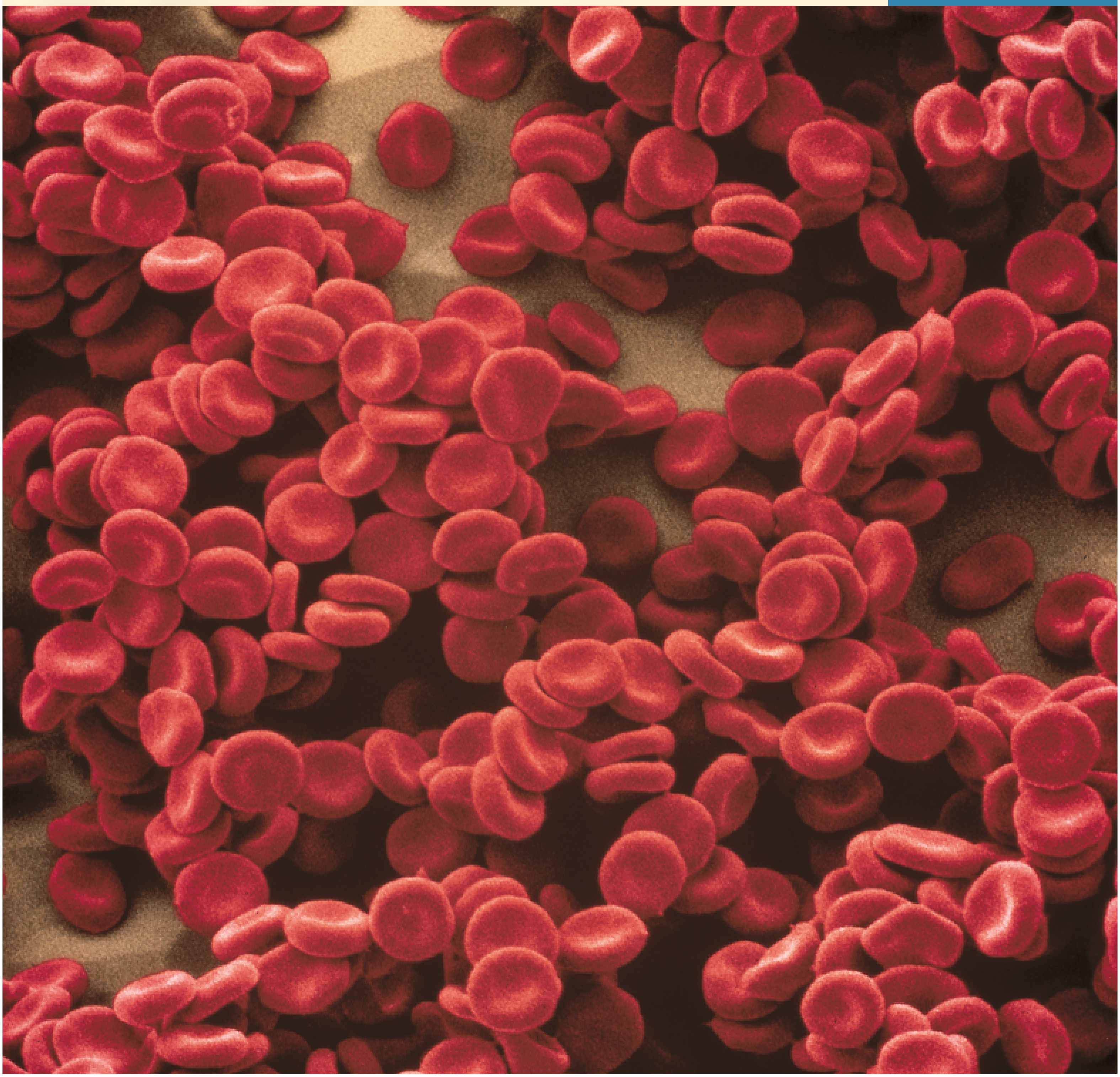
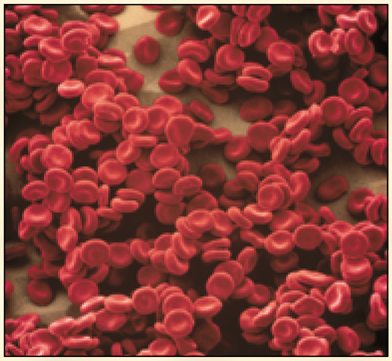
Coordination Compounds

25





Red blood cells (1200x). The red blood cells that transport O_2 throughout our bodies contain hemoglobin, a coordination compound.

OUTLINE

OBJECTIVES

After you have studied this chapter, you should be able to

- *Recognize coordination compounds*
- *Recognize metals that form soluble ammine complexes in aqueous solutions and write the formulas for common ammine complexes*
- *Use the terminology that describes coordination compounds*
- *Apply the rules for naming coordination compounds*
- *Recognize common structures of coordination compounds*
- *Describe various kinds of structural (constitutional) isomerism and distinguish among structural isomers*
- *Recognize stereoisomers*
- *Describe the crystal field theory of bonding in coordination compounds*
- *Explain the origin of color in complex species*
- *Use the spectrochemical series to explain colors of a series of complexes*

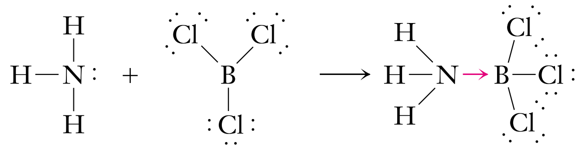
Coordination compounds are found in many places on the earth's surface. Every living system includes many coordination compounds. They are also important components of everyday products as varied as cleaning materials, medicines, inks, and paints. A list of important coordination compounds appears to be endless because new ones are discovered every year.

25-1 COORDINATION COMPOUNDS

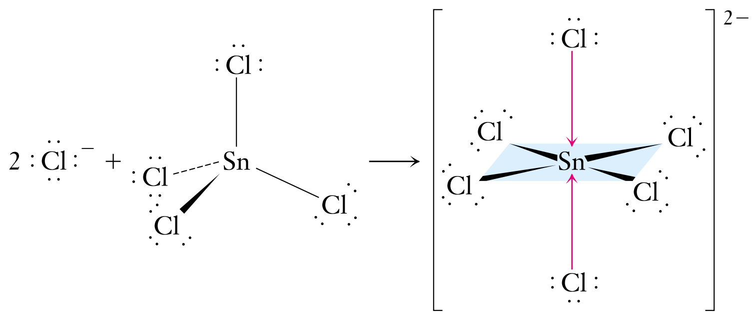
Covalent bonds in which the shared electron pair is provided by one atom are called *coordinate covalent bonds.*

In Section 10-10 we discussed Lewis acid–base reactions. A *base* makes available a share in an electron pair, and an *acid* accepts a share in an electron pair, to form a **coordinate**

covalent bond. Such bonds are often represented by arrows that point from the electron pair donor (Lewis base) to the acceptor (Lewis acid).



ammonia, a Lewis base; boron trichloride, a Lewis acid



chloride ion, a Lewis base; tin(IV) chloride, a Lewis acid; hexachlorostannate(IV) ion

The red arrows represent coordinate covalent bonds. These arrows do not imply that two Sn—Cl bonds are different from the others. Once formed, all the Sn—Cl bonds in the $[SnCl_6]^{2-}$ ion are alike.

Electron configurations of the elements of the three *d*-transition series are given in Table 25-1 and in Appendix B. Most *d*-transition metal ions have vacant *d* orbitals that can accept shares in electron pairs. Many act as Lewis acids by forming coordinate covalent bonds in **coordination compounds (coordination complexes,** or **complex ions).** Complexes of transition metal ions or molecules include cationic species (e.g., $[Cr(OH_2)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Ag(NH_3)_2]^+$), anionic species (e.g., $[Ni(CN_4)]^{2-}$, $[MnCl_5]^{3-}$), and neutral species (e.g., $[Fe(CO)_5]$, $[Pt(NH_3)_2Cl_2]$). Many complexes are very stable, as indicated by their low dissociation constants, K_d (Section 20-6 and Appendix I).

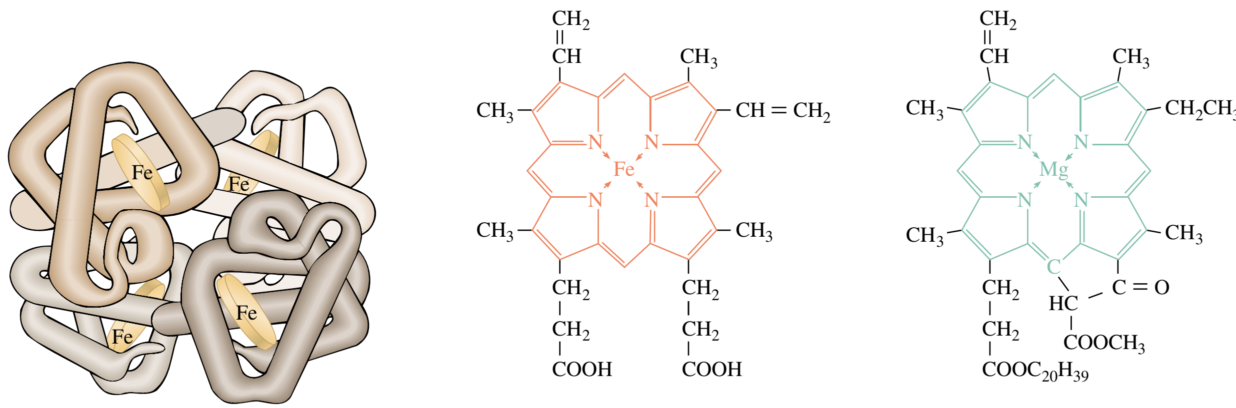
We often write water as OH_2 rather than H_2O when we want to emphasize that oxygen is the donor atom.

We now understand from molecular orbital theory that all substances have some vacant orbitals—they are *potential* Lewis acids. Most substances have unshared pairs of electrons—they are *potential* Lewis bases.

TABLE 25-1 ***Ground State Electron Configurations of d-Transition Metals***

Period 4		Period 5		Period 6	
$_{21}$Sc	$[Ar]3d^14s^2$	$_{39}$Y	$[Kr]4d^15s^2$	$_{57}$La	$[Xe]5d^16s^2$
$_{22}$Ti	$[Ar]3d^24s^2$	$_{40}$Zr	$[Kr]4d^25s^2$	$_{72}$Hf	$[Xe]4f^{14}5d^26s^2$
$_{23}$V	$[Ar]3d^34s^2$	$_{41}$Nb	$[Kr]4d^45s^1$	$_{73}$Ta	$[Xe]4f^{14}5d^36s^2$
$_{24}$Cr	$[Ar]3d^54s^1$	$_{42}$Mo	$[Kr]4d^55s^1$	$_{74}$W	$[Xe]4f^{14}5d^46s^2$
$_{25}$Mn	$[Ar]3d^54s^2$	$_{43}$Tc	$[Kr]4d^55s^2$	$_{75}$Re	$[Xe]4f^{14}5d^56s^2$
$_{26}$Fe	$[Ar]3d^64s^2$	$_{44}$Ru	$[Kr]4d^75s^1$	$_{76}$Os	$[Xe]4f^{14}5d^66s^2$
$_{27}$Co	$[Ar]3d^74s^2$	$_{45}$Rh	$[Kr]4d^85s^1$	$_{77}$Ir	$[Xe]4f^{14}5d^76s^2$
$_{28}$Ni	$[Ar]3d^84s^2$	$_{46}$Pd	$[Kr]4d^{10}$	$_{78}$Pt	$[Xe]4f^{14}5d^96s^1$
$_{29}$Cu	$[Ar]3d^{10}4s^1$	$_{47}$Ag	$[Kr]4d^{10}5s^1$	$_{79}$Au	$[Xe]4f^{14}5d^{10}6s^1$
$_{30}$Zn	$[Ar]3d^{10}4s^2$	$_{48}$Cd	$[Kr]4d^{10}5s^2$	$_{80}$Hg	$[Xe]4f^{14}5d^{10}6s^2$

Several of the apparent irregularities in these electron configurations can be explained by the special stability of half-filled and filled sets of *d* orbitals (Section 5-17).



(a) Porphyrin ring system + iron = heme group (shown as disks at left) (b) Chlorophyll a

Figure 25-1 (a) A model of a hemoglobin molecule (MW = 64,500 amu). Individual atoms are not shown. The four heme groups in a hemoglobin molecule are represented by disks. Each heme group contains one Fe^{2+} ion and porphyrin rings. A single red blood cell contains more than 265 million hemoglobin molecules and more than 1 billion Fe^{2+} ions. (b) The structure of chlorophyll a, which also contains a porphyrin ring with a Mg^{2+} ion at its center. Chlorophyll is necessary for photosynthesis. The porphyrin ring is the part of the molecule that absorbs light. The structure of chlorophyll b is slightly different.

Many important biological substances are coordination compounds. Hemoglobin and chlorophyll are two examples (Figure 25-1). Hemoglobin is a protein that carries O_2 in blood. It contains iron(II) ions bound to large porphyrin rings. The transport of oxygen by hemoglobin involves the coordination and subsequent release of O_2 molecules by the Fe(II) ions. Chlorophyll is necessary for photosynthesis in plants. It contains magnesium ions bound to porphyrin rings. Vitamin B_{12} is a large complex of cobalt. Coordination compounds have many practical applications in such areas as medicine, water treatment, soil and plant treatment, protection of metal surfaces, analysis of trace amounts of metals, electroplating, and textile dyeing.

Bonding in transition metal complexes was not understood until the pioneering research of Alfred Werner (1866–1919), a Swiss chemist who received the Nobel Prize in chemistry in 1913. Great advances have been made since in the field of coordination chemistry, but Werner's work remains the most important contribution by a single researcher.

Double salts are ionic solids resulting from the cocrystallization of two salts from the same solution into a single structure. In the example given, the solid is produced from an aqueous solution of iron(II) sulfate, $FeSO_4$, and ammonium sulfate, $(NH_4)_2SO_4$.

Prior to Werner's work, the formulas of transition metal complexes were written with dots, $CrCl_3 \cdot 6H_2O$, $AgCl \cdot 2NH_3$, just like double salts such as iron(II) ammonium sulfate hexahydrate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. The properties of solutions of double salts are the properties expected for solutions made by mixing the individual salts. However, a solution of $AgCl \cdot 2NH_3$, or more properly $[Ag(NH_3)_2]Cl$, behaves differently from either a solution of (very insoluble) silver chloride or a solution of ammonia. The dots have been called "dots of ignorance," because they signified that the mode of bonding was unknown. Table 25-2 summarizes the types of experiments Werner performed and interpreted to lay the foundations for modern coordination theory.

