$\text{I}^-$	iodo
$\text{CN}^-$	cyano
	nitrate
$\text{OH}^-$	hydroxo
$\text{O}^{2-}$	oxo
	oxalato
	carbonato

3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses *bis-* to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups ( $\text{C}_5\text{H}_4\text{N}$ ).

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state ([Table 41.2](#) and [Table 41.3](#)). When the complex is an anion, the suffix *-ate* is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state ([Table 41.4](#)). Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead of *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Br}$ , the coordination sphere (in brackets) has a charge of  $1+$  to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of  $1-$  each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal:  $+1 = -2 + x$ , so the oxidation state ( $x$ ) is equal to  $3+$ .

**Table 40.18**

*Examples in Which the Complex Is a Cation*

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	hexaamminecobalt(III) chloride
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	tetraamminedichloroplatinum(IV) ion
$[\text{Ag}(\text{NH}_3)_2]^+$	diamminesilver(I) ion
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	tetraaquadichlorochromium(III) chloride
$[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$	tris(ethylenediamine)cobalt(III) sulfate

**Table 40.19**

*Examples in Which the Complex Is Neutral*

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	diamminetetrachloroplatinum(IV)
$[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]$	dichlorobis(ethylenediamine)nickel(II)

**Table 40.20**

*Examples in Which the Complex Is an Anion*

$[\text{PtCl}_6]^{2-}$	hexachloroplatinate(IV) ion
$\text{Na}_2[\text{SnCl}_6]$	sodium hexachlorostannate(IV)

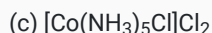
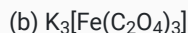
## LINK TO LEARNING

Do you think you understand naming coordination complexes? You can look over more examples and test yourself with [online quizzes](#) at the University of Sydney's site.

## EXAMPLE 40.7.1

### Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.



### Solution

(a) There are two  $\text{Na}^+$  ions, so the coordination sphere has a negative two charge:  $[\text{PtCl}_6]^{2-}$ . There are six anionic chloride ligands, so  $-2 = -6 + x$ , and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six. (b) The coordination sphere has a charge of 3- (based on the potassium) and the oxalate ligands each have a charge of 2-, so the metal oxidation state is given by  $-3 = -6 + x$ , and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six. (c) In this example, the coordination sphere has a cationic charge of 2+. The  $\text{NH}_3$  ligand is neutral, but the chloro ligand has a charge of 1-. The oxidation state is found by  $+2 = -1 + x$  and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

### Check Your Learning

The complex potassium dicyanoargentate(I) is used to make antiseptic compounds. Give the formula and coordination number.

### ✓ Answer

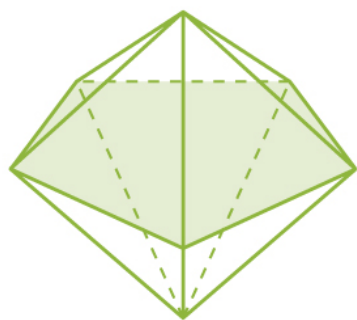
$\text{K}[\text{Ag}(\text{CN})_2]$ ; coordination number two

## The Structures of Complexes

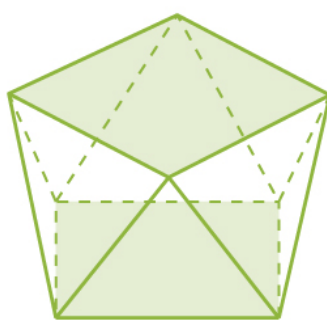
For transition metal complexes, the coordination number determines the geometry around the central metal ion. The most common structures of the complexes in coordination compounds are square planar, tetrahedral, and octahedral, corresponding to coordination numbers of four, four, and six, respectively. Coordination numbers greater than six are less common and yield a variety of structures (see [Figure 40.18](#) and [Table 40.5](#)):

**Figure 40.21**

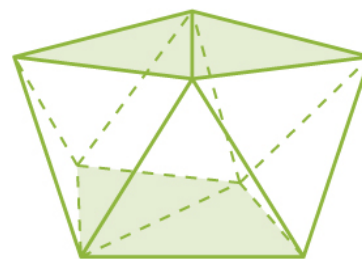
*These are geometries of some complexes with coordination numbers of seven and eight.*



Pentagonal bipyramid



Square antiprism



Dodecahedral

**Table 40.22**

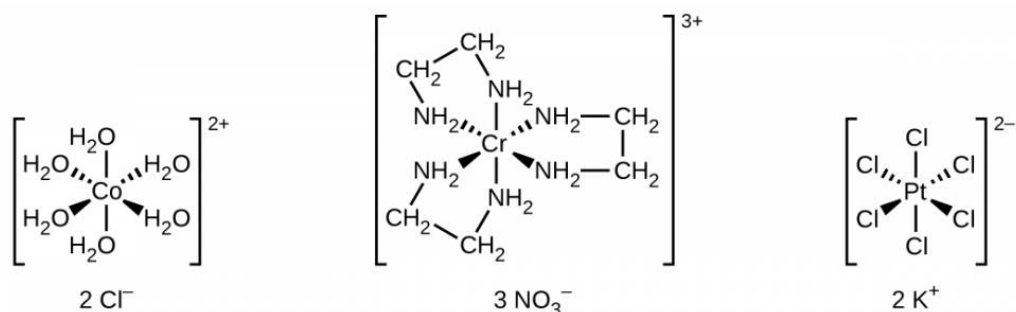
*Coordination Numbers and Molecular Geometry*

Coordination Number	Molecular Geometry	Example
2	linear	$[\text{Ag}(\text{NH}_3)_2]^+$
3	trigonal planar	$[\text{Cu}(\text{CN})_3]^{2-}$
4	tetrahedral ( $d^0$ or $d^{10}$ ), low oxidation states for M	$[\text{Ni}(\text{CO})_4]$
4	square planar ( $d^8$ )	$[\text{Ni}(\text{CN})_4]^{2-}$
5	trigonal bipyramidal	$[\text{CoCl}_5]^{2-}$
5	square pyramidal	$[\text{VO}(\text{CN})_4]^{2-}$
6	octahedral	$[\text{CoCl}_6]^{3-}$
7	pentagonal bipyramid	$[\text{ZrF}_7]^{3-}$
8	square antiprism	$[\text{ReF}_8]^{2-}$
8	dodecahedron	$[\text{Mo}(\text{CN})_8]^{4-}$
9 and above	more complicated structures	$[\text{ReH}_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding  $d$ -electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in [Figure 40.19](#). The chloride and nitrate anions in  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$  and  $[\text{Cr}(\text{en})_3](\text{NO}_3)_3$ , and the potassium cations in  $\text{K}_2[\text{PtCl}_6]$ , are outside the brackets and are not bonded to the metal ion.

