

Chelation, Biological Effects

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.

32.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. As shown in [Figure 32.1](#), 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 32.1

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

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

Atomic number → 1

Symbol → **H**

Atomic mass → 1.008

Name → hydrogen

1

H

1.008

hydrogen

Color Code

Metal	Solid
Metalloid	Liquid
Nonmetal	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 32.1.1

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) Ti^{2+}

(d) Am^{3+}

(e) 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) $\text{Ce}^{3+}[\text{Xe}]4f^1$; 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

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

32.1.2 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

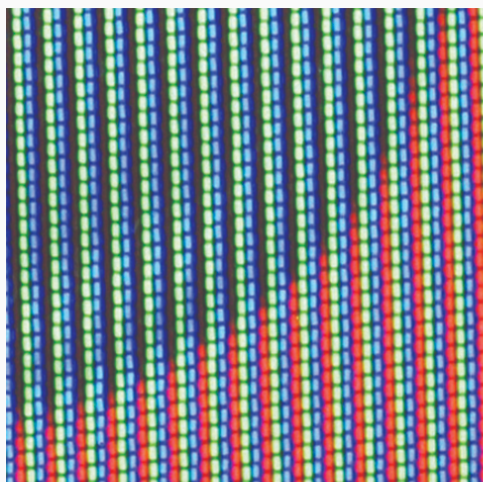
×

$10^{-5}\%$ 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.

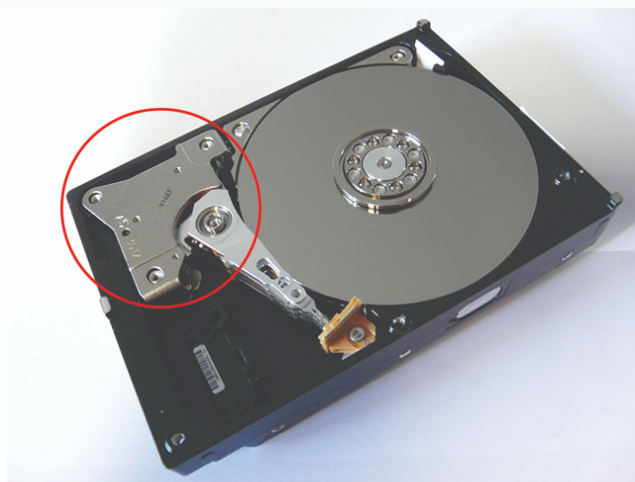
The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline ([Figure 32.2](#)). 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 32.2

(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.

32.1.3 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 Be^{2+} and 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 Cr^{3+} , Fe^{3+} , and Co^{2+} , form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+} , Ru^{3+} , and 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 oxoanions 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 oxoanions.

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 32.3](#). 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 32.3

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

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

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 Cr³⁺ ions in water and, in the absence of air, less stable Cr²⁺ ions. The sulfide with the highest oxidation state for chromium is Cr₂S₃, which contains the Cr³⁺ ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

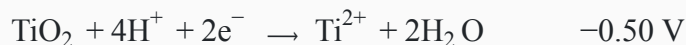
EXAMPLE 32.1.4

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^+

32.1.5 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 32.4](#)). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). 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 32.4

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>)



(a)



(b)



(c)

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.