Werner isolated platinum(IV) compounds with the formulas that appear in the first column of Table 25-2. He added excess $AgNO_3$ to solutions of carefully weighed amounts of the five salts. The precipitated AgCl was collected by filtration, dried, and weighed.

TABLE 25-2 *Interpretation of Experimental Data by Werner*

Formula	Moles AgCl Precipitated per Formula Unit	Number of Ions per Formula Unit (based on conductance)	True Formula	Ions/Formula Unit	
$PtCl_4 \cdot 6NH_3$	4	5	$[Pt(NH_3)_6]Cl_4$	$[Pt(NH_3)_6]^{4+}$	4 Cl^-
$PtCl_4 \cdot 5NH_3$	3	4	$[Pt(NH_3)_5Cl]Cl_3$	$[Pt(NH_3)_5Cl]^{3+}$	3 Cl^-
$PtCl_4 \cdot 4NH_3$	2	3	$[Pt(NH_3)_4Cl_2]Cl_2$	$[Pt(NH_3)_4Cl_2]^{2+}$	2 Cl^-
$PtCl_4 \cdot 3NH_3$	1	2	$[Pt(NH_3)_3Cl_3]Cl$	$[Pt(NH_3)_3Cl_3]^{+}$	Cl^-
$PtCl_4 \cdot 2NH_3$	0	0	$[Pt(NH_3)_2Cl_4]$	no ions	

He determined the number of moles of AgCl produced. This told him the number of Cl^- ions precipitated per formula unit. The results are in the second column. Werner reasoned that the precipitated Cl^- ions must be free (uncoordinated), whereas the unprecipitated Cl^- ions must be bonded to Pt so they could not be precipitated by Ag^+ ions. He also measured the conductances of solutions of these compounds of known concentrations. By comparing these with data on solutions of simple electrolytes, he found the number of ions per formula unit. The results are shown in the third column. Piecing the evidence together, he concluded that the correct formulas are the ones listed in the last two columns. The NH_3 and Cl^- within the brackets are bonded by coordinate covalent bonds to the Lewis acid, Pt(IV) ion.

The conductance of a solution of an electrolyte is a measure of its ability to conduct electricity. It is related to the number of ions and the charges on ions in solution.

The charge on a complex is the sum of its constituent charges.

We can use this relationship to determine or confirm the charge on a complex species. For example, the charge on $[Pt(NH_3)_6]^{4+}$ can be calculated as

$$\begin{aligned}\text{Charge} &= [\text{charge on Pt(IV)}] + 6 \times (\text{charge on } NH_3)\\ &= (4+) + 6 \times (0) = 4+\end{aligned}$$

The charge on $[Pt(NH_3)_4Cl_2]^{2+}$ is

$$\begin{aligned}\text{Charge} &= [\text{charge on Pt(IV)}] + 4 \times (\text{charge on } NH_3) + 2 \times (\text{charge on } Cl^-)\\ &= (4+) + 4 \times (0) + 2 \times (1-) = 2+\end{aligned}$$

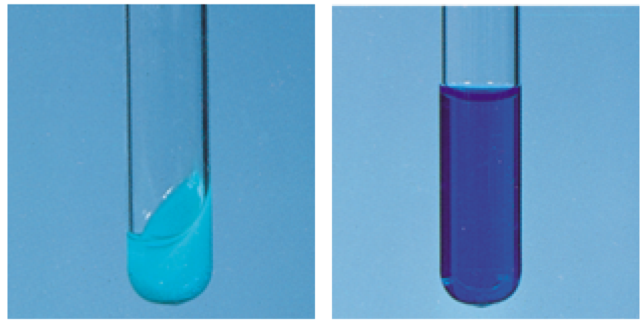
25-2 AMMINE COMPLEXES

Ammine complexes contain NH_3 molecules bonded to metal ions. Because the ammine complexes are important compounds, we will describe some of them briefly.

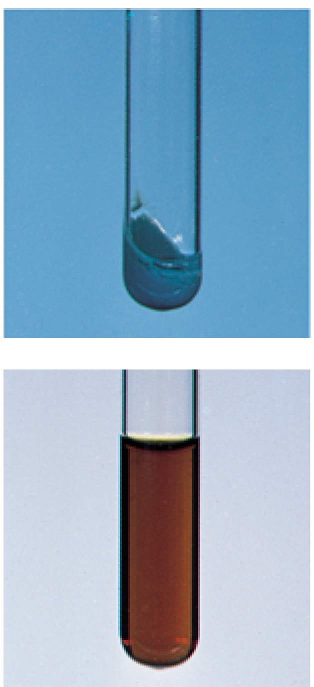
Most metal hydroxides are insoluble in water, and so aqueous NH_3 reacts with nearly all metal ions to form insoluble metal hydroxides, or hydrated oxides.

$$\begin{array}{rcl} 2[(NH_3(aq) + H_2O(\ell) & \rightleftharpoons & NH_4^+(aq) + OH^-(aq)] \\ Cu^{2+}(aq) + 2OH^-(aq) & \longrightarrow & Cu(OH)_2(s) \\ \hline Cu^{2+}(aq) + 2NH_3(aq) + 2H_2O(\ell) & \longrightarrow & Cu(OH)_2(s) + 2NH_4^+(ag) \end{array}$$

Colors of coordination compounds depend on which metals and ligands are present. From left: the $[Ni(NH_3)_6]^{2+}$ ion is purple; the $[Ni(H_2O)_6]^{2+}$ ion is green; the $[Cu(H_2O)_4]^{2+}$ ion is light blue; and the $[Cu(NH_3)_4]^{2+}$ ion is deep blue.



$Cu(OH)_2$ (*light blue*) dissolves in excess aqueous NH_3 to form $[Cu(NH_3)_4]^{2+}$ ions (*deep blue*).



$Co(OH)_2$ (a blue compound that turns gray quickly) dissolves in excess aqueous NH_3 to form $[Co(NH_3)_6]^{2+}$ ions (*yellow-orange*).

Similarly,

$$Cr^{3+} + 3NH_3 + 3H_2O \longrightarrow Cr(OH)_3(s) + 3NH_4^+$$

In general terms we can represent this reaction as

$$M^{n+} + nNH_3 + nH_2O \longrightarrow M(OH)_n(s) + nNH_4^+$$

where M^{n+} represents all of the common metal ions *except* the cations of the strong bases (Group IA cations and the heavier members of Group IIA: Ca^{2+}, Sr^{2+}, and Ba^{2+}).

The hydroxides of some metals and some metalloids are amphoteric (Section 10-6). Aqueous NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$), so the $[OH^-]$ is too low to dissolve amphoteric hydroxides to form hydroxo complexes.

However, several metal hydroxides do dissolve in an excess of aqueous NH_3 to form ammine complexes. For example, the hydroxides of copper and cobalt are readily soluble in an excess of *aqueous* ammonia solution.

TABLE 25-3 ***Common Metal Ions That Form Soluble Complexes with an Excess of Aqueous Ammonia***[a]

Metal Ion	Insoluble Hydroxide Formed by Limited Aq. NH_3	Complex Ion Formed by Excess Aq. NH_3
Co^{2+}	$Co(OH)_2$	$[Co(NH_3)_6]^{2+}$
Co^{3+}	$Co(OH)_3$	$[Co(NH_3)_6]^{3+}$
Ni^{2+}	$Ni(OH)_2$	$[Ni(NH_3)_6]^{2+}$
Cu^{+}	$CuOH \longrightarrow \frac{1}{2}Cu_2O$[b]	$[Cu(NH_3)_2]^{+}$
Cu^{2+}	$Cu(OH)_2$	$[Cu(NH_3)_4]^{2+}$
Ag^{+}	$AgOH \longrightarrow \frac{1}{2}Ag_2O$[b]	$[Ag(NH_3)_2]^{+}$
Zn^{2+}	$Zn(OH)_2$	$[Zn(NH_3)_4]^{2+}$
Cd^{2+}	$Cd(OH)_2$	$[Cd(NH_3)_4]^{2+}$
Hg^{2+}	$Hg(OH)_2$	$[Hg(NH_3)_4]^{2+}$

[a] *The ions of Rh, Ir, Pd, Pt, and Au show similar behavior.*

[b] *CuOH and AgOH are unstable and decompose to the corresponding oxides.*

TABLE 25-4 *Typical Simple Ligands with Their Donor Atoms Shaded*

Molecule	Name	Name as Ligand	Ion	Name	Name as Ligand
$:NH_3$	ammonia	ammine	$:\ddot{\underset{..}{Cl}}:^-$	chloride	chloro
$:\ddot{O}H_2$	water	aqua	$:\ddot{\underset{..}{F}}:^-$	fluoride	fluoro
$:C{\equiv}O:$	carbon monoxide	carbonyl	$:C{\equiv}N:^-$	cyanide	cyano[a]
$:PH_3$	phosphine	phosphine	$:\ddot{\underset{..}{O}}H^-$	hydroxide	hydroxo
$:\dot{N}{=}\ddot{\underset{..}{O}}$	nitrogen oxide	nitrosyl	$:NO_2^-$	nitrite	nitro[b]

[a]*Nitrogen atoms can also function as donor atoms, in which case the ligand name is "isocyano."*
[b]*Oxygen atoms can also function as donor atoms, in which case the ligand name is "nitrito."*

$$Cu(OH)_2(s) + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 2OH^-$$
$$Co(OH)_2(s) + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 2OH^-$$

Interestingly, the metal hydroxides that exhibit this behavior are derived from the 12 metals of the cobalt, nickel, copper, and zinc families. All the common cations of these metals except Hg_2^{2+} (which disproportionates) form soluble complexes in the presence of excess aqueous ammonia (Table 25-3).

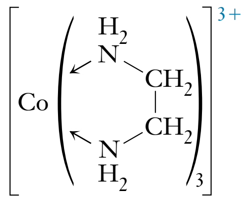
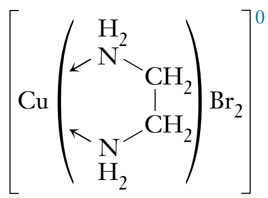
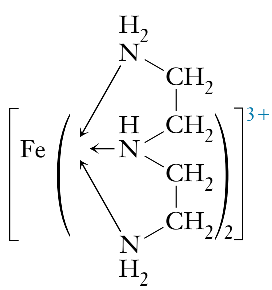
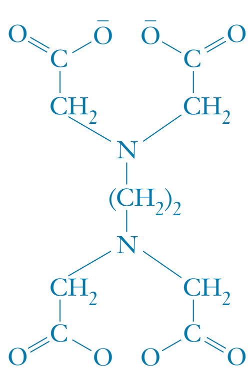
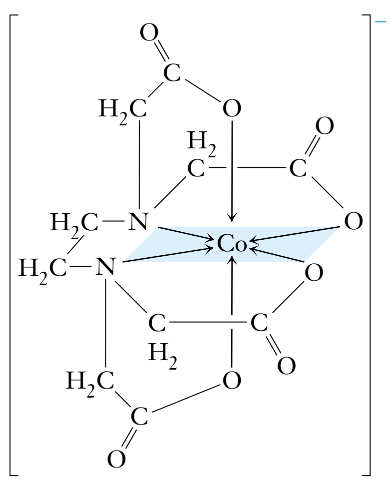
25-3 IMPORTANT TERMS

The Lewis bases in coordination compounds may be molecules, anions, or (rarely) cations. They are called **ligands** (Latin *ligare*, "to bind"). The **donor atoms** of the ligands are the atoms that donate shares in electron pairs to metals. In some cases it is not possible to identify donor atoms, because the bonding electrons are not localized on specific atoms. Some small organic molecules such as ethylene, $H_2C{=}CH_2$, bond to a transition metal through the electrons in their double bonds. Examples of typical simple ligands are listed in Table 25-4.

Ligands that can bond to a metal through only one donor atom at a time are **monodentate** (Latin *dent*, "tooth"). Ligands that can bond simultaneously through more than one donor atom are **polydentate.** Polydentate ligands that bond through two, three, four, five, or six donor atoms are called *bidentate*, *tridentate*, *quadridentate*, *quinquedentate*, and *hexadentate*, respectively. Complexes that consist of a metal atom or ion and polydentate ligands are called **chelate complexes** (Greek *chele*, "claw").

The **coordination number** of a metal atom or ion in a complex is the number of donor atoms to which it is coordinated, not necessarily the number of ligands. The **coordination sphere** includes the metal or metal ion (called the **central atom**) and its ligands, but no uncoordinated counterions. For example, the coordination sphere of hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, is the hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$. These terms are illustrated in Table 25-5.

TABLE 25-5 *Some Ligands and Coordination Spheres (complexes)*

Ligand(s)	Classification	Coordination Sphere	Oxidation Number of M	Coordination Number of M
NH_3 ammine	monodentate	$[Co(NH_3)_6]^{3+}$ hexaamminecobalt(III)	+3	6
$H_2N—CH_2—CH_2—NH_2$ (or N N) ethylenediamine (en)	bidentate	 $[Co(en)_3]^{3+}$ tris(ethylenediamine)-cobalt(III) ion	+3	6
Br^- bromo $H_2N—CH_2—CH_2—NH_2$ ethylenediamine (en)	monodentate bidentate	 $[Cu(en)Br_2]$ dibromoethylenediamine-copper(II)	+2	4
$H_2N—(CH_2)_2—N(H)—(CH_2)_2—NH_2$ (or N N N) diethylenetriamine (dien)	tridentate	 $[Fe(dien)_2]^{3+}$ bis(diethylenetriamine)-iron(III) ion	+3	6
 ethylenediaminetetraacetato (edta)	hexadentate	 $[Co(edta)]^-$ (ethylenediaminetetraacetato)-cobaltate(III) ion	+3	6

25-4 NOMENCLATURE

The International Union of Pure and Applied Chemistry (IUPAC) has adopted a set of rules for naming coordination compounds. The rules are based on those originally devised by Werner.