**Figure 40.23**

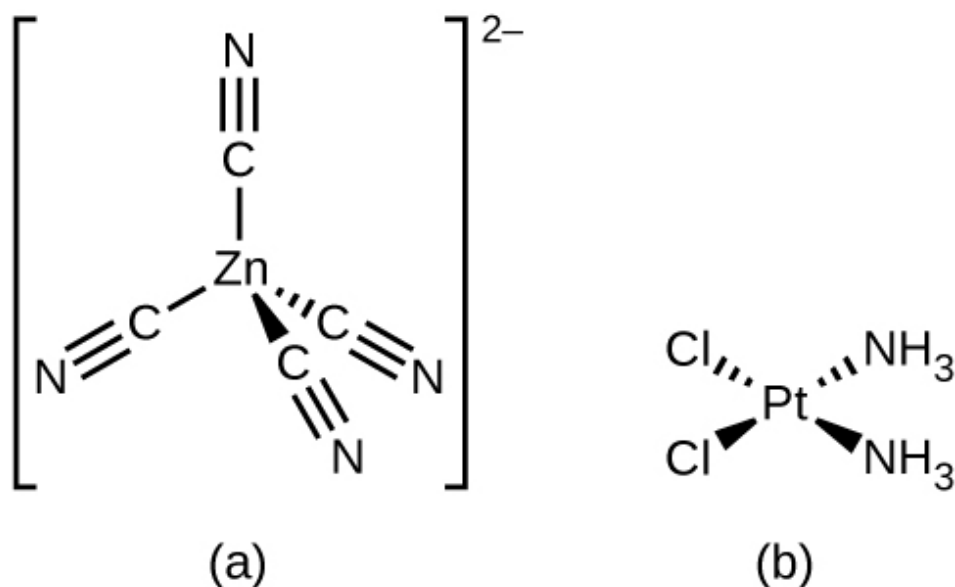
*Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of  $90^\circ$  about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.*



For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as  $[\text{Zn}(\text{CN})_4]^{2-}$  (Figure 40.20), each of the ligand pairs forms an angle of  $109.5^\circ$ . In square planar complexes, such as  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , each ligand has two other ligands at  $90^\circ$  angles (called the *cis* positions) and one additional ligand at an  $180^\circ$  angle, in the *trans* position.

**Figure 40.24**

Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in  $\text{K}_2[\text{Zn}(\text{CN})_4]$  or a square planar geometry (b) as shown in  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .

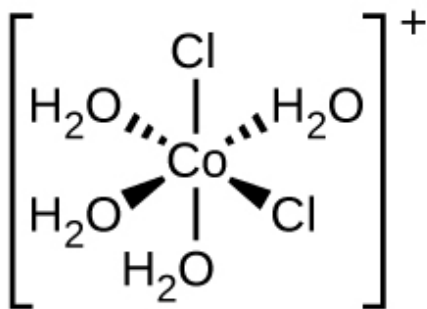
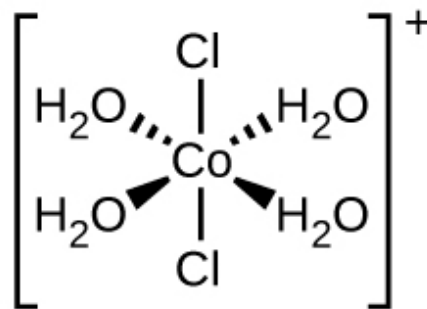


## 40.8 Isomerism in Complexes

Isomers are different chemical species that have the same chemical formula. Transition metal complexes often exist as **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  ion has two isomers. In the *cis* configuration, the two chloride ligands are adjacent to each other (Figure 40.21). The other isomer, the *trans* configuration, has the two chloride ligands directly across from one another.

**Figure 40.25**

The *cis* and *trans* isomers of  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

Violet, *cis* formGreen, *trans* form

Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$  differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$  isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

## EXAMPLE 40.8.1

### Geometric Isomers

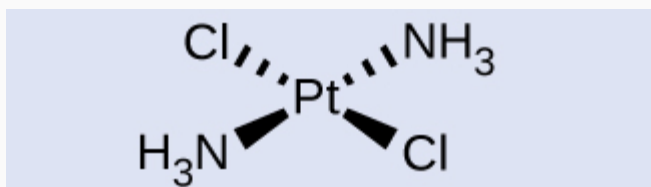
Identify which geometric isomer of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is shown in [Figure 40.20](#). Draw the other geometric isomer and give its full name.

### Solution

In the [Figure 40.20](#), the two chlorine ligands occupy *cis* positions. The other form is shown in [Figure 40.22](#). When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).

#### Figure 40.26

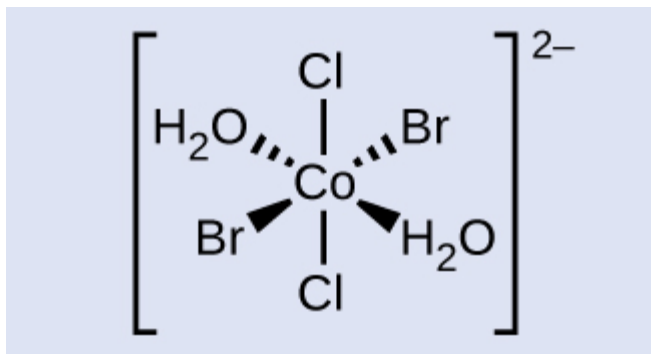
The *trans* isomer of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  has each ligand directly across from an adjacent ligand.



### Check Your Learning

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

### ✓ Answer



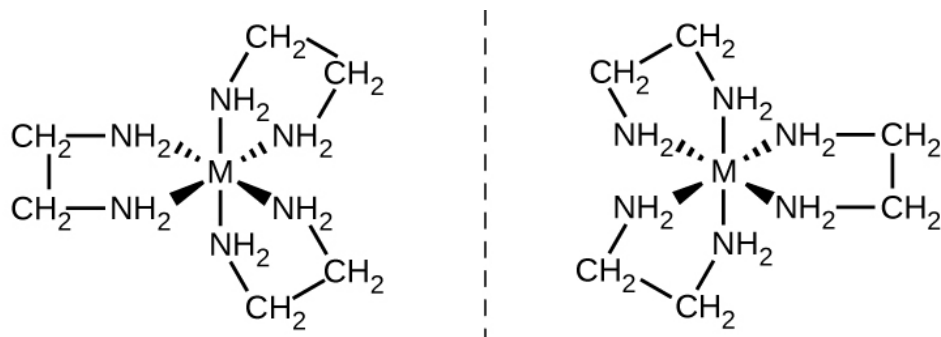
Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as  $[\text{M}(\text{en})_3]^{n+}$  [in which  $\text{M}^{n+}$  is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in [Figure 40.23](#). These two isomers will react differently with other optical isomers. For example, DNA helices are



optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of  $[M(en)_3]^{n+}$  and not the other.