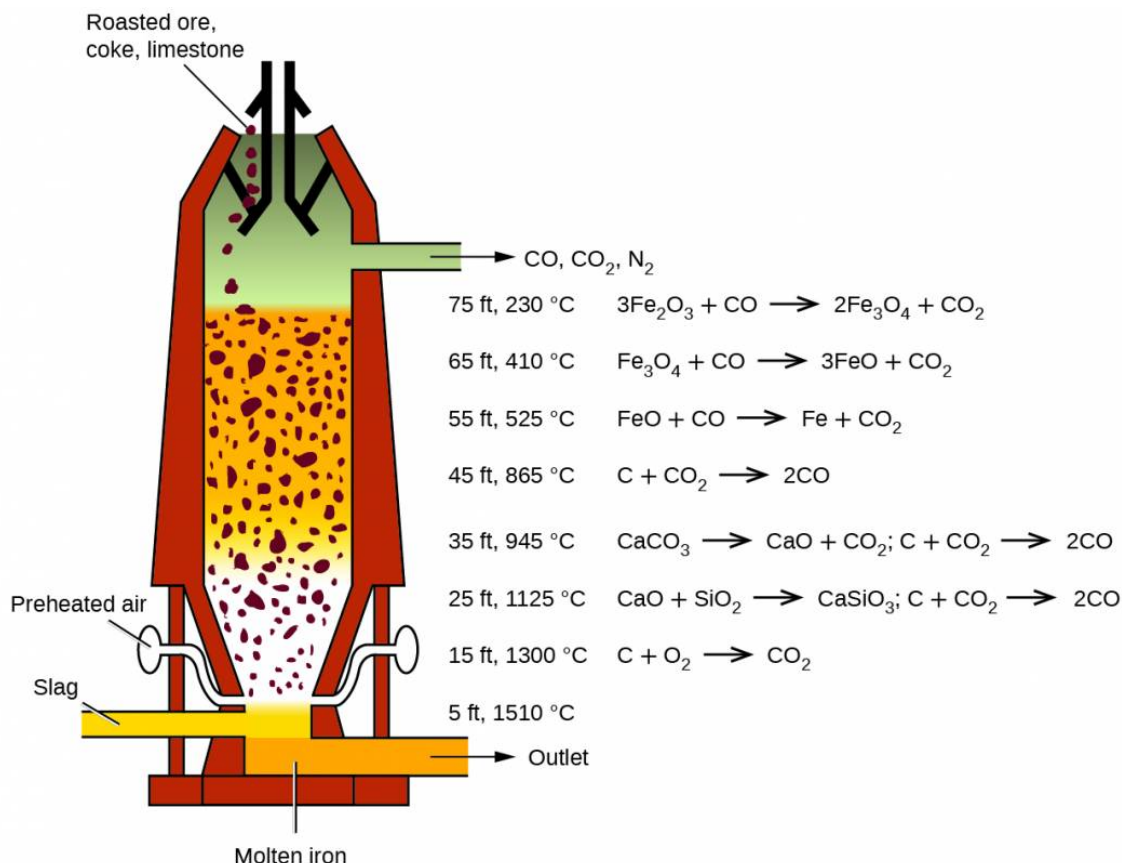
32.1.6 Isolation of Iron

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.

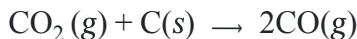
The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter ([Figure 32.5](#)) in which the roasted ore, coke, and limestone (impure 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 32.5

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.

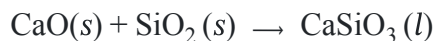


Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer 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 32.5](#).

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 32.6](#)).

Figure 32.6

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.

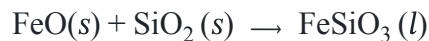
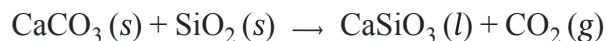
LINK TO LEARNING

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

32.1.7 Isolation of Copper

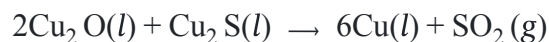
The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu_2S , FeS , FeO , and SiO_2 , 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_2S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu_2S into Cu_2O . 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 32.7](#)). 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 32.7

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



32.1.8 Isolation of Silver

Silver sometimes occurs in large nuggets ([Figure 32.8](#)) 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 Ag_2S and AgCl . Representative equations are:

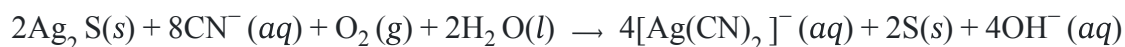
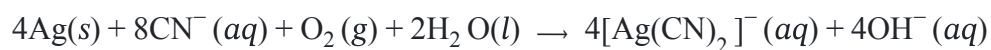
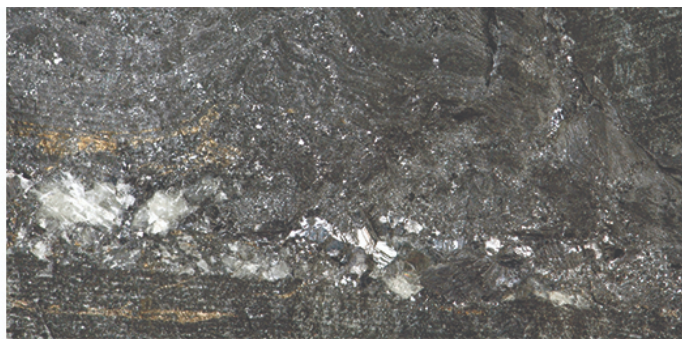


Figure 32.8

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)

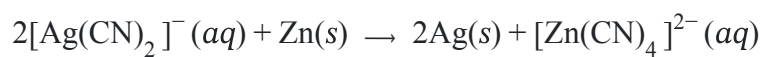


(a)



(b)

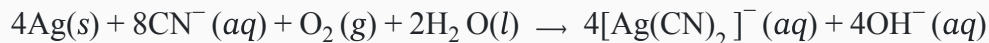
The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:



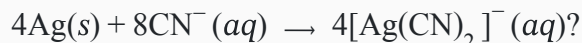
EXAMPLE 32.1.9

Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(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

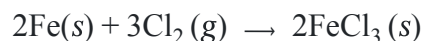
The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

32.1.10 Transition Metal Compounds

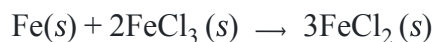
The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by 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.