1. Cations are always named before anions, with a space between their names.
2. In naming the coordination sphere, ligands are named in alphabetical order. The prefixes di = 2, tri = 3, tetra = 4, penta = 5, hexa = 6, and so on specify the number of each kind of *simple* (monodentate) ligand. For example, in dichloro, the "di" indicates that two Cl^- ions act as ligands. For complicated ligands (polydentate chelating agents), other prefixes are used, including: bis = 2, tris = 3, tetrakis = 4, pentakis = 5, and hexakis = 6. The names of complicated ligands are enclosed in parentheses. The numeric prefixes are not used in alphabetizing. When a prefix denotes the number of substituents on a single ligand, as in dimethylamine, $NH(CH_3)_2$, it *is* used to alphabetize ligands.
3. The names of anionic ligands end in the suffix -o. Examples are F^-, fluoro; OH^-, hydroxo; O^{2-}, oxo; S^{2-}, sulfido; CO_3^{2-}, carbonato; CN^-, cyano; SO_4^{2-}, sulfato; NO_3^-, nitrato; $S_2O_3^{2-}$, thiosulfato.
4. The names of neutral ligands are usually unchanged. Four important exceptions are NH_3, ammine; H_2O, aqua; CO, carbonyl; and NO, nitrosyl.
5. Some metals exhibit variable oxidation states. The oxidation number of such a metal is designated by a Roman numeral in parentheses following the name of the complex ion or molecule.
6. The suffix "-ate" at the end of the name of the complex signifies that it is an anion. If the complex is neutral or cationic, no suffix is used. The English stem is usually used for the metal, but where the naming of an anion is awkward, the Latin stem is substituted. For example, "ferrate" is used rather than "ironate," and "plumbate" rather than "leadate" (Table 25-6).

TABLE 25-6 ***Names for Some Metals in Complex Anions***

Metal	Name* of Metal in Complex Anions
aluminum	aluminate
antimony	antimonate
chromium	chromate
cobalt	cobaltate
copper	*cupr*ate
gold	*aur*ate
iron	*ferr*ate
lead	*plumb*ate
manganese	manganate
nickel	nickelate
platinum	platinate
silver	*argent*ate
tin	*stann*ate
zinc	zincate

**Stems derived from Latin names for metals are shown in italics.*

The term *ammine* (two m's) signifies the presence of ammonia as a ligand. It is different from the term *amine* (one m), which describes some organic compounds (Section 27-12) that are derived from ammonia.

The following examples illustrate these rules.

$K_2[Cu(CN)_4]$	potassium tetracyanocuprate(II)
$[Ag(NH_3)_2]Cl$	diamminesilver chloride
$[Cr(OH_2)_6](NO_3)_3$	hexaaquachromium(III) nitrate
$[Co(en)_2Br_2]Cl$	dibromobis(ethylenediamine)cobalt(III) chloride
$[Ni(CO)_4]$	tetracarbonylnickel(0)
$Na[Al(OH)_4]$	sodium tetrahydroxoaluminate
$[Pt(NH_3)_4][PtCl_6]$	tetraammineplatinum(II) hexachloroplatinate(IV)
$[Cu(NH_3)_2(en)]Br_2$	diammine(ethylenediamine)copper(II) bromide
$Na_2[Sn(OH)_6]$	sodium hexahydroxostannate(IV)
$[Co(en)_3](NO_3)_3$	tris(ethylenediamine)cobalt(III) nitrate
$K_4[Ni(CN)_2(ox)_2]$	potassium dicyanobis(oxalato)nickelate(II)
$[Co(NH_3)_4(OH_2)Cl]Cl_2$	tetraammineaquachlorocobalt(III) chloride

The oxidation state of aluminum is not given because it is always +3.

The abbreviation *ox* represents the oxalate ion $(COO)_2^{2-}$ or $C_2O_4^{2-}$.

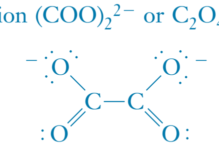
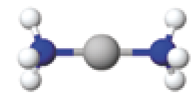
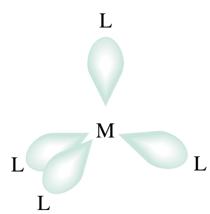
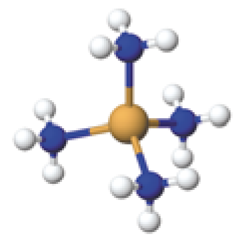
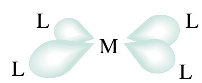
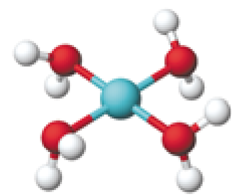
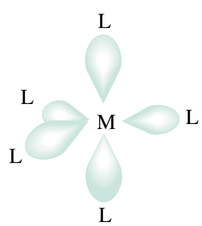
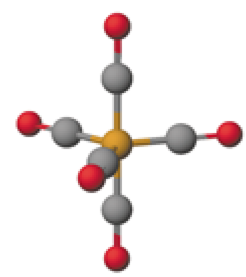
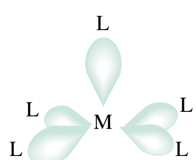
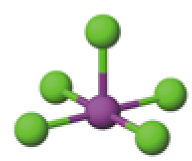
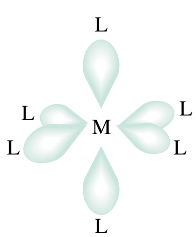
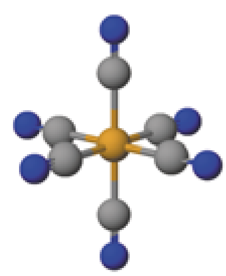


TABLE 25-7 *Idealized Geometries for Various Coordination Numbers*

Coordination Number	Geometry	Examples	Model	
2	 linear	$[Ag(NH_3)_2]^+$ $[Cu(CN)_2]^-$	$[Ag(NH_3)_2]^+$	
4	 tetrahedral	$[Zn(CN)_4]^{2-}$ $[Cd(NH_3)_4]^{2+}$	$[Cd(NH_3)_4]^{2+}$	
4	 square planar	$[Ni(CN)_4]^{2-}$ $[Cu(OH_2)_4]^{2+}$ $[Pt(NH_3)_2Cl_2]$	$[Cu(OH_2)_4]^{2+}$	
5	 trigonal bipyramidal	$[Fe(CO)_5]$ $[CuCl_5]^{3-}$	$[Fe(CO)_5]$	
5	 square pyramidal	$[Ni(CN)_5]^{3-}$ $[MnCl_5]^{3-}$	$[MnCl_5]^{3-}$	
6	 octahedral	$[Fe(CN)_6]^{4-}$ $[Fe(OH_2)_6]^{2+}$	$[Fe(CN)_6]^{4-}$	

25-5 STRUCTURES

The structures of coordination compounds are governed largely by the coordination number of the metal. Many have structures similar to the simple molecules and ions we studied in Chapter 8. Unshared pairs of electrons in *d* orbitals usually have only small influences on geometry because they are not in the outer shell. Table 25-7 summarizes the geometries for common coordination numbers.

Both tetrahedral and square planar geometries are common for complexes with coordination number 4. For coordination number 5, the trigonal bipyramidal structure and the square pyramidal structure are both common. Transition metal complexes with coordination numbers as high as 7, 8, and 9 are known. The geometries tabulated are ideal geometries. Actual structures are sometimes distorted, especially if the ligands are not all the same. The distortions are due to compensations for the unequal electric fields generated by the different ligands.

ISOMERISM IN COORDINATION COMPOUNDS

Isomers are different compounds that have the same molecular formula; they have the same number and kinds of atoms arranged differently. The term *isomers* comes from the Greek word meaning "equal weights." *Because their structures are different, isomers have different physical and chemical properties.* Here we shall restrict our discussion of isomerism to that caused by different arrangements of ligands about central metal ions.

There are two major classes of isomers: structural (constitutional) isomers and stereoisomers. For coordination compounds, each can be further subdivided as follows.

Structural Isomers	Stereoisomers
1. ionization isomers	1. geometric (positional) isomers
2. hydrate isomers	2. optical isomers
3. coordination isomers	
4. linkage isomers	

Some coordination compounds. Starting at the top left and moving clockwise:

$[Cr(CO)_6]$ (*white*), CO is the ligand.

$K_3\{Fe[(COO)_2]_3\}$ (*green*), $(COO)_2^{2-}$ (oxalate ion) is the ligand.

$[Co(H_2N{-}CH_2{-}CH_2{-}NH_2)_3]I_3$ (*yellow-orange*), ethylenediamine is the ligand.

$[Co(NH_3)_5(OH_2)]Cl_3$ (*red*), NH_3 and H_2O are ligands.

$K_3[Fe(CN)_6]$ (*red-orange*), CN^- is the ligand. (A drop of water fell on this sample.)

Differences between **structural isomers** involve either more than one coordination sphere or different donor atoms on the same ligand. They contain *different atom-to-atom bonding sequences.* Simple stereoisomers of coordination compounds involve only one coordination sphere and the same ligands and donor atoms. Before considering stereoisomers, we will describe the four types of structural isomers.

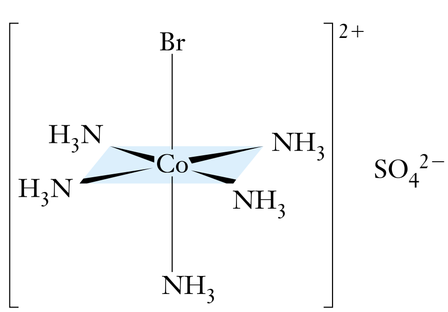
25-6 STRUCTURAL (CONSTITUTIONAL) ISOMERS

Ionization (Ion–Ion Exchange) Isomers

These isomers result from the interchange of ions inside and outside the coordination sphere. For example, red-violet $[Co(NH_3)_5Br]SO_4$ and red $[Co(NH_3)_5SO_4]Br$ are ionization isomers.

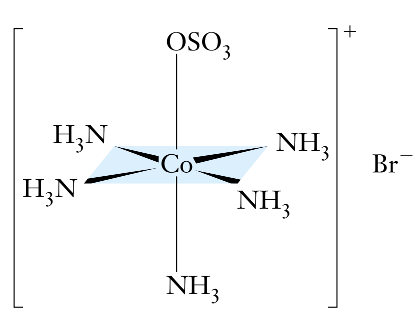
Isomers such as those shown here may or *may not* exist in the same solution in equilibrium. Such isomers are formed by *different* reactions.

We write the sulfato ligand as OSO_3 to emphasize that it is coordinated through a lone pair on one of the O atoms.



$[Co(NH_3)_5Br]SO_4$
pentaamminebromocobalt(III) sulfate

A



$[Co(NH_3)_5SO_4]Br$
pentaamminesulfatocobalt(III) bromide

B

In structure A the SO_4^{2-} ion is free and is not bound to the cobalt(III) ion. A solution of A reacts readily with a solution of barium, $BaCl_2$, to precipitate $BaSO_4$, but does not react readily with $AgNO_3$. In structure B the SO_4^{2-} ion is bound to the cobalt(III) ion and so it does not react with $BaCl_2$ in aqueous solution. The Br^- ion is free, however, and a solution of B reacts with $AgNO_3$ to precipitate AgBr. *Equimolar* solutions of A and B also have different electrical conductivities. The sulfate solution, A, conducts electric current better because its ions have 2+ and 2− charges rather than 1+ and 1−. Other examples of this type of isomerism include

$[Pt(NH_3)_4Cl_2]Br_2$	and	$[Pt(NH_3)_4Br_2]Cl_2$
$[Pt(NH_3)_4SO_4](OH)_2$	and	$[Pt(NH_3)_4(OH)_2]SO_4$
$[Co(NH_3)_5NO_2]SO_4$	and	$[Co(NH_3)_5SO_4]NO_2$
$[Cr(NH_3)_5SO_4]Br$	and	$[Cr(NH_3)_5Br]SO_4$

Recall that $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) and AgBr ($K_{sp} = 3.3 \times 10^{-13}$) are classified as insoluble in H_2O, whereas $BaBr_2$ is soluble and Ag_2SO_4 ($K_{sp} = 1.7 \times 10^{-5}$) is moderately soluble.

In A:

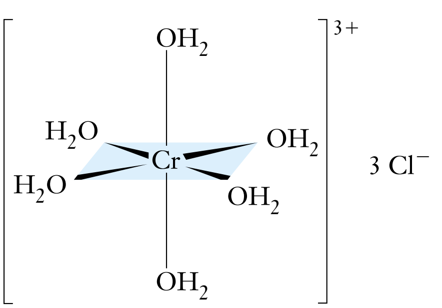
$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4(s)$$
$$Ag^{+} + SO_4^{2-} \longrightarrow \text{no rxn}$$

In B:

$$Ag^{+} + Br^{-} \longrightarrow AgBr(s)$$
$$Ba^{2+} + Br^{-} \longrightarrow \text{no rxn}$$

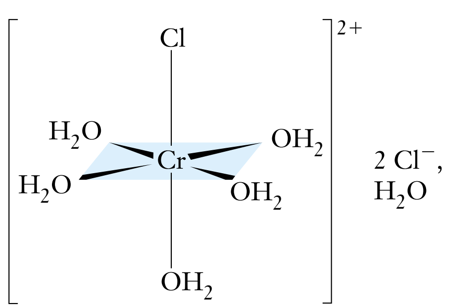
Hydrate Isomers

In some crystalline complexes, water can be *inside* and *outside* the coordination sphere. For example, when treated with excess $AgNO_3(aq)$, solutions of the following three hydrate isomers yield three, two, and one mole of AgCl precipitate, respectively, per mole of complex.



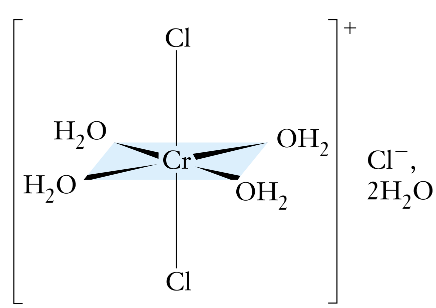
$[Cr(OH_2)_6]Cl_3$
hexaaquachromium(III) chloride

violet



$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$
pentaaquachlorochromium(III) chloride hydrate

blue-green

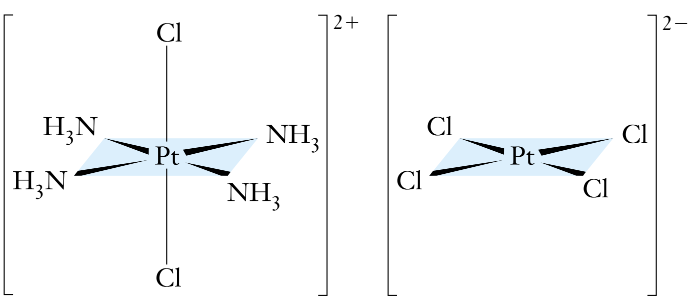


$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$
tetraaquadichlorochromium(III) chloride dihydrate

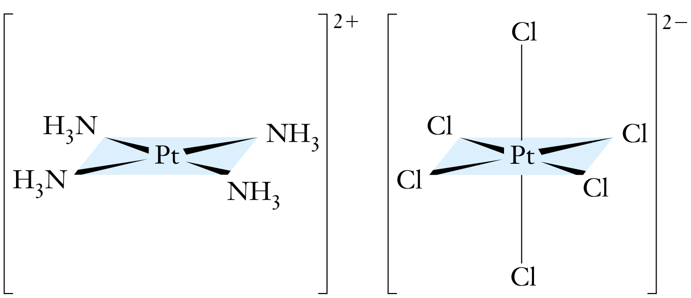
green

Coordination Isomers

Coordination isomerism can occur in compounds containing both complex cations and complex anions. Such isomers involve exchange of ligands between cation and anion, that is, between coordination spheres.



