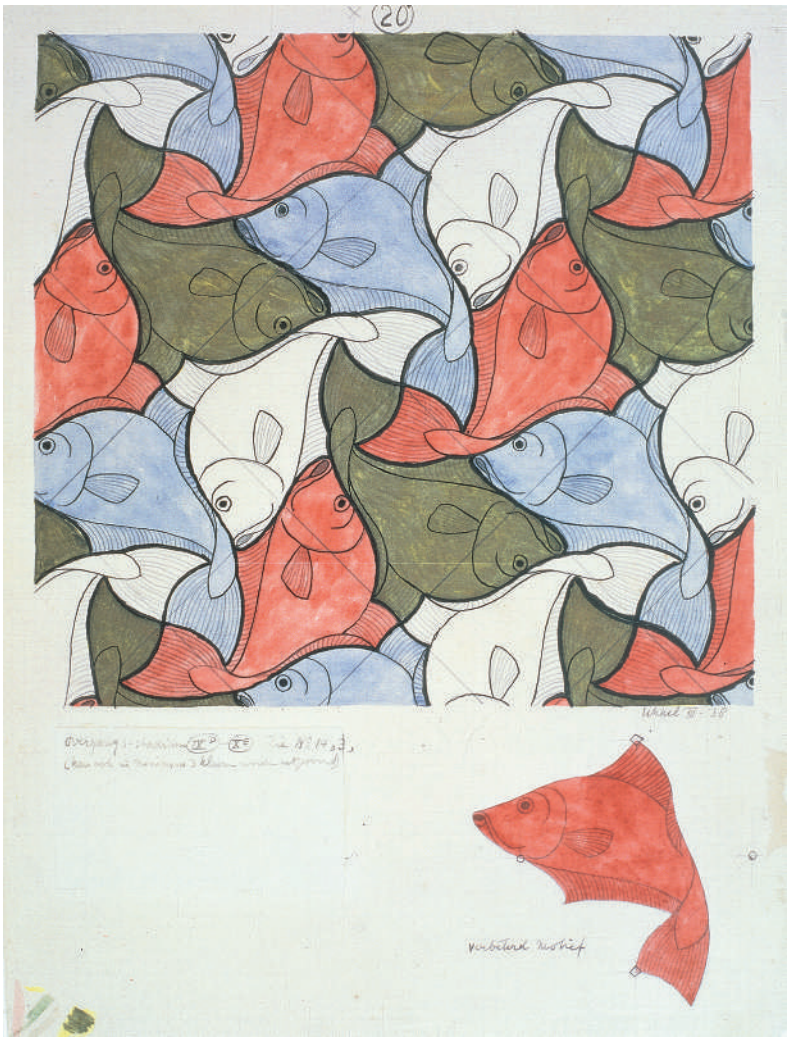
Complex Ions

19



When a tetrahedron is reflected or rotated, a structure indistinguishable from the original is obtained. Chemists call the tetrahedron a *symmetric* structure. Escher, in his painting *Symmetry No. 20,* shows a translational repeating symmetry. He flips or moves his objects, creating a pattern.

Copper's red 'cause d electrons
Preferentially get the blues
And absorption 'cross the band gaps
Gives the pigments gorgeous hues

—DR. JAMES D. LIVINGSTON
Physics at Its Best

In previous chapters we have referred from time to time to compounds of the transition metals. Many of these have relatively simple formulas such as $CuSO_4$, $CrCl_3$, and $Fe(NO_3)_3$. These compounds are ionic. The transition metal is present as a simple cation (Cu^{2+}, Cr^{3+}, Fe^{3+}). In that sense, they resemble the ionic compounds formed by the main-group metals, such as $CaSO_4$ and $Al(NO_3)_3$.

It has been known for more than a century, however, that transition metals also form a variety of ionic compounds with more complex formulas such as

$$[Cu(NH_3)_4]SO_4 \qquad [Cr(NH_3)_6]Cl_3 \qquad K_3[Fe(CN)_6]$$

In these so-called *coordination compounds,* the transition metal is present as a complex ion, enclosed within the brackets. In the three compounds listed above, the following complex ions are present:

$$Cu(NH_3)_4^{2+} \qquad Cr(NH_3)_6^{3+} \qquad Fe(CN)_6^{3-}$$

The charges of these complex ions are balanced by those of simple anions or cations (e.g., SO_4^{2-}, $3Cl^-$, $3K^+$).