**Figure 40.27**

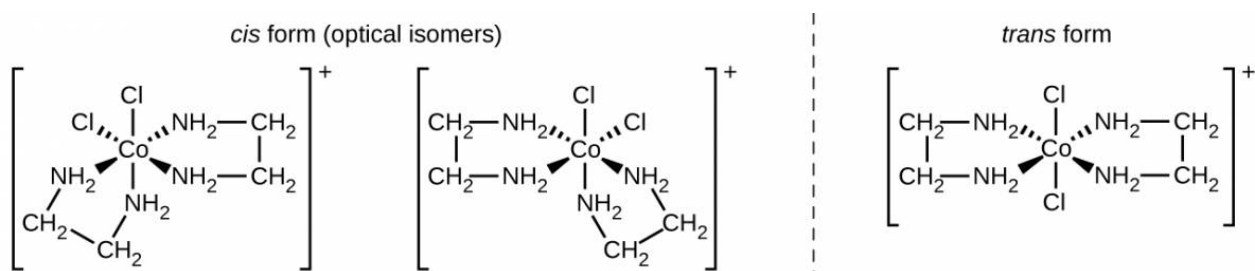
The complex  $[M(en)_3]^{n+}$  ( $M^{n+}$  = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.



The  $[Co(en)_2Cl_2]^+$  ion exhibits geometric isomerism (*cis/trans*), and its *cis* isomer exists as a pair of optical isomers ([Figure 40.24](#)).

**Figure 40.28**

Three isomeric forms of  $[Co(en)_2Cl_2]^+$  exist. The *trans* isomer, formed when the chlorines are positioned at a  $180^\circ$  angle, has very different properties from the *cis* isomers. The mirror images of the *cis* isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.



Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly,  $SCN^-$  can be bound through the sulfur or nitrogen atom, affording two distinct compounds ( $[Co(NH_3)_5SCN]^{2+}$  or  $[Co(NH_3)_5NCS]^{2+}$ ).

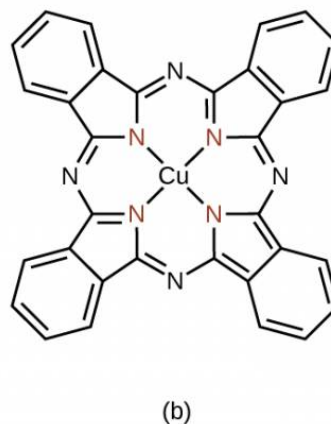
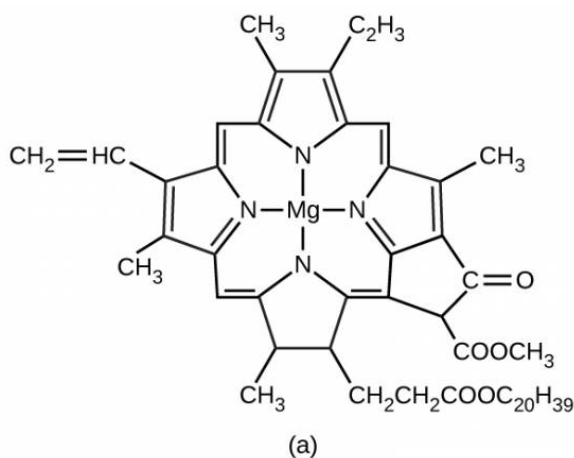
Ionization isomers (or coordination isomers) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are  $[CoCl_6][Br]$  and  $[CoCl_5Br][Cl]$ .

## 40.9 Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium ([Figure 40.25](#)). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

**Figure 40.29**

- (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center.  
 (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.



## 40.9.1 CHEMISTRY IN EVERYDAY LIFE

### Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see [Figure 40.26](#)). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

**Figure 40.30**

(a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)



(a)



(b)



(c)

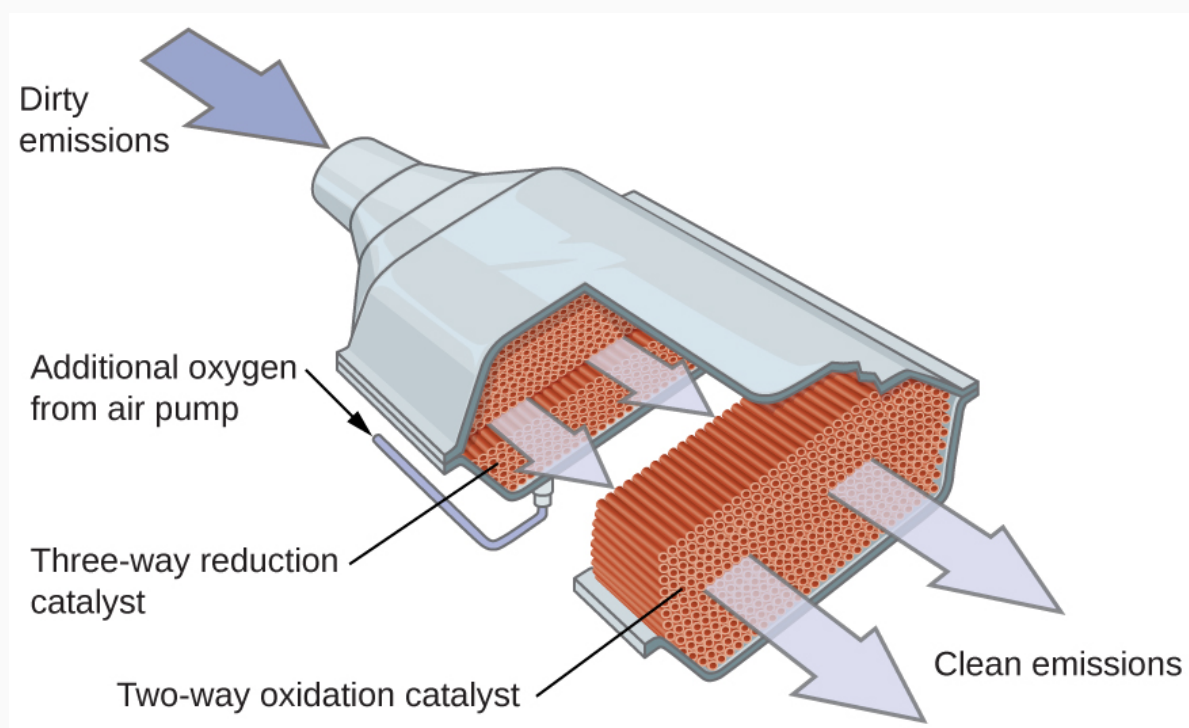
## 40.9.2 PORTRAIT OF A CHEMIST

### Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see [Figure 19.27](#)).