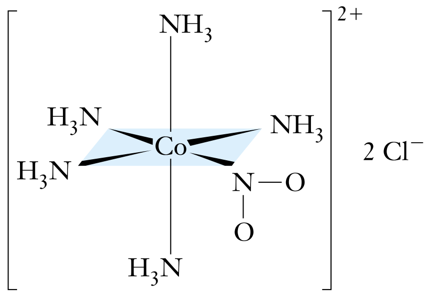
$[Pt(NH_3)_4Cl_2][PtCl_4]$,
tetraamminedichloroplatinum(IV) tetrachloroplatinate(II)



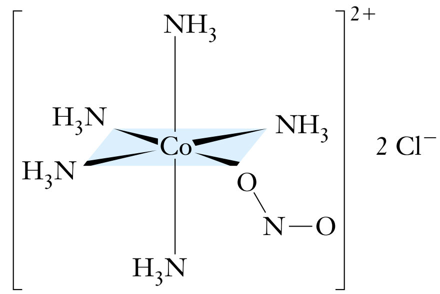
$[Pt(NH_3)_4][PtCl_6]$,
tetraammineplatinum(II) hexachloroplatinate(IV)

Linkage Isomers

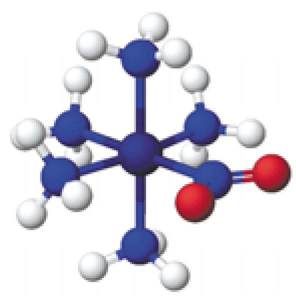
Certain ligands can bind to metal ions in more than one way. Examples of such ligands are cyano, $—CN^-$, and isocyano, $—NC^-$; nitro, $—NO_2^-$, and nitrito, $—ONO^-$. The donor atoms are on the left in these representations.



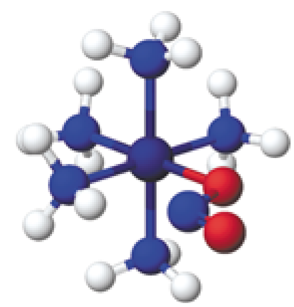
$[Co(NH_3)_5NO_2]Cl_2$
pentaamminenitrocobalt(III) chloride
yellow, stable in acids



$[Co(NH_3)_5ONO]Cl_2$
pentaamminenitritocobalt(III) chloride
red, decomposes in acids



Pentaamminenitrocobalt(III) ion, $[Co(NH_3)_5NO_2]^{2+}$



Pentaamminenitritocobalt(III) ion, $[Co(NH_3)_5ONO]^{2+}$

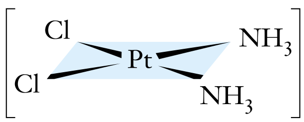
25-7 STEREOISOMERS

A complex with coordination number 2 or 3 that contains only *simple ligands* can have only one spatial arrangement. Try building models to see this.

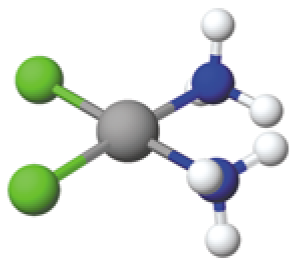
Compounds that contain the same atoms and the same atom-to-atom bonding sequences, but that differ only in the spatial arrangements of the atoms relative to the central atom, are **stereoisomers.** Complexes with only *simple* ligands can exist as stereoisomers *only if* they have coordination number 4 or greater. The most common coordination numbers among coordination complexes are 4 and 6, and so they will be used to illustrate stereoisomerism.

Geometric (*cis–trans*) Isomers

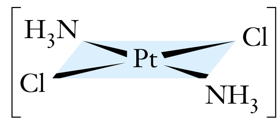
In **geometric isomers,** or ***cis-trans*** **isomers,** of *coordination compounds*, the same ligands are arranged in different orders within the coordination sphere. Geometric isomerism occurs when atoms or groups of atoms can be arranged on two sides of a rigid structure. *Cis* means "adjacent to" and *trans* means "on the opposite side of." *Cis*- and *trans*-diamminedichloroplatinum(II) are shown below.



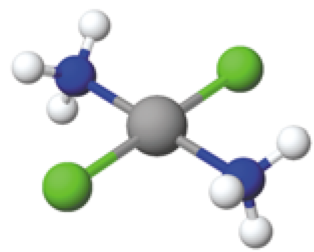
cis
pale yellow
Cl—Pt—Cl angle ≈ 90°
N—Pt—N angle ≈ 90°



cis-diamminedichloroplatinum(II), *cis*-$[Pt(NH_3)_2Cl_2]$



trans
dark yellow
Cl—Pt—Cl angle ≈ 180°
N—Pt—N angle ≈ 180°



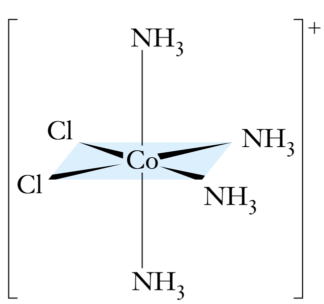
trans-diamminedichloroplatinum(II), *trans*-$[Pt(NH_3)_2Cl_2]$

The *cis* isomer has been used successfully in cancer chemotherapy. The *trans* isomer has no such activity.

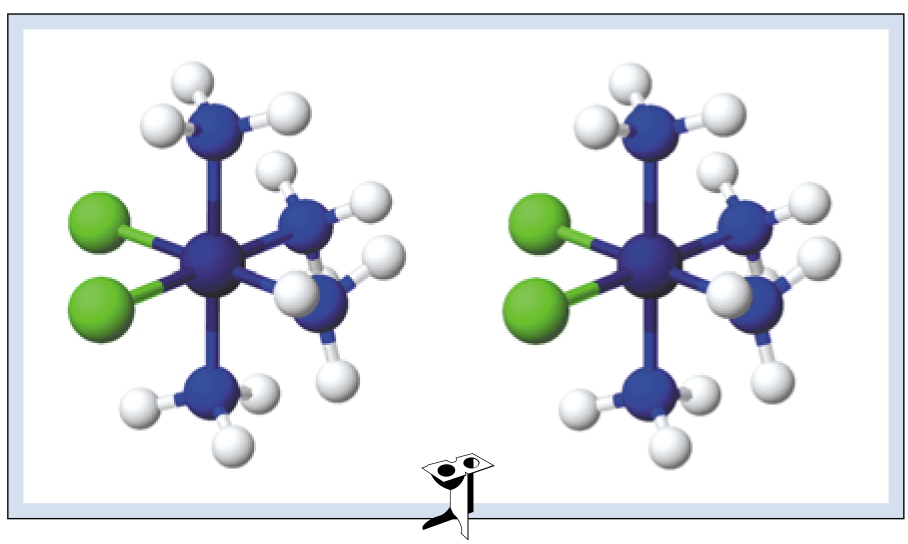
In the *cis* isomer, the chloro groups are closer to each other (on the same side of the square) than they are in the *trans* isomer. The ammine groups are also closer together in the *cis* complex.

Geometric isomerism is possible for octahedral complexes. For example, complexes of the type MA_4B_2 can exist in two isomeric forms. Consider as an example the complex ion $[Co(NH_3)_4Cl_2]^+$. The two like ligands (Cl^-) can be either *cis* or *trans* to each other. These two complexes are different colors: solutions and salts of the *cis* isomer are violet and those of the *trans* isomer are green.

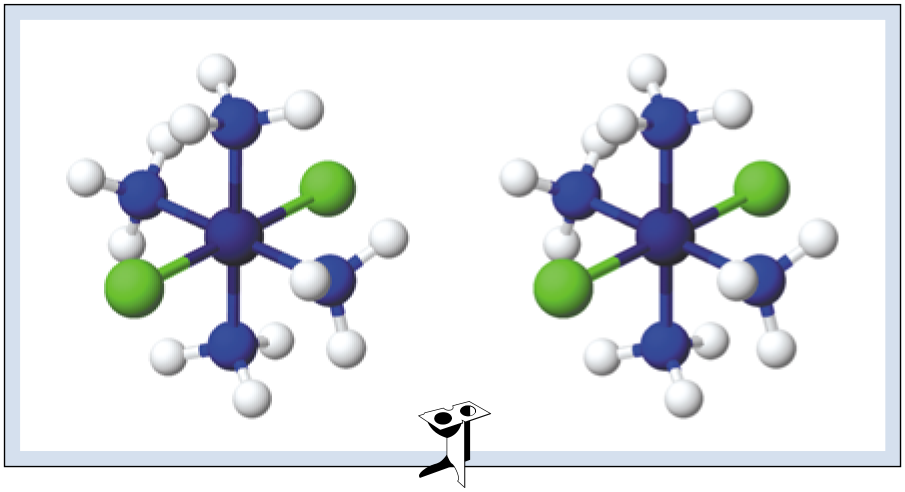
Cis–trans isomerism is not possible for tetrahedral complexes, in which all angles are (ideally) 109.5°.



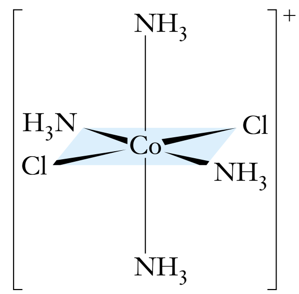
cis-tetraamminedichlorocobalt(III) ion, *cis*-$[Co(NH_3)_4Cl_2]^+$



A stereoview of *cis*-tetraamminedichlorocobalt(III) ion, *cis*-$[Co(NH_3)_4Cl_2]^+$. The two chloro ligands are adjacent to each other.



A stereoview of *trans*-tetraamminedichlorocobalt(III) ion, *trans*-$[Co(NH_3)_4Cl_2]^+$. The two chloro ligands are across from each other.



trans-tetraamminedichlorocobalt(III) ion, *trans*-$[Co(NH_3)_4Cl_2]^+$

Complexes involving bidentate ligands, such as ethylenediamine, can also exhibit this kind of isomerism, as shown in Figure 25-2.

Octahedral complexes with the general formula MA_3B_3 can exhibit another type of geometric isomerism, called *mer–fac* isomerism. This can be illustrated with the complex ion $[Pt(NH_3)_3Cl_3]^+$ (see Table 25-2). In one isomer the three similar ligands (e.g., the Cl^- ligands) lie at the corners of a triangular face of the octahedron; this is called the *fac* isomer (for *facial*).

In the other isomer, the three similar ligands lie in the same plane; this is called the *mer* isomer (so called because the plane is analogous to a meridian on a globe).

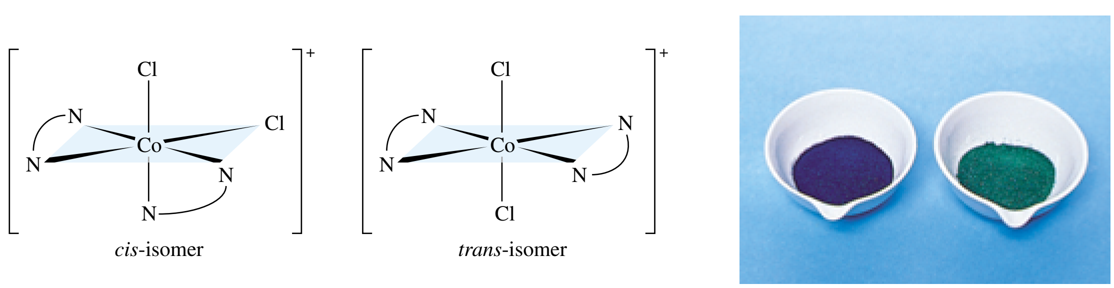
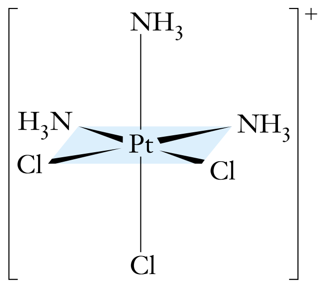
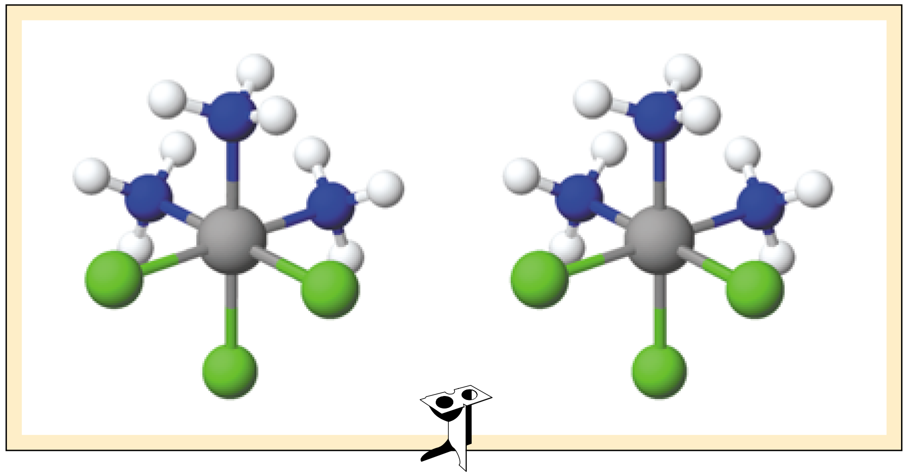


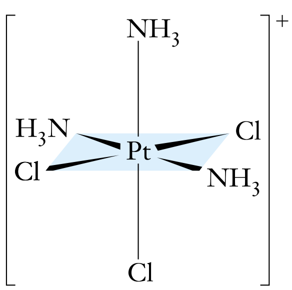
Figure 25-2 The dichlorobis(ethylenediamine)cobalt(III) ion, $[Co(en)_2Cl_2]^+$, exists as a pair of *cis–trans* isomers. Ethylenediamine is represented as N N. *Cis*-dichlorobis(ethylenediamine)cobalt(III) perchlorate, $[Co(en)_2Cl_2]ClO_4$, is purple. *Trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, $[Co(en)_2Cl_2]Cl$, is green.