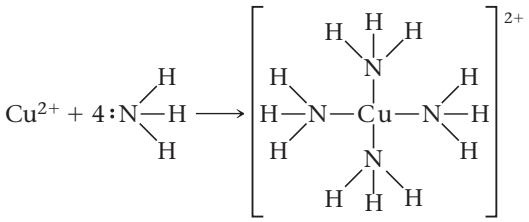
Chapter Outline

This chapter is devoted to complex ions and the important role they play in inorganic chemistry. We consider in turn

- the composition and names of complex ions and the coordination compounds that they form (Sections 19-1 and 19-2).
- the geometry of complex ions (Section 19-3).
- the electronic structure of the central metal ion (or atom) in a complex (Section 19-4).

19-1 Composition of Complex Ions

When ammonia is added to an aqueous solution of a copper(II) salt, a deep, almost opaque, blue color develops (Figure 19.1). This color is due to the formation of the $Cu(NH_3)_4^{2+}$ ion, in which four NH_3 molecules are bonded to a central Cu^{2+} ion. The formation of this species can be represented by the equation



The nitrogen atom of each NH_3 molecule contributes a pair of unshared electrons to form a covalent bond with the Cu^{2+} ion. This bond and others like it, where both electrons are contributed by the same atom, are referred to as *coordinate covalent bonds*.

The $Cu(NH_3)_4^{2+}$ ion is commonly referred to as a **complex ion**. We use the term complex ion to indicate a charged species in which a metal atom is bonded to neutral molecules and/or anions referred to collectively as **ligands**. The number of bonds formed by the **central atom** is called its **coordination number**. In the $Cu(NH_3)_4^{2+}$ complex ion

- the central atom is Cu^{2+}.
- the ligands are NH_3 molecules.
- the coordination number is 4.

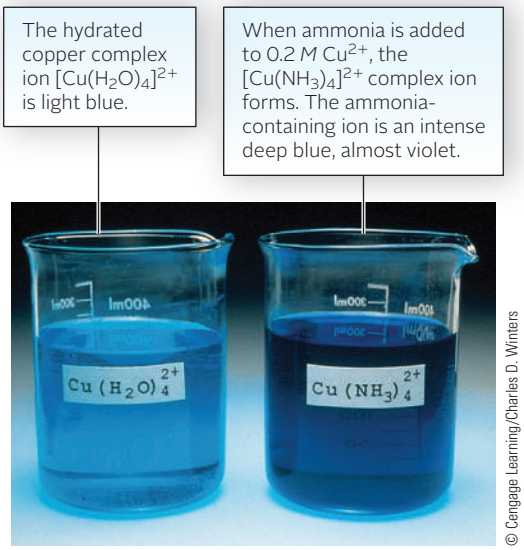


Figure 19.1 Colors of copper complexes.

Species such as $Al(H_2O)_6^{3+}$ and $Zn(H_2O)_3(OH)^+$, found in previous chapters, are further examples of complex ions. The metals that show the greatest tendency to form complex ions are those that form small cations with a charge of +2 or greater. Typically, these are the metals toward the right of the transition series (in the first transition series, $_{24}Cr$ through $_{30}Zn$). Nontransition metals, including Al, Sn, and Pb, form a more limited number of stable complex ions.

Cations of these metals invariably exist in aqueous solution as complex ions. Consider, for example, the zinc(II) cation. In a water solution of $Zn(NO_3)_2$, the $Zn(H_2O)_4^{2+}$ ion is present. Treatment with ammonia converts this to $Zn(NH_3)_4^{2+}$; addition of sodium hydroxide forms $Zn(OH)_4^{2-}$.

An ion such as $Cu(NH_3)_4^{2+}$ cannot exist by itself in the solid state. The +2 charge of this ion must be balanced by anions with a total charge of −2. A typical compound containing the $Cu(NH_3)_4^{2+}$ ion is

$$[Cu(NH_3)_4^{2+}]Cl_2: \qquad 1\ Cu(NH_3)_4^{2+}\ \text{ion},\ 2\ Cl^-\ \text{ions}$$

Compounds such as the one above, which contain a complex ion, are referred to as **coordination compounds.** The formula of the complex ion is set off by brackets, [ ], to make the structure of the compound clear.