**Figure 40.31**

*Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.*



Another project involves the development of porous, sponge-like materials that are "photoactive." The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this [video](#) to learn more about this research and listen to Dr. D'Alessandro (shown in [Figure 40.28](#)) describe what it is like being a research chemist.

**Figure 40.32**

*Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).*



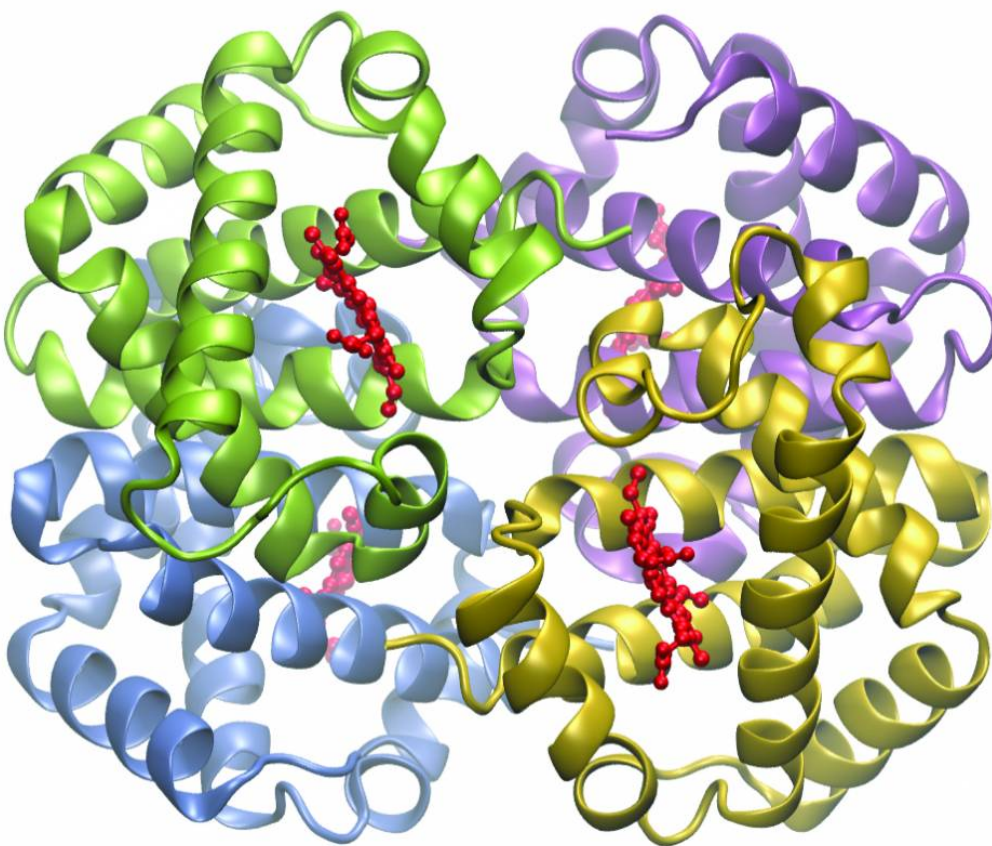
Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from [Figure 40.25](#)) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme ([Figure 40.29](#)), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is  $\text{Fe}^{2+}$ ; oxidation of the iron to  $\text{Fe}^{3+}$  prevents oxygen transport.

**Figure 40.33**

*Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.*

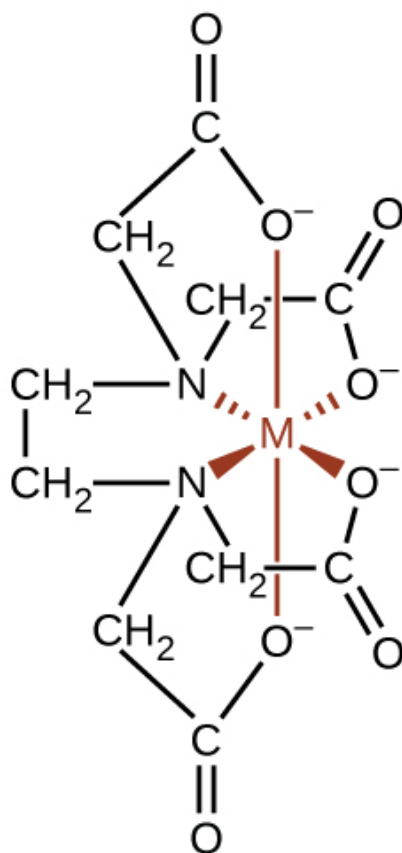




Complexing agents often are used for water softening because they tie up such ions as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ , which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA,  $(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ , coordinates to metal ions through six donor atoms and prevents the metals from reacting ([Figure 40.30](#)). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

**Figure 40.34**

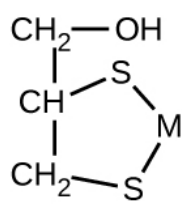
*The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.*



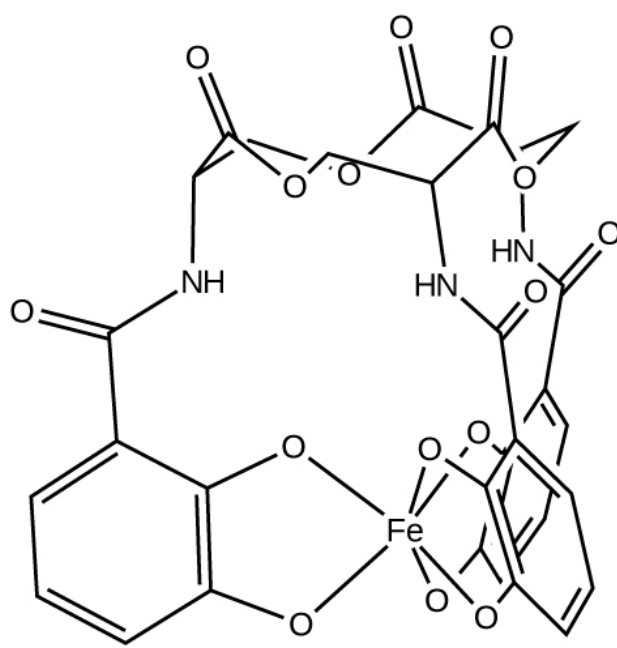
Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL),  $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OH}$ , is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate ([Figure 40.31](#)). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

**Figure 40.35**

*Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.*



(a)



(b)