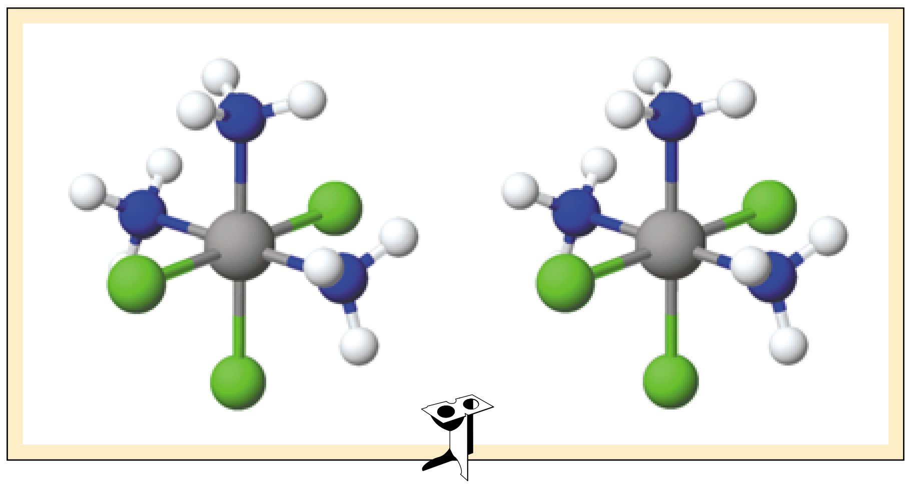
fac-triamminetrichloroplatinum(IV) ion,
fac-$[Pt(NH_3)_3Cl_3]^+$



A stereoview of *fac*-triamminetrichloroplatinum(IV) ion, *fac*-$[Pt(NH_3)_3Cl_3]^+$. The three chloro ligands are all on one triangular face of an octahedron, and the three ammine ligands are all on the opposite triangular face.

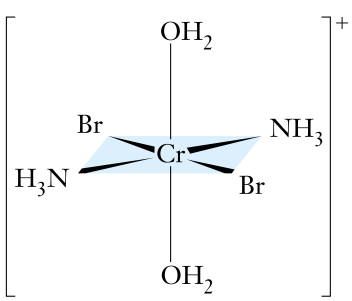


mer-triamminetrichloroplatinum(IV) ion,
mer-$[Pt(NH_3)_3Cl_3]^+$



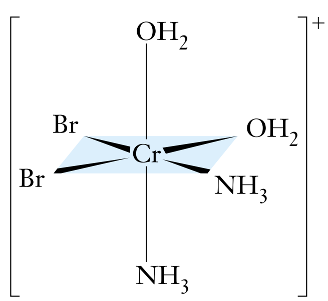
A stereoview of *mer*–triammine-trichloroplatinum(IV) ion, *mer*-$[Pt(NH_3)_3Cl_3]^+$. The three chloro ligands are all one meridian (in a plane), and the three ammine ligands are all on a perpendicular meridian (a plane perpendicular to the first).

Complexes of the type $[MA_2B_2C_2]$ can exist in several isomeric forms. Consider as an example $[Cr(OH_2)_2(NH_3)_2Br_2]^+$. First, the members of all three pairs of like ligands may be either *trans* to each other (A) or *cis* to each other (B).



trans-diammine-*trans*-diaqua-*trans*-dibromochromium(III) ion

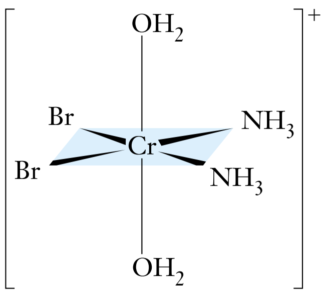
A



cis-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

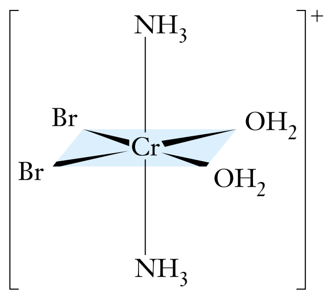
B

Then, members of one of the pairs may be *trans* to each other, but the members of the other two pairs are *cis*.



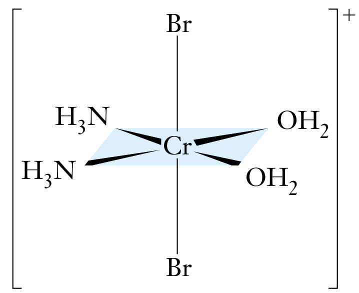
cis-diammine-*trans*-diaqua-*cis*-dibromochromium(III) ion

C



trans-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

D



cis-diammine-*cis*-diaqua-*trans*-dibromochromium(III) ion

E

In C, only the two H_2O ligands are in a *trans* arrangement; in D, only the NH_3 ligands are *trans*; and in E, only the two Br^- ligands are *trans*.

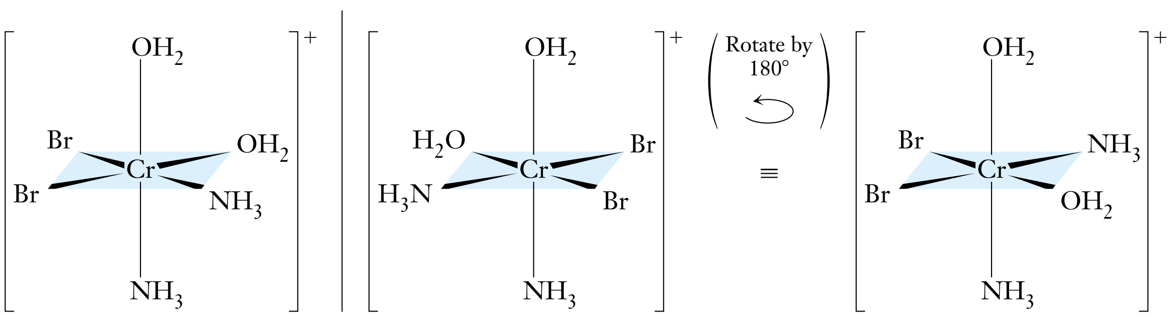
There is no *trans–trans–cis* isomer. Why?

Further interchange of the positions of the ligands produces no new geometric isomers. However, one of the five geometric isomers (B) can exist in two distinct forms called *optical isomers*.

Optical Isomers

An object that is not superimposable with its mirror image is said to be *chiral.*

The *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) geometrical isomer (B) exists in two forms that bear the same relationship to each other as left and right hands. They are *nonsuperimposable* mirror images of each other and are called **optical isomers** or **enantiomers.**

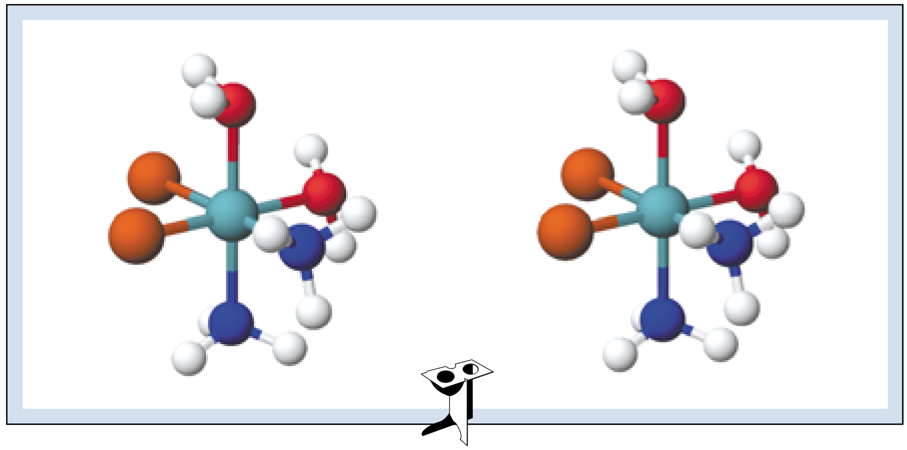


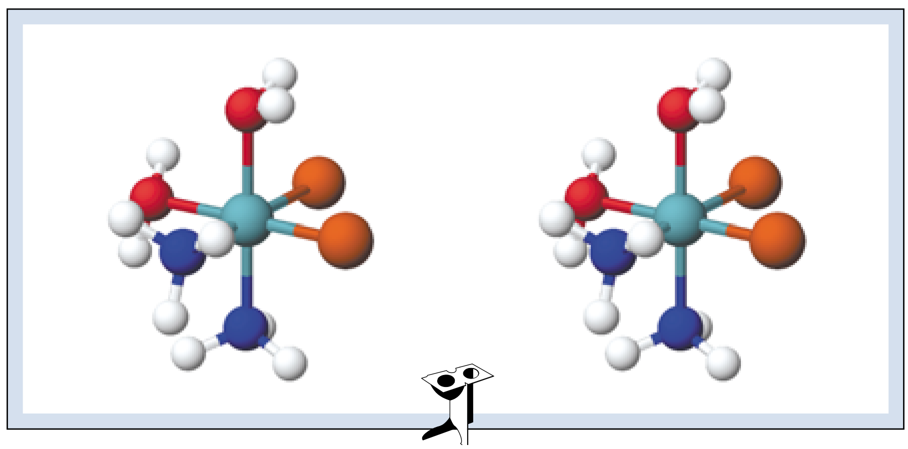
B-I **B-II** **B-II′**

Optical isomers of *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

Complexes B-I and B-II are mirror images of each other. To see that they are not identical, imagine rotating B-II about its vertical axis by 180° (B-II′), so that the two Br^- ligands are at the left, as they are in B-I. Then B-II′ has the OH_2 ligand at the right front position and the NH_3 ligand at the right rear position, which is not the same as in B-I. No rotation of B-II makes it identical to B-I. Thus these two arrangements are nonsuperimposable mirror images of each other. Stereo images of these two complexes appear in Figure 25-3.

Figure 25-3 The optical isomers of the *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion.





Optical isomers interact with polarized light in different ways. Separate equimolar solutions of each rotate a plane of polarized light (see Figures 25-4 and 25-5) by equal amounts but in opposite directions. One solution is **dextrorotatory** (rotates to the *right*) and the other is **levorotatory** (rotates to the *left*). Optical isomers are called *dextro* and *levo* isomers. The phenomenon by which a plane of polarized light is rotated is called **optical activity.** It can be measured with a device called a polarimeter (Figure 25-5) or with more sophisticated instruments. A single solution containing equal amounts of the two isomers is a **racemic mixture.** This solution does not rotate a plane of polarized light. The equal and opposite effects of the two isomers exactly cancel. To exhibit optical activity, the *dextro* and *levo* isomers must be separated from each other. This is done by one of a number of chemical or physical processes broadly called **optical resolution.**

Alfred Werner was also the first person to demonstrate optical activity in an inorganic compound (not of biological origin). This demonstration silenced critics of his theory of coordination compounds, and in his opinion, it was his greatest achievement. Louis Pasteur had demonstrated the phenomenon of optical activity many years earlier in organic compounds of biological origin.

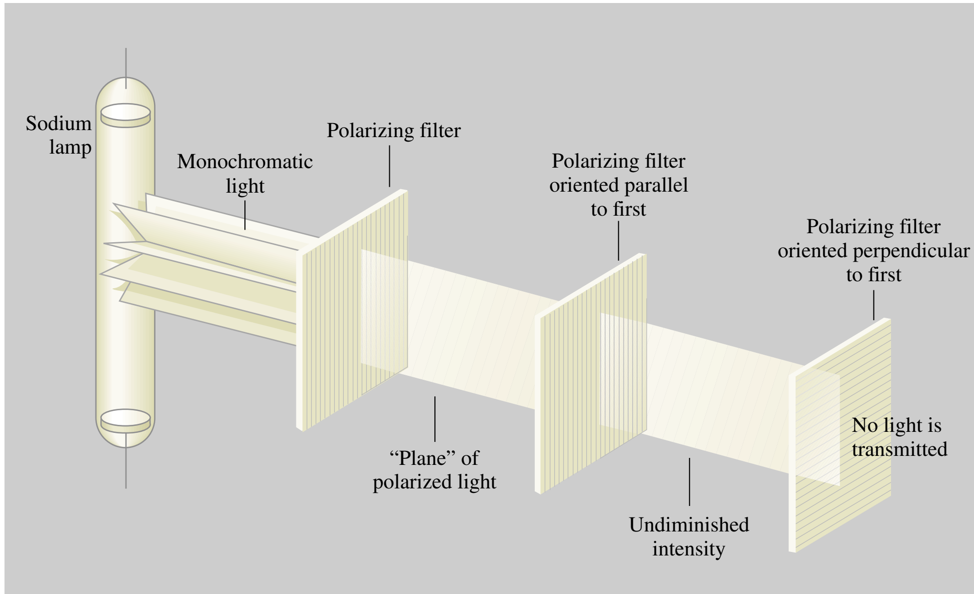


Figure 25-4 Light from a lamp or from the sun consists of electromagnetic waves that vibrate in all directions perpendicular to the direction of travel. Polarizing filters absorb all waves except those that vibrate in a single plane. The third polarizing filter, with a plane of polarization at right angles to the first, absorbs the polarized light completely.