32.1.10.1 Halides

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

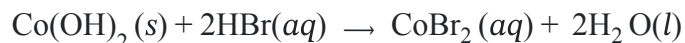


Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:



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:

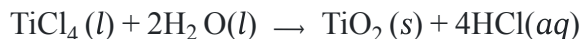


Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:



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 (TiCl_2 and TiCl_3) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride (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:

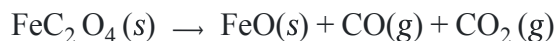


32.1.10.2 Oxides

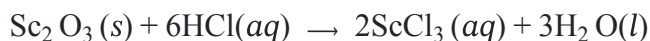
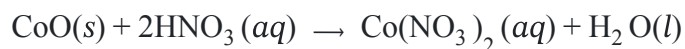
As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more covalent. These variations in bonding are because the electronegativities 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 Sc_2O_3 , TiO_2 , V_2O_5 , Cr_2O_3 , Mn_3O_4 , Fe_3O_4 , Co_3O_4 , NiO , and CuO .

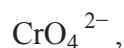
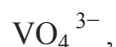
Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating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



With the exception of CrO_3 and Mn_2O_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



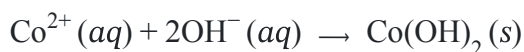
For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:



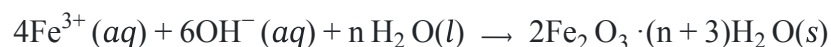
Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and HMnO_4 , respectively.

32.1.10.3 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:



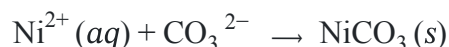
In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:



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.

32.1.10.4 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:

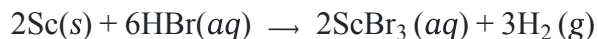


The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metal salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

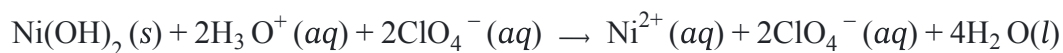
32.1.10.5 Other Salts

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.

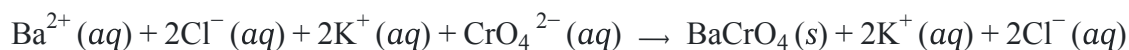
A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:



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.

32.1.11 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 Nb₃Sn, 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.

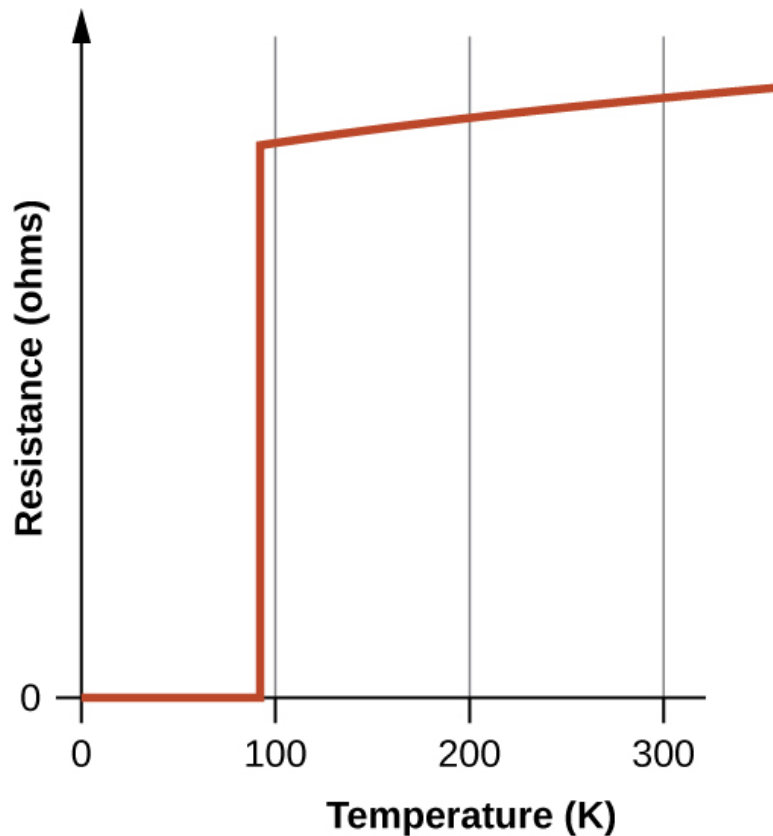
One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is YBa₂Cu₃O₇.