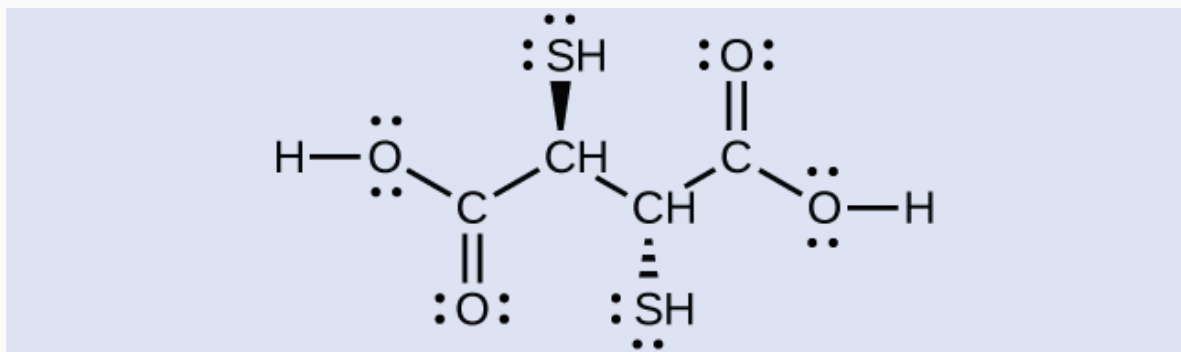
### EXAMPLE 40.9.3

#### Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in [Figure 40.32](#). Identify which atoms in this molecule could act as donor atoms.

**Figure 40.36**

*Dimercaptosuccinic acid is used to treat heavy metal poisoning.*



#### Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

#### Check Your Learning

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.<sup>1</sup> Identify at least two biologically important metals that could be disrupted by chelation therapy.

#### ✓ Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II),  $[\text{Pt}(\text{NH}_3)_2(\text{Cl})_2]$ ,

and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine (NH<sub>3</sub>)<sub>2</sub> portion is retained with other groups, replacing the dichloro [(Cl)<sub>2</sub>] portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

## Learning Objectives

By the end of this section, you will be able to:

- Outline the basic premise of crystal field theory (CFT)
- Identify molecular geometries associated with various d-orbital splitting patterns
- Predict electron configurations of split d orbitals for selected transition metal atoms or ions
- Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

## 40.10 Crystal Field Theory

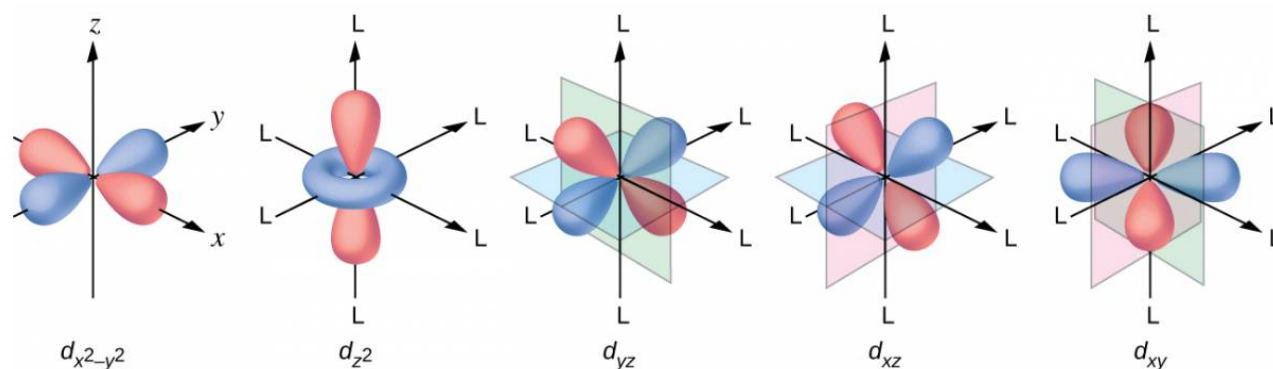
To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is crystal field theory (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in [Figure 19.33](#). In an octahedral complex, the six ligands coordinate along the axes.

### Figure 40.37

*The directional characteristics of the five d orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the orbital so that the axis labels could be shown.*



In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five  $d$  orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the  $d$  orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five  $d$  orbitals, the

and

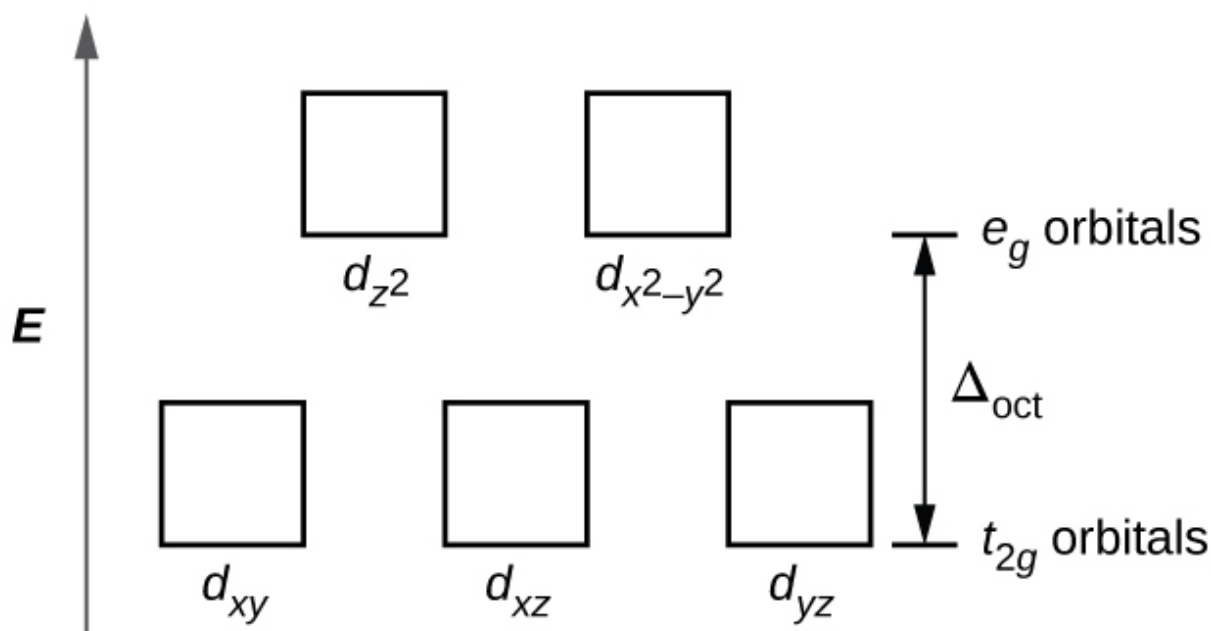
orbitals, point toward the ligands ([Figure 40.33](#)). These two orbitals are called the  $e_g$  orbitals (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, have lobes that point between the ligands and are called the  $t_{2g}$  orbitals (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the  $d$  orbitals of the metal ion. However, the repulsions between the electrons in the  $e_g$  orbitals (the

and

orbitals) and the ligands are greater than the repulsions between the electrons in the  $t_{2g}$  orbitals (the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals) and the ligands. This is because the lobes of the  $e_g$  orbitals point directly at the ligands, whereas the lobes of the  $t_{2g}$  orbitals point between them. Thus, electrons in the  $e_g$  orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the  $t_{2g}$  orbitals. The difference in energy may be represented as shown in [Figure 40.34](#).