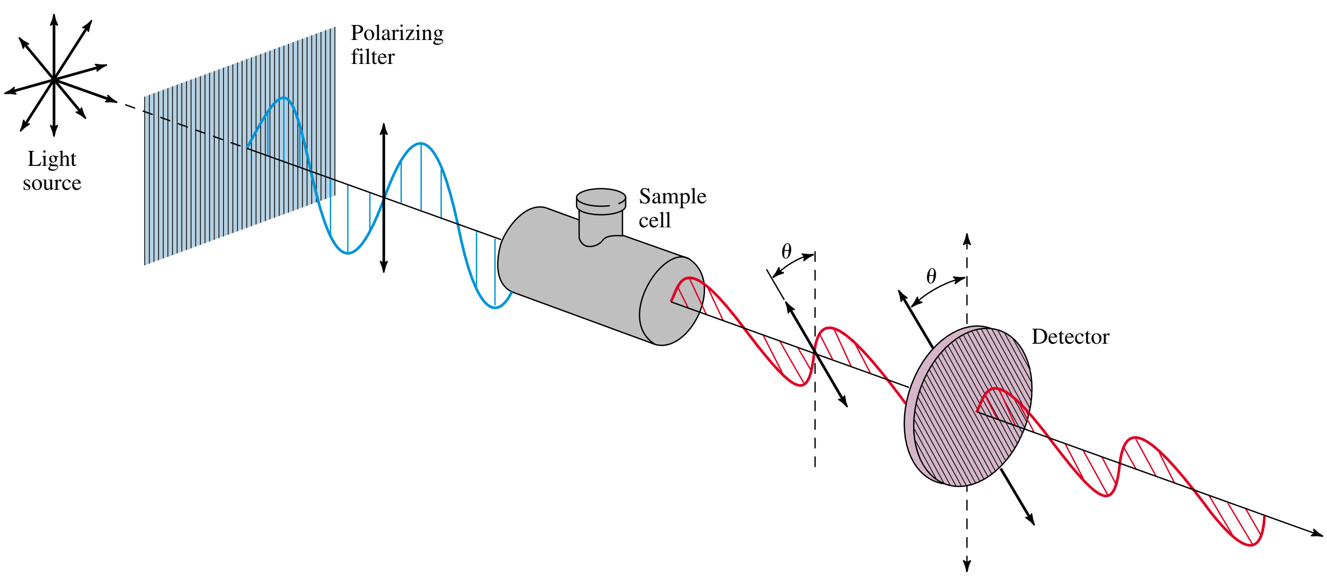
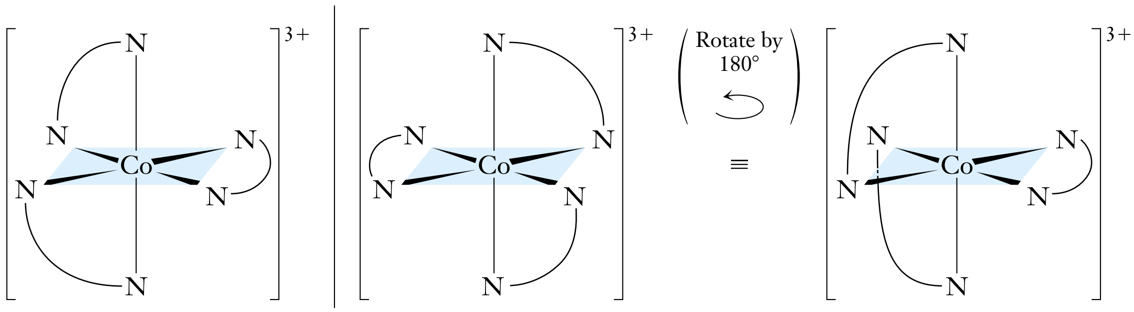
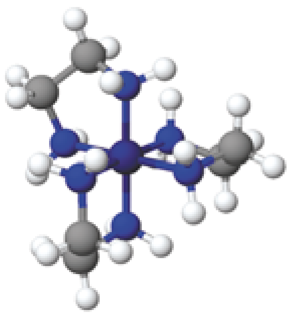


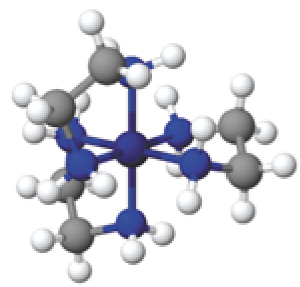
Figure 25-5 The plane of polarization of plane-polarized light is rotated through an angle (θ) as it passes through an optically active medium. Species that rotate the plane to the right (clockwise) are dextrorotatory, and those that rotate it to the left are levorotatory.

Another pair of optical isomers follows, each of which contains three molecules of ethylenediamine, a bidentate ligand.



The two optical isomers of the *tris*(ethylenediamine)cobalt(III) ion





BONDING IN COORDINATION COMPOUNDS

Bonding theories for coordination compounds should be able to account for structural features, colors, and magnetic properties. The earliest accepted theory was the valence bond theory (Chapter 8). It can account for structural and magnetic properties, but it offers no explanation for the wide range of colors of coordination compounds. The **crystal field theory** gives satisfactory explanations of color as well as of structure and magnetic properties for many coordination compounds. We will therefore discuss only this more successful theory in the remainder of this chapter.

25-8 CRYSTAL FIELD THEORY

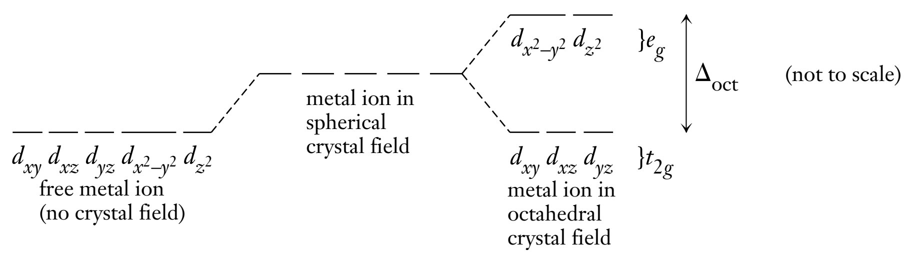
Hans Bethe (1906–) and J. H. van Vleck (1899–1980) developed the crystal field theory between 1919 and the early 1930s. It was not widely used, however, until the 1950s. In its original form, it assumed that the bonds between ligand and metal were completely ionic.

Modern ligand field theory is based on crystal field theory. It attributes partial covalent character and partial ionic character to bonds. It is a more sophisticated theory, beyond the scope of this text.

In a metal ion surrounded by other atoms, the *d* orbitals are at higher energy than they are in an isolated metal ion. If the surrounding electrons were uniformly distributed about the metal ion, the energies of *all* five *d* orbitals would increase by the same amount (a *spherical crystal field*). Because the ligands approach the metal ion from different directions, they affect different *d* orbitals in different ways. Here we illustrate the application of these ideas to complexes with coordination number 6 (*octahedral crystal field*).

The $d_{x^2-y^2}$, and d_{z^2} orbitals are directed along a set of mutually perpendicular x, y, and z axes (p. 212). As a group, these orbitals are called $\boldsymbol{e_g}$ **orbitals.** The d_{xy}, d_{yz}, and d_{xz} orbitals, collectively called $\boldsymbol{t_{2g}}$ **orbitals,** lie between the axes. The ligand donor atoms approach the metal ion along the axes to form octahedral complexes. Crystal field theory proposes that the approach of the six donor atoms (point charges) along the axes sets up an electric field (the crystal field). Electrons on the ligands repel electrons in e_g orbitals on the metal ion more strongly than they repel those in t_{2g} orbitals (Figure 25-6). This removes the degeneracy of the set of d orbitals and splits them into two sets, the e_g set at higher energy and the t_{2g} set at lower energy.

Recall that degenerate orbitals are orbitals of equal energy.



The energy separation between the two sets is called the **crystal field splitting energy,** $\Delta_{octahedral}$, or Δ_{oct}. It is proportional to the *crystal field strength* of the ligands—that is, how strongly the ligand electrons repel the electrons on the metal ion.

Typical values of Δ_{oct} are between 100 and 400 kJ/mol.

The d electrons on a metal ion occupy the t_{2g} set in preference to the higher energy e_g set. Electrons that occupy the e_g orbitals are strongly repelled by the relatively close approach of ligands. The occupancy of these orbitals tends to destabilize octahedral complexes.

As always, electrons occupy the orbitals in the arrangement that results in the lowest energy. The **electron pairing energy,** P, is the expenditure of energy that is necessary to pair electrons by bringing two negatively charged particles into the same region of space. We must compare this with the crystal field splitting energy, Δ_{oct}, the difference in energy between t_{2g} and e_g. Weak field ligands such as F^- cause only small splitting energies, whereas strong field ligands such as CN^- give large values of Δ_{oct}.

If the splitting energy, Δ_{oct}, is smaller than the pairing energy, P, the electrons occupy all five nondegenerate orbitals singly before pairing. After all d orbitals are half-filled,

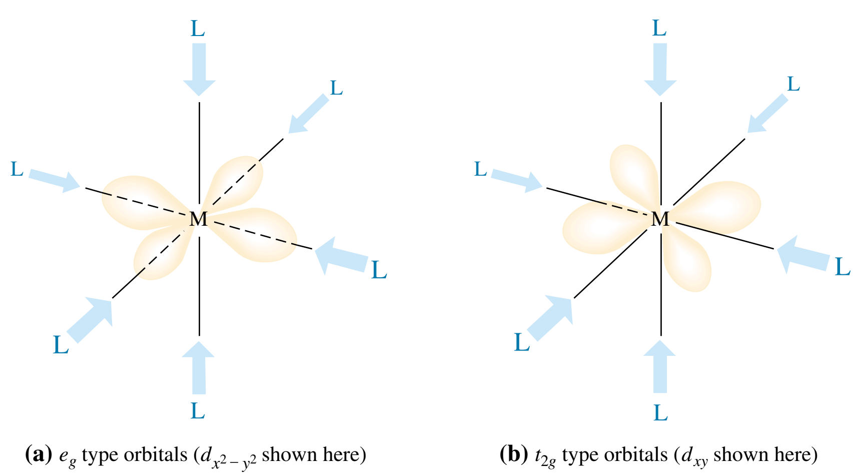


Figure 25-6 Effects of the approach of ligands on the energies of d orbitals on the metal ion. In an octahedral complex, the ligands (L) approach the metal ion (M) along the x, y, and z axes, as indicated by the blue arrows. (a) The orbitals of the e_g type—$d_{x^2-y^2}$ (shown here) and d_{z^2}—point directly toward the incoming ligands, so electrons in these orbitals are strongly repelled. (b) The orbitals of the t_{2g} type—d_{xy} (shown here), d_{xz} and d_{yz}—do not point toward the incoming ligands, so electrons in these orbitals are less strongly repelled.

additional electrons then pair with electrons in the t_{2g} set. Such a complex would have the same number of *unpaired* electrons on the metal atom or ion as when the metal is uncomplexed; this is called a **high spin complex.** But if the splitting energy is greater than the pairing energy, the electrons will be at lower energy if they pair in the t_{2g} orbital before any electrons occupy the higher energy e_g orbitals. Such a complex could have fewer unpaired electrons on the metal atom than when the metal is uncomplexed, so it is called a **low spin complex.**

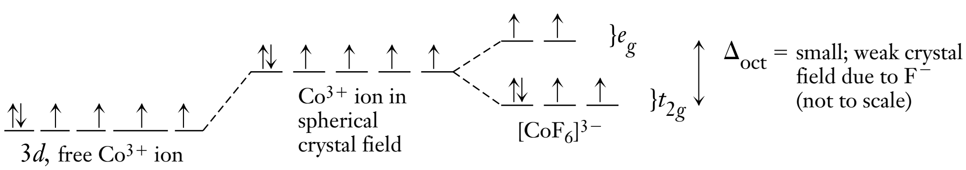
Let us now describe the hexafluorocobaltate(III) ion, $[CoF_6]^{3-}$, and the hexacyanocobalt(III) ion, $[Co(CN)_6]^{3-}$. Both contain the d^6 Co^{3+} ion. The $[CoF_6]^{3-}$ ion is a paramagnetic complex, whereas $[Co(CN)_6]^{3-}$ is a diamagnetic complex. We will focus our attention on the *d* electrons.

A diamagnetic species has no unpaired electrons. A paramagnetic species has unpaired electrons, and the strength of the paramagnetism depends on the number of unpaired electrons. See Chapter 5.

The Co^{3+} ion has six electrons (four unpaired) in its 3*d* orbitals.

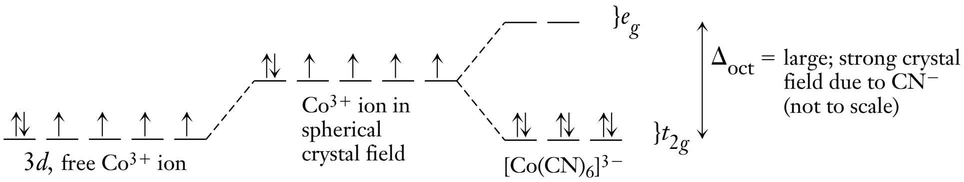
		3*d*
Co^{3+}	[Ar]	$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

Magnetic measurements indicate that $[CoF_6]^{3-}$ also has four unpaired electrons per ion. So there must be four electrons in t_{2g} orbitals and two in e_g orbitals. Fluoride, F^-, is a weak field ligand, so the crystal field splitting energy is very small ($\Delta_{oct} < P$) and electron pairing is unfavorable. Thus $[CoF_6]^{3-}$ is a *high spin* complex.



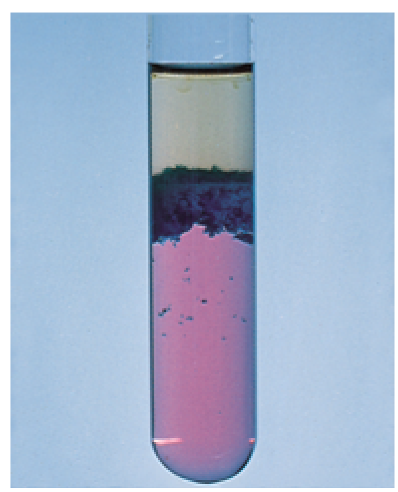
$[CoF_6]^{3-}$ is a *high spin* complex.

On the other hand, $[Co(CN)_6]^{3-}$ is diamagnetic, so all six *d* electrons must be paired in the t_{2g} orbitals. Cyanide ion, CN^-, is a strong field ligand, which generates a large crystal field splitting energy ($\Delta_{oct} > P$), making electron pairing more favorable; $[Co(CN)_6]^{3-}$ is a low spin complex.



$[Co(CN)_6]^{3-}$ is a *low spin* complex.

The difference in configurations between $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$ is due to the relative magnitudes of the crystal field splitting, Δ_{oct}, caused by the different crystal field strengths of F^- and CN^-. The CN^- ion interacts with vacant metal orbitals more strongly than the F^- ion does. As a result, the crystal field splitting generated by the close approach of six CN^- ions (strong field ligands) to the metal ion is greater than that generated by the approach of six F^- ions (weak field ligands).



►$[Co(OH_2)_6]^{2+}$ ions are pink (*bottom*). A limited amount of aqueous ammonia produces $Co(OH)_2$, a blue compound that quickly turns gray (*middle*). $Co(OH)_2$ dissolves in excess aqueous ammonia to form $[Co(NH_3)_6]^{2+}$ ions, which are yellow-orange (*top*).