Table 19.1 Complexes of Pt^{2+} with NH_3 and Cl^-

Complex	O.N. of Pt	Ligands	Total Charge of Ligands	Charge of Complex
$Pt(NH_3)_4^{2+}$	+2	$4NH_3$	0	+2
$Pt(NH_3)_3Cl^+$	+2	$3NH_3$, $1Cl^-$	−1	+1
$Pt(NH_3)_2Cl_2$	+2	$2NH_3$, $2Cl^-$	−2	0
$Pt(NH_3)Cl_3^-$	+2	$1NH_3$, $3Cl^-$	−3	−1
$PtCl_4^{2-}$	+2	$4Cl^-$	−4	−2

Charges of Complexes

The charge of a complex is readily determined by applying a simple principle (Figure 19.2):

charge of complex = O.N. central metal + charges of ligands

("O.N." in the above is the abbreviation for "oxidation number.") The application of this principle is shown in Table 19.1, where we list the formulas of several complexes formed by platinum(II), which shows a coordination number of 4. Notice that one of the species, $Pt(NH_3)_2Cl_2$, is a neutral complex rather than a complex ion; the charges of the two Cl^- ions just cancel that of the central Pt^{2+} ion.

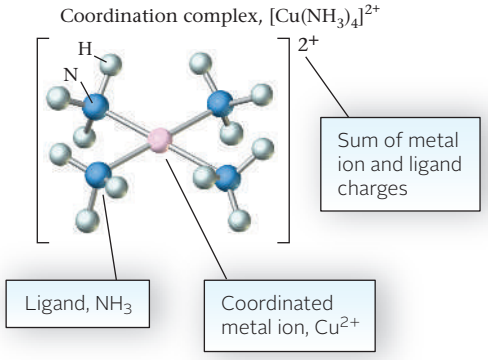


Figure 19.2 The $[Cu(NH_3)_4]^{2+}$ complex ion.

EXAMPLE 19.1

Consider the $Co(H_2O)_3Cl_3^-$ ion.

a What is the oxidation number of cobalt?

STRATEGY

Apply the relation

charge = oxidation number (O.N.) of the central atom + charge of ligands

SOLUTION

Charge of the complex ion	−1
Charge of the ligands	H_2O = 0; Cl: 3(−1) = −3
Oxidation number of the metal	charge = O.N. + charge of ligands −1 = O.N. + [0 + 3(−1)]; O.N. = +2

b What is the formula of the coordination compound containing this anion and the Na^+ cation? The Ca^{2+} cation?

STRATEGY

1. You know the charge of the complex ion (−1) and the charge of the cations (+1 for Na; +2 for Ca). Apply the principle of electrical neutrality to write the formula of the coordination compound.
2. Use square brackets to enclose the formula of the complex ion.

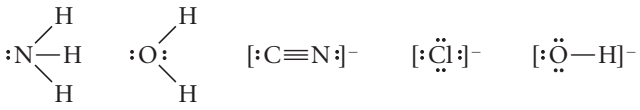
SOLUTION

Compound with the Na^+ cation	$Na^+\ Co(H_2O)_3Cl_3^{-1} \longrightarrow Na[Co(H_2O)_3Cl_3]$
Compound with the Ca^{2+} cation	$Ca^{2+}\ Co(H_2O)_3Cl_3^{-1} \longrightarrow Ca[Co(H_2O)_3Cl_3]_2$

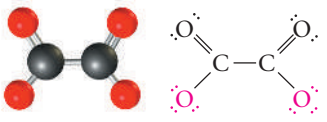
Ligands; Chelating Agents

Unshared pair = lone pair.

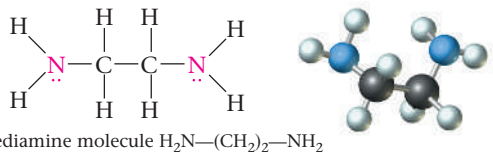
In principle, any molecule or anion with an unshared pair of electrons can act as a Lewis base (see Chapter 13). In other words, it can donate a lone pair to a metal cation to form a coordinate covalent bond. In practice, a ligand usually contains an atom of one of the more electronegative elements (C, N, O, S, F, Cl, Br, I). Several hundred different ligands are known. Those most commonly encountered in general chemistry are NH_3 and H_2O molecules and CN^-, Cl^-, and OH^- ions.