#### Figure 40.38

*In octahedral complexes, the  $e_g$  orbitals are destabilized (higher in energy) compared to the  $t_{2g}$  orbitals because the ligands interact more strongly with the  $d$  orbitals at which they are pointed directly.*



The difference in energy between the  $e_g$  and the  $t_{2g}$  orbitals is called the crystal field splitting and is symbolized by  $\Delta_{\text{oct}}$ , where oct stands for octahedral.

The magnitude of  $\Delta_{\text{oct}}$  depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using  $3d$ ,  $4d$ , or  $5d$  orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the spectrochemical series, a short version of which is given here:

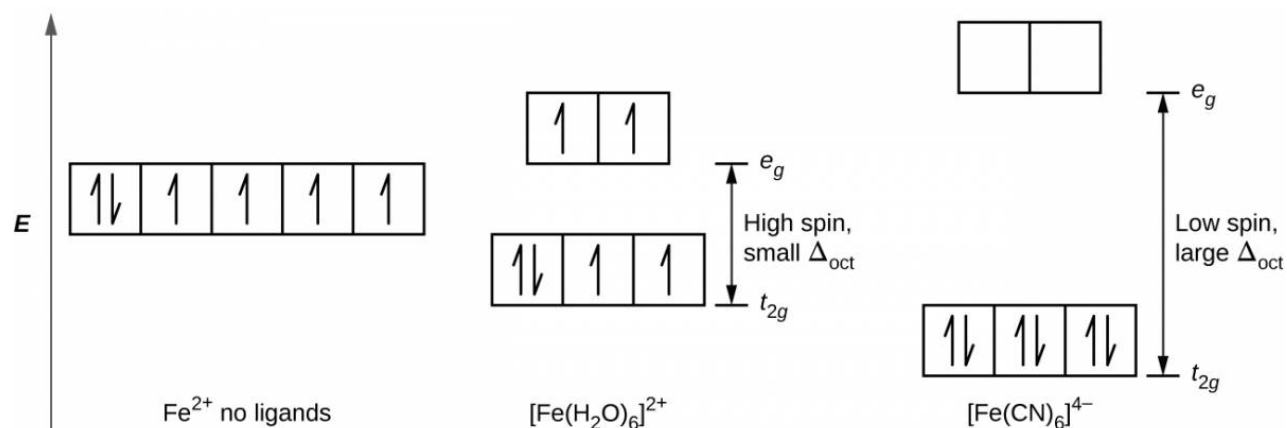
In this series, ligands on the left cause small crystal field splittings and are weak-field ligands, whereas those on the right cause larger splittings and are strong-field ligands. Thus, the  $\Delta_{\text{oct}}$  value for an octahedral complex with iodide ligands ( $\text{I}^-$ ) is much smaller than the  $\Delta_{\text{oct}}$  value for the same metal with cyanide ligands ( $\text{CN}^-$ ).

Electrons in the  $d$  orbitals follow the aufbau ("filling up") principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the pairing energy ( $P$ ). Electrons will always singly occupy each orbital in a degenerate set before pairing.  $P$  is similar in magnitude to  $\Delta_{\text{oct}}$ . When electrons fill the  $d$  orbitals, the relative magnitudes of  $\Delta_{\text{oct}}$  and  $P$  determine which orbitals will be occupied.

In  $[\text{Fe}(\text{CN})_6]^{4-}$ , the strong field of six cyanide ligands produces a large  $\Delta_{\text{oct}}$ . Under these conditions, the electrons require less energy to pair than they require to be excited to the  $e_g$  orbitals ( $\Delta_{\text{oct}} > P$ ). The six  $3d$  electrons of the  $\text{Fe}^{2+}$  ion pair in the three  $t_{2g}$  orbitals (Figure 40.35). Complexes in which the electrons are paired because of the large crystal field splitting are called low-spin complexes because the number of unpaired electrons (spins) is minimized.

#### Figure 40.39

*Iron(II) complexes have six electrons in the  $5d$  orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\Delta_{\text{oct}}$  is greater than  $P$ , and the electrons pair in the lower energy  $t_{2g}$  orbitals before occupying the  $e_g$  orbitals. With weak-field ligands such as  $\text{H}_2\text{O}$ , the ligand field splitting is less than the pairing energy,  $\Delta_{\text{oct}}$  less than  $P$ , so the electrons occupy all  $d$  orbitals singly before any pairing occurs.*



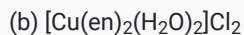
In  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , on the other hand, the weak field of the water molecules produces only a small crystal field splitting ( $\Delta_{\text{oct}} < P$ ). Because it requires less energy for the electrons to occupy the *e<sub>g</sub>* orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , there will be one pair of electrons and four unpaired electrons ([Figure 40.35](#)). Complexes such as the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion is a low-spin complex with only one unpaired electron, whereas both the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{FeF}_6]^{3-}$  ions are high-spin complexes with five unpaired electrons.

## EXAMPLE 40.10.1

### High- and Low-Spin Complexes

Predict the number of unpaired electrons.



### Solution

The complexes are octahedral.

(a)  $\text{Cr}^{3+}$  has a  $d^3$  configuration. These electrons will all be unpaired.

(b)  $\text{Cu}^{2+}$  is  $d^9$ , so there will be one unpaired electron.

(c)  $\text{Co}^{3+}$  has  $d^6$  valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the  $t_{2g}$  orbitals, leaving 0 unpaired.