TABLE 25-8 ***High and Low Spin Octahedral Configurations***

d^n	Examples	High Spin	Low Spin	d^n	Examples	High Spin	Low Spin
d^1	Ti^{3+}	— — e_g $\uparrow$ — — t_{2g}	same as high spin	d^6	Fe^{2+}, Ru^{2+}, Pd^{4+}, Rh^{3+}, Co^{3+}	$\uparrow$ $\uparrow$ e_g $\uparrow\downarrow$ $\uparrow$ $\uparrow$ t_{2g}	— — e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ t_{2g}
d^2	Ti^{2+}, V^{3+}	— — e_g $\uparrow$ $\uparrow$ — t_{2g}	same as high spin	d^7	Co^{2+}, Rh^{2+}	$\uparrow$ $\uparrow$ e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ t_{2g}	$\uparrow$ — e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ t_{2g}
d^3	V^{2+}, Cr^{3+}	— — e_g $\uparrow$ $\uparrow$ $\uparrow$ t_{2g}	same as high spin	d^8	Ni^{2+}, Pt^{2+}	$\uparrow$ $\uparrow$ e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ t_{2g}	same as high spin
d^4	Mn^{3+}, Re^{3+}	$\uparrow$ — e_g $\uparrow$ $\uparrow$ $\uparrow$ t_{2g}	— — e_g $\uparrow\downarrow$ $\uparrow$ $\uparrow$ t_{2g}	d^9	Cu^{2+}	$\uparrow\downarrow$ $\uparrow$ e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ t_{2g}	same as high spin
d^5	Mn^{2+}, Fe^{3+} Ru^{3+}	$\uparrow$ $\uparrow$ e_g $\uparrow$ $\uparrow$ $\uparrow$ t_{2g}	— — e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ t_{2g}	d^{10}	Zn^{2+}, Ag^{+}, Hg^{2+}	$\uparrow\downarrow$ $\uparrow\downarrow$ e_g $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ t_{2g}	same as high spin

$$\Delta_{oct} \text{ for } [Co(CN)_6]^{3-} > \Delta_{oct} \text{ for } [CoF_6]^{3-}$$

A convenient way to describe *d*-transition metal ions is to indicate the number of nonbonding electrons in *d* orbitals.

Low spin configurations exist only for octahedral complexes having metal ions with d^4, d^5, d^6, and d^7 configurations. For d^1–d^3 and d^8–d^{10} ions, only one possibility exists. In these cases, the configuration is designated as high spin. All d^n possibilities are shown in Table 25-8.

25-9 COLOR AND THE SPECTROCHEMICAL SERIES

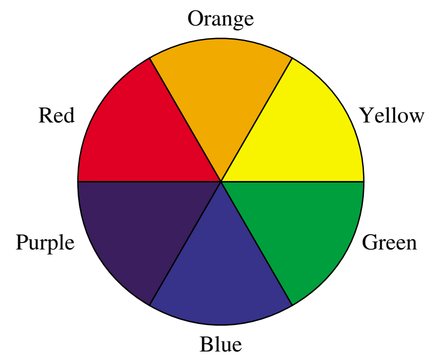
A substance appears colored because it absorbs light that corresponds to one or more of the wavelengths in the visible region of the electromagnetic spectrum (4000 to 7000 Å) and transmits or reflects the other wavelengths. Our eyes are detectors of light in the visible region, and so each wavelength in this region appears as a different color. A combination of all wavelengths in the visible region is called “white light”; sunlight is an example. The absence of all wavelengths in the visible region is blackness.

In Table 25-9 we show the relationships among colors absorbed and colors transmitted or reflected in the visible region. The first column displays the wavelengths absorbed. The **spectral color** is the color associated with the wavelengths of light absorbed by the sample. When certain visible wavelengths are absorbed from incoming “white” light, the light *not absorbed* remains visible to us as transmitted or reflected light. For instance, a sample that absorbs orange light appears blue. The **complementary color** is the color associated with the wavelengths that are not absorbed by the sample. The complementary color is seen when the spectral color is removed from white light.

Most transition metal compounds are colored, a characteristic that distinguishes them from most compounds of the representative elements. In transition metal *compounds*, the *d* orbitals in any one energy level of the metals are not degenerate. No longer do all have the same energy, as they do in isolated atoms. They are often split into two sets of orbitals separated by energies, Δ_{oct}, that correspond to wavelengths of light in the visible region.

TABLE 25-9 *Complementary Colors*

Wavelength Absorbed (Å)	Spectral Color (color absorbed)	Complementary Color (color observed)
4100	violet	lemon yellow
4300	indigo	yellow
4800	blue	orange
5000	blue-green	red
5300	green	purple
5600	lemon yellow	violet
5800	yellow	indigo
6100	orange	blue
6800	red	blue-green



A color wheel shows colors and their complementary colors. For example, green is the complementary color of red. The data in Table 25-9 are given for specific wavelengths. Broad bands of wavelengths are shown in this color wheel.

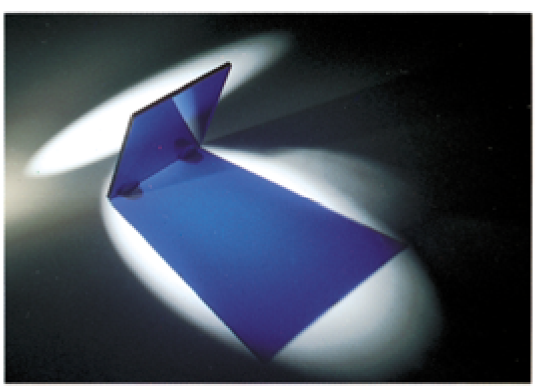
The absorption of visible light causes electronic transitions between orbitals in these sets. Table 25-10 gives the colors of some transition metal nitrates in aqueous solution. Solutions of representative (A group) metal nitrates are colorless.

One transition of a high spin octahedral Co(III) complex is depicted as follows.

Ground State		Excited State	Energy of Light Absorbed
e_g ↑ ↑	Absorption of light →	⇅ ↑	$\Delta E = h\nu$ depends on Δ_{oct}
t_{2g} ⇅ ↑ ↑		↑ ↑ ↑	

Planck's constant is $h = 6.63 \times 10^{-34}$ J·s.

The frequency (ν), and therefore the wavelength and color, of the light absorbed are related to Δ_{oct}.[1] This, in turn, depends on the crystal field strength of the ligands. So the colors and visible absorption spectra of transition metal complexes, as well as their magnetic properties, provide information about the strengths of the ligand–metal interactions.



Adding a Co(II) salt to molten glass gives the glass a deep blue color.

TABLE 25-10 *Colors of Aqueous Solutions of Some Transition Metal Nitrates*

Transition Metal Ion	Color of Aq. Solution
Cr^{3+}	Deep blue
Mn^{2+}	Pale pink
Fe^{2+}	Pale green
Fe^{3+}	Orchid
Co^{2+}	Pink
Ni^{2+}	Green
Cu^{2+}	Blue

[1]The numerical relationship between Δ_{oct} and the wavelength, λ, of the absorbed light is found by combining the expressions $E = h\nu$ and $\nu = c/\lambda$, where c is the speed of light. For *one* mole of a complex,

$$\Delta_{oct} = EN_A = \frac{hcN_A}{\lambda} \quad \text{where } N_A \text{ is Avogadro's number}$$

The colors of complex compounds that contain a given metal depend on the ligands. The yellow compound at the left is a salt that contains $[Co(NH_3)_6]^{3+}$ ions. In the next three compounds, left to right, one NH_3 ligand in $[Co(NH_3)_6]^{3+}$ has been replaced by NCS^- (*orange*), H_2O (*red*), and Cl^- (*purple*). The green compound at the right is a salt that contains $[Co(NH_3)_4Cl_2]^+$ ions.

By interpreting the visible spectra of many complexes, it is possible to arrange common ligands in order of increasing crystal field strengths.

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < (COO)_2^{2-} < NH_3 < en < NO_2^- < CN^-$$

Increasing crystal field strength

This arrangement is called the **spectrochemical series.** Strong field ligands, such as CN^-, produce large crystal field splittings and usually produce low spin complexes, where possible. Weak field ligands, such as Cl^-, produce small crystal field splittings and high spin complexes. Low spin complexes usually absorb higher-energy (shorter-wavelength) light than do high spin complexes. The colors of several six-coordinate Cr(III) complexes are listed in Table 25-11.

In $[Cr(NH_3)_6]Cl_3$, the Cr(III) is bonded to six ammonia ligands, which produce a relatively high value of Δ_{oct}. This causes the $[Cr(NH_3)_6]^{3+}$ ion to absorb relatively high energy visible light in the blue and violet regions. Thus, we see yellow-orange, the complementary color.

We see the light that is transmitted (passes through the sample) or that is reflected by the sample.

Water is a weaker field ligand than ammonia, and therefore Δ_{oct} is less for $[Cr(OH_2)_6]^{3+}$ than for $[Cr(NH_3)_6]^{3+}$. As a result, $[Cr(OH_2)_6]Br_3$ absorbs lower energy (longer wavelength) light. This causes the reflected and transmitted light to be higher energy bluish gray, the color that describes $[Cr(OH_2)_6]Br_3$.

Different anions sometimes cause compounds containing the same complex cation to have different colors. For example, two different-colored compounds in this table both contain the $[Cr(OH_2)_6]^{3+}$ ion.

TABLE 25-11 *Colors of Some Chromium(III) Complexes*

$[Cr(OH_2)_6]Cl_3$	violet	$[Cr(NH_3)_6]Cl_3$	yellow
$[Cr(OH_2)_6]Br_3$	bluish gray	$[Cr(NH_3)_5Cl]Cl_2$	purple
$[Cr(OH_2)_4Cl_2]Cl$	green	$[Cr(NH_3)_4Cl_2]Cl$	violet
$[Cr(OH_2)_4Br_2]Br$	green	$[Cr(CON_2H_4)_6][SiF_6]_3$	green

Key Terms

Ammine complexes Complex species that contain ammonia molecules bonded to metal ions.

Central atom The atom or ion to which the ligands are bonded in a complex species.

Chelate A ligand that utilizes two or more donor atoms in bonding to metals.

***cis–trans* isomerism** See *Geometric isomerism.*

Complementary color The color associated with the wavelengths of light that are not absorbed—that is, the color transmitted or reflected.

Coordinate covalent bond A covalent bond in which both shared electrons are donated by the same atom; a bond between a Lewis base and a Lewis acid.

Coordination compound or complex A compound containing coordinate covalent bonds between electron pair donors and a metal.

Coordination isomers Isomers involving exchange of ligands between a complex cation and a complex anion of the same coordination compound.

Coordination number The number of donor atoms coordinated to a metal.

Coordination sphere The metal ion and its coordinated ligands, but not any uncoordinated counterions.

Crystal field theory A theory of bonding in transition metal complexes in which ligands and metal ions are treated as point charges; a purely ionic model. Ligand point charges represent the crystal (electric) field perturbing the metal's *d* orbitals that contain nonbonding electrons.

Δ_{oct} The energy separation between e_g and t_{2g} sets of metal *d* orbitals caused by octahedral complexation of ligands.

Dextrorotatory Describes an optically active substance that rotates the plane of plane-polarized light to the right; also called dextro.

Donor atom A ligand atom whose electrons are shared with a Lewis acid.

e_g orbitals A set of $d_{x^2-y^2}$ and d_{z^2} orbitals; those *d* orbitals within a set with lobes directed along the *x*, *y*, and *z* axes.

Enantiomers Stereoisomers that differ only by being nonsuperimposable mirror images of each other, like left and right hands; also called optical isomers.

Geometric isomerism Occurs when atoms or groups of atoms can be arranged in different ways on two sides of a rigid structure; also called *cis–trans* isomerism. In geometric isomers of coordination compounds, the same ligands are arranged in different orders within the coordination sphere.

High spin complex The crystal field designation for a complex in which all t_{2g} and e_g orbitals are singly occupied before any pairing occurs.

Hydrate isomers Isomers of crystalline complexes that differ in terms of the presence of water inside or outside the coordination sphere.

Ionization isomers Isomers that result from interchange of ions inside and outside the coordination sphere.

Isomers Different compounds that have the same formula.

Levorotatory Refers to an optically active substance that rotates the plane of plane-polarized light to the left; also called levo.

Ligand A Lewis base in a coordination compound.

Linkage isomers Isomers in which a particular ligand bonds to a metal ion through different donor atoms.

Low spin complex The crystal field designation for a complex in which pairing occurs to fill the t_{2g} orbitals before any electrons occupy the e_g orbitals.

Optical activity The ability of one of a pair of optical isomers to rotate the plane of polarized light.

Optical isomers See *Enantiomers.*

Pairing energy The energy required to pair two electrons in the same orbital.

Plane-polarized light Light waves in which all the electric vectors are oscillating in one plane.

Polarimeter A device used to measure optical activity.

Polydentate Describes ligands with more than one donor atom.

Racemic mixture An equimolar mixture of optical isomers that is, therefore, optically inactive.

Spectral color The color associated with the wavelengths of light that are absorbed.

Spectrochemical series An arrangement of ligands in order of increasing ligand field strength.

Square planar complex A complex in which the metal atom or ion is in the center of a square plane, with a ligand donor atom at each of the four corners.

Stereoisomers Isomers that differ only in the way in which atoms are oriented in space; they include geometric and optical isomers.

Strong field ligand A ligand that exerts a strong crystal or ligand electric field and generally forms low spin complexes with metal ions when possible.

Structural (constitutional) isomers (Applied to coordination compounds.) Isomers whose differences involve more than a single coordination sphere or else different donor atoms; they include ionization isomers, hydrate isomers, coordination isomers, and linkage isomers.

t_{2g} orbitals A set of d_{xy}, d_{yz}, and d_{xz} orbitals; those *d* orbitals within a set with lobes bisecting the *x*, *y*, and *z* axes.

Weak field ligand A ligand that exerts a weak crystal or ligand field and generally forms high spin complexes with metals.

Exercises

Basic Concepts

1. What property of transition metals allows them to form coordination compounds easily?

2. Suggest more appropriate formulas for $NiSO_4 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 4NH_3$, and $Co(NO_3)_2 \cdot 6NH_3$.

3. What are the two constituents of a coordination complex? What type of chemical bonding occurs between these constituents?

4. Define the term "coordination number" for the central atom or ion in a complex. What values of the coordination numbers for metal ions are most common?

5. Distinguish among the terms *ligands*, *donor atoms*, and *chelates*.

6. Identify the ligands and give the coordination number and the oxidation number for the central atom or ion in each of the following: (a) $[Co(NH_3)_2(NO_2)_4]^-$; (b) $[Cr(NH_3)_5Cl]Cl_2$; (c) $K_4[Fe(CN)_6]$; (d) $[Pd(NH_3)_4]^{2+}$.

7. Repeat Exercise 6 for (a) $Na[AuCl_2]$; (b) $[Ag(NH_3)_2]^+$; (c) $[Pt(NH_3)_2Cl_4]$; (d) $[Co(en)_3]^{3+}$

8. What is the term given to the phenomenon of ring formation by a ligand in a complex? Describe a specific example.

9. Describe the experiments of Alfred Werner on the compounds of the general formula $PtCl_4 \cdot nNH_3$, where $n = 2$, 3, 4, 5, 6. What was his interpretation of these experiments?