The new materials become superconducting at temperatures close to 90 K ([Figure 32.9](#)), 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 32.9

The resistance of the high-temperature superconductor YBa₂Cu₃O₇ 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.

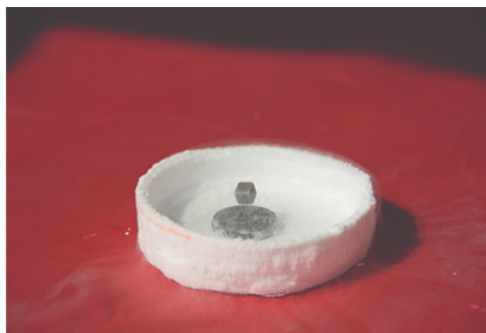
Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors ([Figure 32.10](#)).

Figure 32.10

(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.

32.2 Coordination Chemistry of Transition Metals

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

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 32.11](#)). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure 32.11

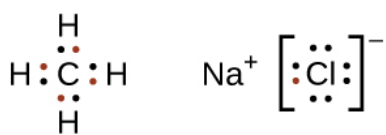
Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with $M = Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$,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



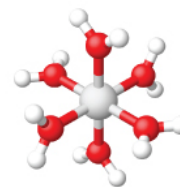
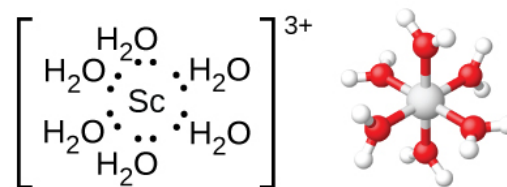
Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4 . The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 32.12). 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 32.12

(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)

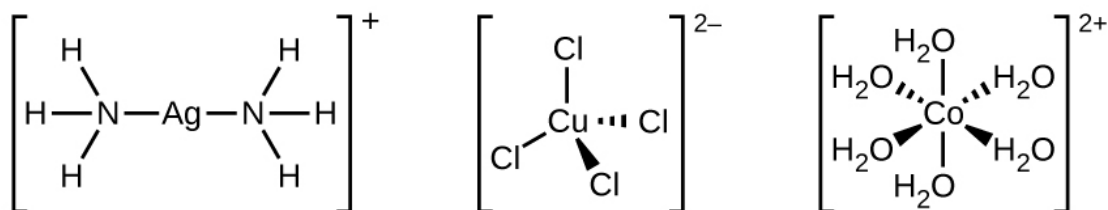


(b)

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 32.13](#)). 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 32.13

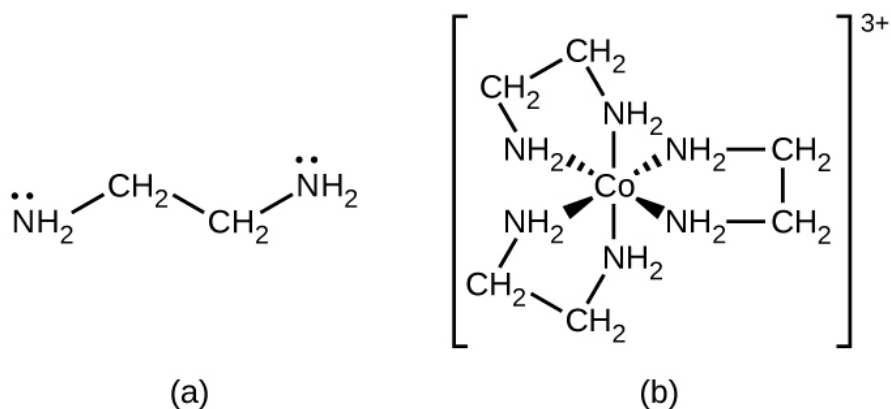
The complexes (a) $[\text{Ag}(\text{NH}_3)_2]^+$, (b) $[\text{CuCl}_4]^{2-}$, and (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, 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 32.14](#)). 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 32.14