### Check Your Learning

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which  $d$ -electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

### ✓ Answer

$d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$

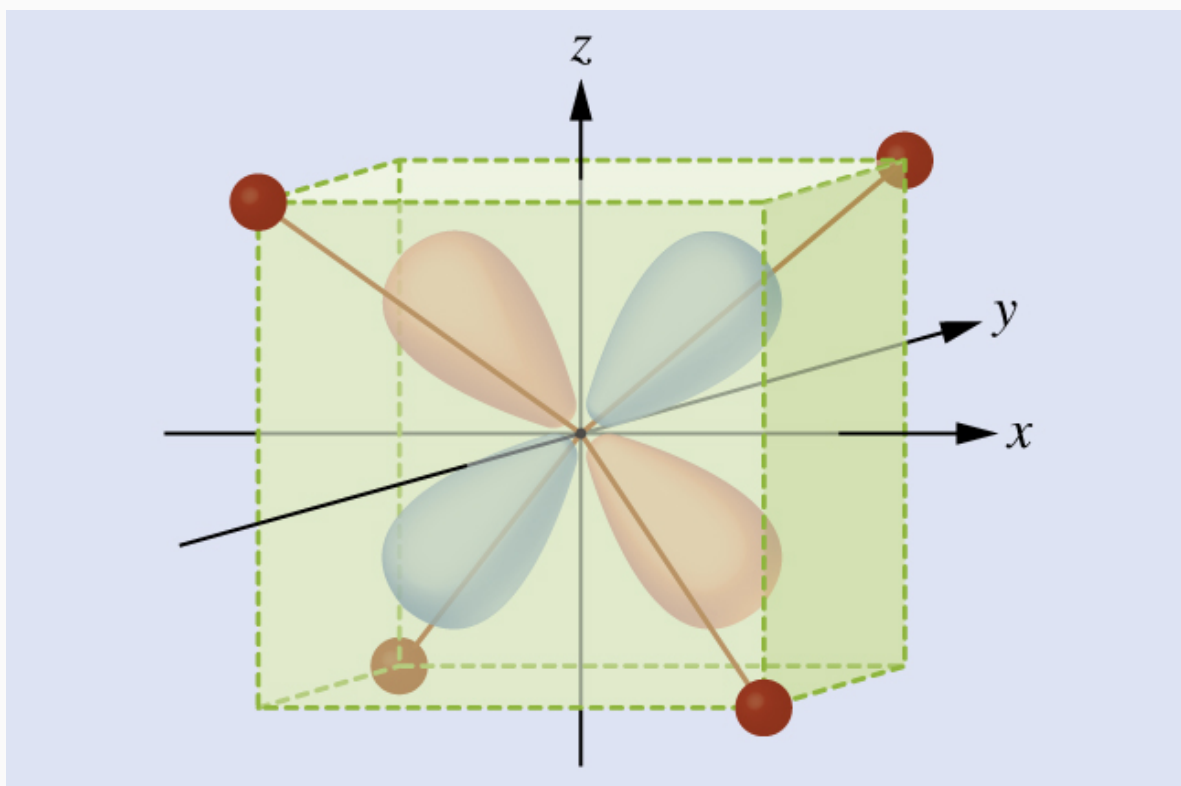
## EXAMPLE 40.10.2

### CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the  $e_g$  set point directly at the ligands. For tetrahedral complexes, the  $d$  orbitals remain in place, but now we have only four ligands located between the axes ([Figure 40.36](#)). None of the orbitals points directly at the tetrahedral ligands. However, the  $e_g$  set (along the Cartesian axes) overlaps with the ligands less than does the  $t_{2g}$  set. By analogy with the octahedral case, predict the energy diagram for the  $d$  orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral  $e_g$  set becomes a tetrahedral  $e$  set, and the octahedral  $t_{2g}$  set becomes a  $t_2$  set.

**Figure 40.40**

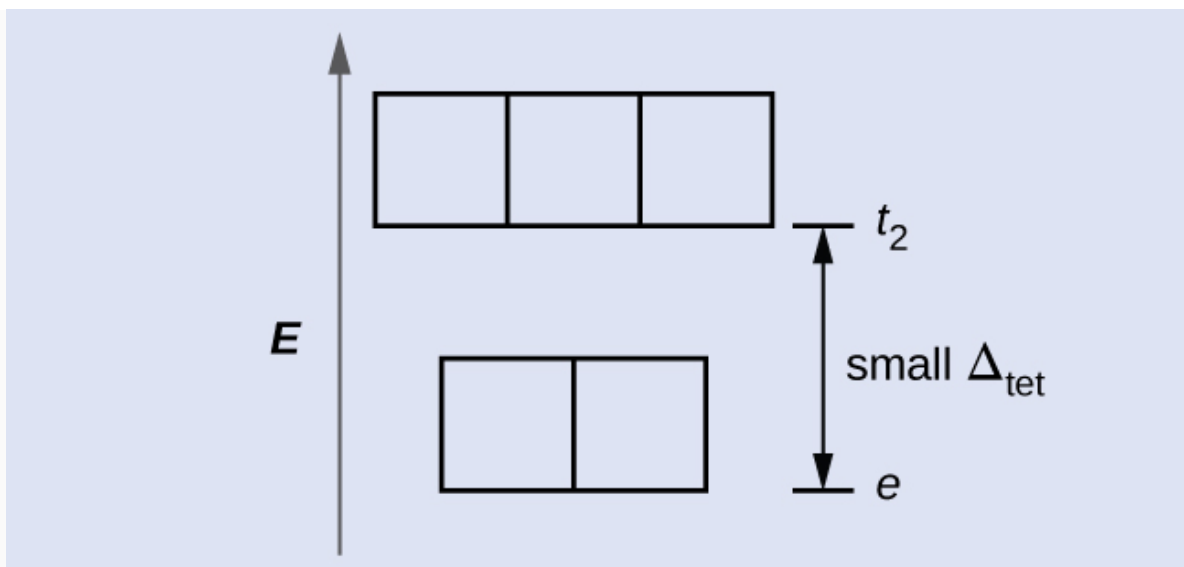
*This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.*



### Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so  $\Delta_{\text{tet}}$  is usually small





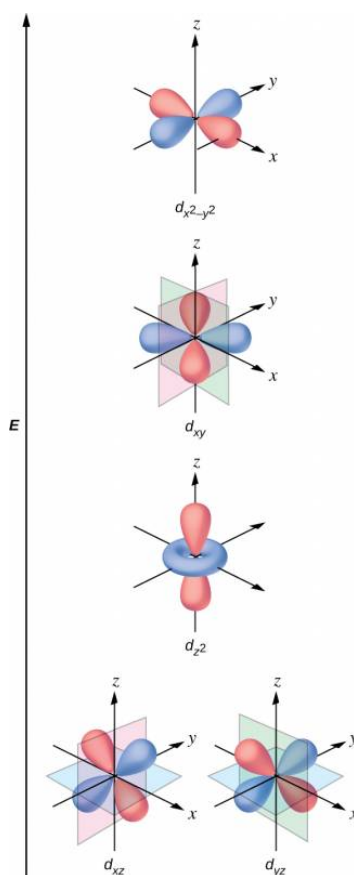
### Check Your Learning

Explain how many unpaired electrons a tetrahedral  $d^4$  ion will have.