10. For each of the compounds of Exercise 9, write formulas indicating the species within the coordination sphere. Also indicate the charges on the complex ions.

11. Write a structural formula showing the ring(s) formed by a bidentate ligand such as ethylenediamine with a metal ion such as Fe^{3+}. How many atoms are in each ring? The formula for this complex ion is $[Fe(en)_3]^{3+}$.

Ammine Complexes

12. Write net ionic equations for reactions of solutions of the following transition metal salts in water with a *limited amount* of aqueous ammonia: (It is not necessary to show the ions as hydrated.) (a) $CuCl_2$; (b) $Zn(NO_3)_2$; (c) $Fe(NO_3)_3$; (d) $Co(NO_3)_2$; (e) $Ni(NO_3)_2$.

13. Write *net ionic* equations for the reactions of the insoluble products of Exercise 12 with an *excess* of aqueous ammonia, if a reaction occurs.

14. Which of the following insoluble metal hydroxides will dissolve in an excess of aqueous ammonia? (a) $Zn(OH)_2$; (b) $Cr(OH)_3$; (c) $Fe(OH)_2$; (d) $Ni(OH)_2$; (e) $Cd(OH)_2$.

15. Write net ionic equations for the reactions in Exercise 14.

Naming Coordination Compounds

16. Give systematic names for the following compounds.
(a) $[Fe(CO)_5]$
(b) $Na_2[Co(OH_2)_2(OH)_4]$
(c) $[Ag(NH_3)_2]Br$
(d) $[Cr(en)_3](NO_3)_3$
(e) $[Pt(NH_3)_4(NO_2)_2]\ F_2$
(f) $K_2[Cu(CN)_4]$
(g) $[Ni(NH_3)_4(H_2O)_2](NO_3)_2$
(h) $Na[Al(H_2O)_2(OH)_4]$
(i) $[Co(NH_3)_4Cl_2][Cr(C_2O_4)_2]$

17. Give systematic names for the following compounds.
(a) $Na[Au(CN)_2]$
(b) $[Ni(CO)_4]$
(c) $[CoCl_6]^{3-}$
(d) $[Co(H_2O)_6]^{3+}$
(e) $Na_2[Pt(CN)_4]$
(f) $K[Cr(NH_3)_2(OH)_2Cl_2]$
(g) $[Mo(NCS)_2(en)_2]ClO_4$
(h) $[Mn(NH_3)_2(OH_2)_3(OH)]SO_4$
(i) $[Co(en)_2Cl_2]I$

18. Give systematic names for the following compounds.
(a) $[Ag(NH_3)_2]Cl$
(b) $[Fe(en)_3]PO_4$
(c) $[Co(NH_3)_6]SO_4$
(d) $[Co(NH_3)_6]_2(SO_4)_3$
(e) $[Pt(NH_3)_4]Cl_2$
(f) $(NH_4)_2[PtCl_4]$
(g) $[Co(NH_3)_5SO_4]NO_2$

19. Give systematic names for the following compounds.
(a) $K_2[PdCl_6]$
(b) $(NH_4)_2[PtCl_6]$
(c) $[Co(en)_3]Cl_2$
(d) $[Co(en)_3]Cl_3$
(e) $[Cr(en)_2(NH_3)_2](NO_3)_2$
(f) $[Co(NH_3)_4Cl_2]Cl$
(g) $(NH_4)_3[CuCl_5]$

20. Write formulas for the following.
(a) diamminedichlorozinc
(b) tin(IV) hexacyanoferrate(II)
(c) tetracyanoplatinate(II) ion
(d) potassium hexachlorostannate(IV)
(e) tetraammineplatinum(II) ion
(f) hexaamminenickel(II) bromide
(g) tetraamminecopper(II) pentacyanohydroxoferrate(III)
(h) diaquadicyanocopper(II)
(i) potassium hexachloropalladate(IV)

21. Write formulas for the following compounds.
(a) *trans*-diamminedinitroplatinum(II)
(b) rubidium tetracyanozincate
(c) triaqua-*cis*-dibromochlorochromium(III)
(d) pentacarbonyliron(0)
(e) sodium pentacyanocobaltate(II)
(f) hexammineruthenium(III) tetrachloronickelate(II)
(g) sodium tetracyanocadmate
(h) hexaamminecobalt(III) chloride

Structures of Coordination Compounds

22. Write formulas, and provide names for three complex cations in each of the following categories.
(a) cations coordinated to only monodentate ligands
(b) cations coordinated to only bidentate ligands
(c) cations coordinated to two bidentate and two monodentate ligands
(d) cations coordinated to one tridentate ligand, one bidentate ligand, and one monodentate ligand
(e) cations coordinated to one tridentate ligand and three monodentate ligands

23. Provide formulas and names for three complex anions that fit each description in Exercise 22.

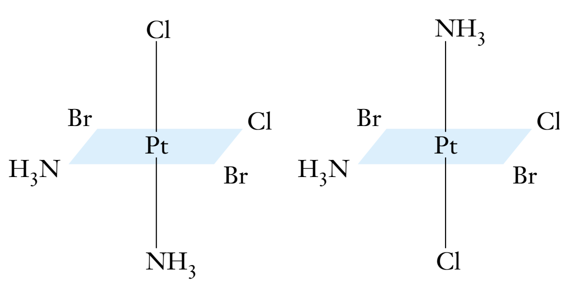
24. How many geometric isomers can be formed by complexes that are (a) octahedral MA_2B_4 and (b) octahedral MA_3B_3? Name any geometric isomers that can exist. Is it possible for any of these isomers to show optical activity (exist as enantiomers)? Explain.

25. Write the structural formulas for (a) two isomers of $[Pt(NH_3)_2Cl_2]$, (b) four isomers (including linkage isomers) of $[Co(NH_3)_3(NO_2)_3]$, and (c) two isomers (including ionization isomers) of $[Pt(NH_3)_3Br]Cl$.

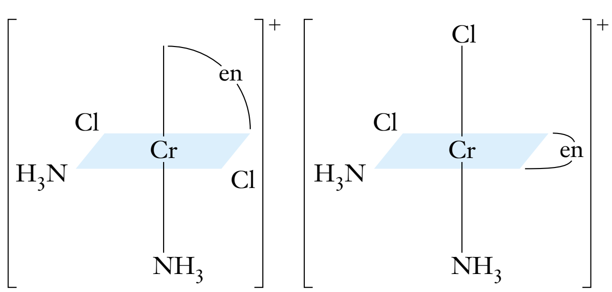
26. Determine the number and types of isomers that would be possible for each of the following complexes.
(a) tetraamminediaquachromium(III) ion
(b) triamminetriaquachromium(III) ion
(c) tris(ethylenediamine) chromium(III) ion
(d) dichlorobis(ethylenediamine)platinum(IV) chloride
(e) diamminedibromodichlorochromate(III) ion

***27.** Indicate whether the complexes in each pair are identical or isomers.

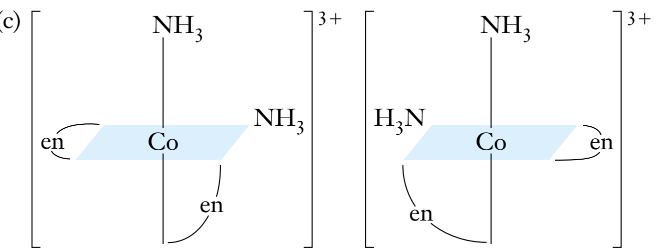
(a)



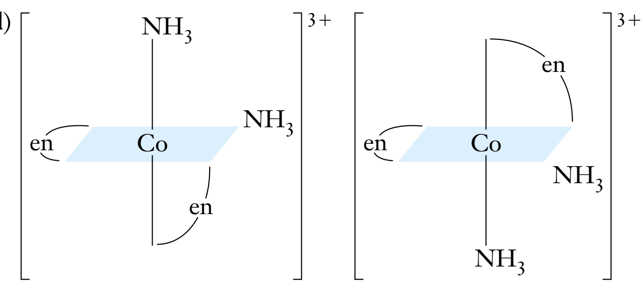
(b)



(c)



(d)



28. Distinguish between constitutional (structural) isomers and stereoisomers.

29. Distinguish between an optically active complex and a racemic mixture.

30. Write the formula for a potential ionization isomer of each of the following compounds. Name each one.
(a) $[Co(NH_3)_4Br_2]Br$
(b) $[Ni(en)_2(NO_2)_2]Cl_2$
(c) $[Fe(NH_3)_5CN]SO_4$

31. Write the formula for a potential hydrate isomer of each of the following compounds. Name each one.
(a) $[Cu(OH_2)_4]Cl_2$ (b) $[Ni(OH_2)_5Br]Br \cdot H_2O$

32. Write the formula for a potential coordination isomer of each of the following compounds. Name each one.
(a) $[Co(NH_3)_6][Cr(CN)_6]$ (b) $[Ni(en)_3][Cu(CN)_4]$

33. Write the formula for a potential linkage isomer of each of the following compounds. Name each one.
(a) $[Co(en)_2(NO_2)_2]Cl$ (b) $[Cr(NH_3)_5(CN)](CN)_2$

Crystal Field Theory

34. Describe clearly what Δ_{oct} is. How is Δ_{oct} actually measured experimentally? How is it related to the spectrochemical series?

35. On the basis of the spectrochemical series, determine whether the following complexes are low spin or high spin.
(a) $[CrCl_4Br_2]^{3-}$
(b) $[Co(en)_3]^{3+}$
(c) $[Fe(OH_2)_6]^{3+}$
(d) $[Fe(NO_2)_6]^{3-}$

36. On the basis of the spectrochemical series, determine whether the following complexes are low spin or high spin.
(a) $[Cu(OH_2)_6]^{2+}$
(b) $[MnF_6]^{3-}$
(c) $[Co(CN)_6]^{3-}$
(d) $[Cr(NH_3)_6]^{3+}$
37. Write out the electron distribution in t_{2g} and e_g orbitals for the following in an octahedral field.

Metal Ions	Ligand Field Strength
V^{2+}	weak
Mn^{2+}	strong
Mn^{2+}	weak
Ni^{2+}	weak
Cu^{2+}	weak
Fe^{3+}	strong
Cu^{+}	weak
Ru^{3+}	strong

38. Write formulas for two complex ions that would fit into each of the categories of Exercise 37. Name the complex ions you list.
39. Determine the electron distribution in (a) $[Co(CN)_6]^{3-}$, a low spin complex ion, and (b) $[CoF_6]^{3-}$, a high spin complex ion.

CONCEPTUAL EXERCISES

40. How can you predict whether a complex is high or low spin? How can you determine whether a complex is high or low spin?
41. Define the terms *diamagnetic* and *paramagnetic*. What feature of electronic structure is directly related to these properties?
42. What are three common metal coordination numbers found in coordination chemistry? Give the shape usually associated with each of the common coordination numbers.
43. Several isomers are possible for $[Co(en)(NH_3)(H_2O)_2Cl]^{2+}$. (Two of the isomers have optical isomers.) How many isomers can you draw? Draw the structure of an isomer that does not have an optical isomer. Draw the structure of an isomer that would have an optical isomer. (*Hint:* "en" is not large enough to bind at *trans* locations.)

BUILDING YOUR KNOWLEDGE

Values of equilibrium constants are listed in Appendix I.

44. Calculate (a) the molar solubility of $Zn(OH)_2$ in pure water, (b) the molar solubility of $Zn(OH)_2$ in 0.25 M NaOH solution, and (c) the concentration of $[Zn(OH)_4]^{2-}$ ions in the solution of (b).
45. The yellow complex oxalatorhodium compound $K_3[Rh(C_2O_4)_3]$ can be prepared from the wine-red complex compound $K_3[RhCl_6]$ by boiling a concentrated aqueous solution of $K_3[RhCl_6]$ and $K_2C_2O_4$ for two hours and then evaporating the solution until the product crystallizes.

$$K_3[RhCl_6](aq) + 3K_2C_2O_4(aq) \xrightarrow{\text{heat}} K_3[Rh(C_2O_4)_3](s) + 6KCl(aq)$$

What is the theoretical yield of the oxalato complex if 1.150 g of the chloro complex is heated with 4.95 g of $K_2C_2O_4$? In an experiment, the actual yield was 0.88 g. What is the percent yield?
46. Consider the formation of the triiodoargentate(I) ion.

$$Ag^+ + 3I^- \longrightarrow [AgI_3]^{2-}$$

Would you expect an increase or decrease in the entropy of the system as the complex is formed? The standard-state absolute entropy at 25°C is 72.68 J/K mol for Ag^+, 111.3 J/K mol for I^-, and 253.1 J/K mol for $[AgI_3]^{2-}$. Calculate ΔS^0 for the reaction and confirm your prediction.
47. Molecular iodine reacts with I^- to form a complex ion.

$$I_2(aq) + I^- \rightleftharpoons [I_3]^-$$

Calculate the equilibrium constant for this reaction given the following data at 25°C.

$$I_2(aq) + 2e^- \longrightarrow 2I^- \qquad E^0 = 0.535\ V$$
$$[I_3]^- + 2e^- \longrightarrow 3I^- \qquad E^0 = 0.5338\ V$$

48. Calculate the pH of a solution prepared by dissolving 0.30 mol of tetraamminecopper(II) chloride, $[Cu(NH_3)_4]Cl_2$, in water to give 1.0 L of solution. Ignore hydrolysis of Cu^{2+}.
49. Use the following standard reduction potential data to answer the questions.

$$Co^{3+} + e^- \rightleftharpoons Co^{2+} \qquad E^0 = 1.808\ V$$
$$Co(OH)_3(s) + e^- \rightleftharpoons Co(OH)_2(s) + OH^-(aq) \qquad E^0 = 0.17\ V$$
$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^0 = 0.108\ V$$
$$[Co(CN)_6]^{3-} + e^- \rightleftharpoons [Co(CN)_5]^{3-} + CN^- \qquad E^0 = -0.83\ V$$
$$O_2(g) + 4H^+(10^{-7}\ M) + 4e^- \rightleftharpoons 2H_2O(\ell) \qquad E^0 = 0.815\ V$$
$$2H_2O(\ell) + 2e^- \rightleftharpoons H_2(g) + 2OH^- \qquad E^0 = -0.828\ V$$

Which cobalt(III) species among those listed would oxidize water? Which cobalt(II) species among those listed would be oxidized by water? Explain your answers.