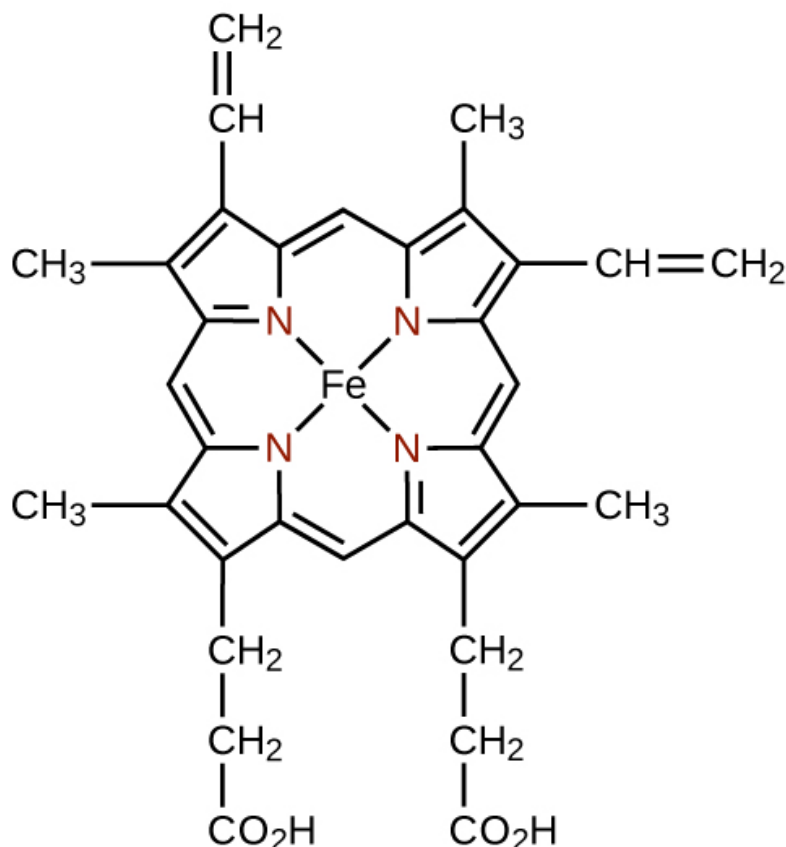
(a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[\text{Co}(\text{en})_3]^{3+}$ contains three of these ligands, each forming two bonds to the cobalt ion.



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 32.14](#) showed one example of a chelate. The heme complex in hemoglobin is another important example ([Figure 32.15](#)). It contains a polydentate ligand with four donor atoms that coordinate to iron.

Figure 32.15

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



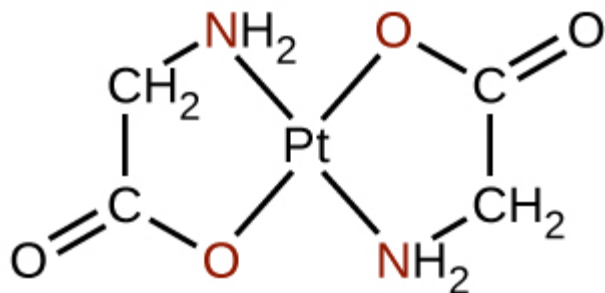
Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3 , Cl^- , and H_2O , are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, and the anion of the acid glycine,



([Figure 32.16](#)) 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 32.15](#)) is a tetradentate ligand.

Figure 32.16

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.



32.2.1 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 32.1](#). For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ as diamminetetrachloroplatinum(IV).

Table 32.17

Examples of Anionic Ligands

Anionic Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
NO_3^-	nitrate
OH^-	hydroxo
O^{2-}	oxo
$\text{C}_2\text{O}_4^{2-}$	oxalato
CO_3^{2-}	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 32.2](#) and [Table 32.3](#)). 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 32.4](#)). 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 32.18

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 32.19

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 32.20

Examples in Which the Complex Is an Anion

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

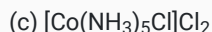
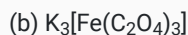
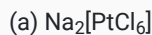
LINK TO LEARNING

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 32.2.2

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 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 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 dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.

✓ Answer

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

Files

[Open in Google Drive](#)

Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. <https://openstax.org/details/books/chemistry-atoms-first-2e> (19.1-19.2)



This content is provided to you freely by BYU Open Learning Network.

Access it online or download it at

https://open.byu.edu/general_college_chemistry_2/chelation_biological.