#### ✓ Answer

4; because  $\Delta_{\text{tet}}$  is small, all tetrahedral complexes are high spin and the electrons go into the  $t_2$  orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the  $z$ -axis. This changes the distribution of the  $d$  orbitals, as orbitals on or near the  $z$ -axis become more stable, and those on or near the  $x$ - or  $y$ -axes become less stable. This results in the octahedral  $t_{2g}$  and the  $e_g$  sets splitting and gives a more complicated pattern, as depicted below:



## 40.11 Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as  $O_2$  that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as  $N_2$  and ions such as  $Na^+$  and  $[Fe(CN)_6]^{4-}$  that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin  $d^6 [Fe(CN)_6]^{4-}$  confirms that iron is diamagnetic, whereas high-spin  $d^6 [Fe(H_2O)_6]^{2+}$  has four unpaired electrons with a magnetic moment that confirms this arrangement.

## 40.12 Colors of Transition Metal Complexes

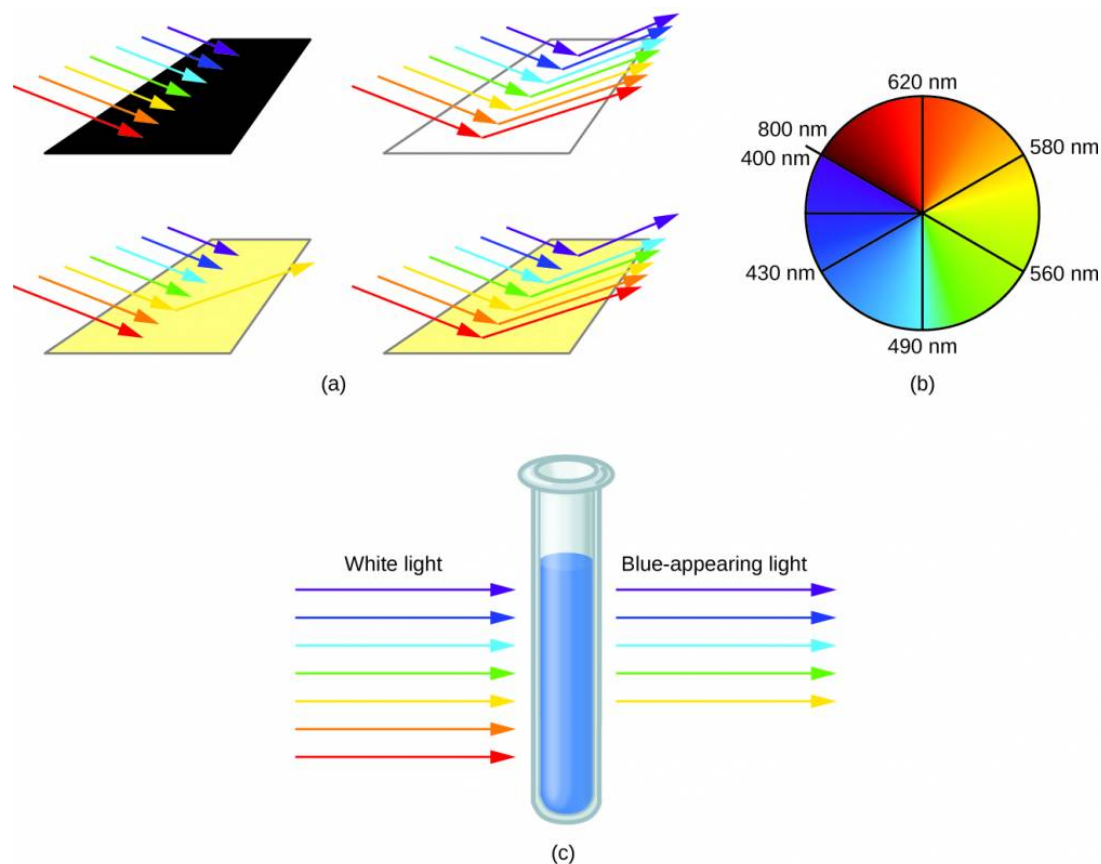
When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the  $d$  orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is

missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 40.37).

**Figure 40.41**

(a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.



## EXAMPLE 40.12.1

### Colors of Complexes

The octahedral complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has a single  $d$  electron. To excite this electron from the ground state  $t_{2g}$  orbital to the  $e_g$  orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to  $\Delta_{\text{oct}}$  and occurs at 499 nm. Calculate the value of  $\Delta_{\text{oct}}$  in Joules and predict what color the solution will appear.

### Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

### Check Your Learning

A complex that appears green, absorbs photons of what wavelengths?

### ✓ Answer

red, 620–800 nm

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in [Figure 40.38](#), different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

#### Figure 40.42

*The partially filled  $d$  orbitals of the stable ions  $\text{Cr}^{3+}(\text{aq})$ ,  $\text{Fe}^{3+}(\text{aq})$ , and  $\text{Co}^{2+}(\text{aq})$  (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)*



The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex  $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$  appears blue-green because the high-spin complex absorbs photons in the red wavelengths ([Figure 40.39](#)). In contrast, the low-spin iron(II) complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$  appears pale yellow because it absorbs higher-energy violet photons.

**Figure 40.43**

Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain  $d^6$  iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.



(a)



(b)

## LINK TO LEARNING

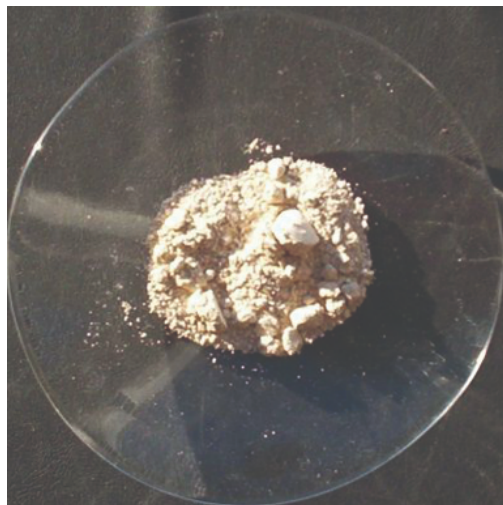
Watch this [video](#) of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of  $d$  orbitals of the central metal atom (large  $\Delta_{\text{oct}}$ ). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the  $\text{Cu}^+$  ion has a  $d^{10}$  configuration, and all the  $e_g$  orbitals are filled. To excite an electron to a higher level, such as the  $4p$  orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing  $[\text{Cu}(\text{CN})_2]^-$ , for example, is colorless. On the other hand, octahedral  $\text{Cu}^{2+}$  complexes have a vacancy in the  $e_g$  orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and  $\text{Cu}^{2+}$  complexes are almost always colored—blue, blue-green violet, or yellow ([Figure 40.40](#)). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

**Figure 40.44**

(a) Copper(I) complexes with  $d^{10}$  configurations such as  $\text{CuI}$  tend to be colorless, whereas (b)  $d^9$  copper(II) complexes such as  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  are brightly colored.



(a)



(b)

## Files

[Open in Google Drive](#)

## Previous Citation(s)

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