Some ligands have more than one atom with an unshared pair of electrons and hence can form more than one bond with a central metal atom. Ligands of this type are referred to as *chelating agents;* the complexes formed are referred to as **chelates** (from the Greek *chela,* crab's claw). Two of the most common chelating agents are the oxalate anion (abbreviated *ox*) and the ethylenediamine molecule (abbreviated *en*), whose Lewis structures are



oxalate ion, $C_2O_4^{2-}$

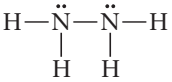


ethylenediamine molecule $H_2N{-}(CH_2)_2{-}NH_2$

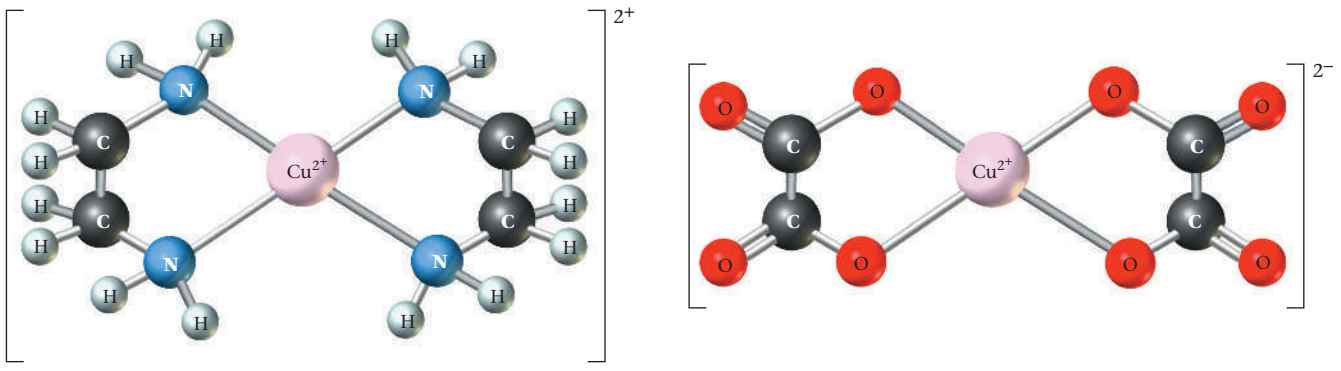
(The atoms that form bonds with the central metal are shown in color.)

Figure 19.3 shows the structure of the chelates formed by copper(II) with these ligands. Notice that in both of these complex ions, the coordination number of copper(II) is 4. The central cation is bonded to four atoms, two from each ligand.

For a ligand to act as a chelating agent, it must have at least two lone pairs of electrons. Moreover, these electron pairs must be far enough removed from one another to give a chelate ring with a stable geometry. In the chelates shown in Figure 19.3, the ring is five-membered, containing a Cu^{2+} ion and four nonmetal atoms. Most chelates contain five- or six-membered rings. Smaller or larger rings are less stable. For example, even though the hydrazine molecule



has two lone pairs, it does not form chelates. To do so, it would have to form a three-membered ring with 60° bond angles.



$Cu(en)_2^{2+}$ $Cu(C_2O_4)_2^{2-}$

Figure 19.3 Chelates formed by Cu^{2+} with the ethylenediamine molecules (*en*) and the oxalate ions ($C_2O_4^{2-}$).

Coordination Number

As shown in Table 19.2, the most common coordination number is 6. A coordination number of 4 is less common. A value of 2 is restricted largely to Cu^+, Ag^+, and Au^+.

Odd coordination numbers are rare.

A few cations show only one coordination number in their complexes. Thus Co^{3+} always shows a coordination number of 6, as in

$$Co(NH_3)_6^{3+} \qquad Co(NH_3)_4Cl_2^{+} \qquad Co(en)_3^{3+}$$

Other cations, such as Al^{3+} and Ni^{2+}, have variable coordination numbers, depending on the nature of the ligand.

Table 19.2 Coordination Number and Geometry of Complex Ions*

Metal Ion	Coordination Number	Geometry	Example
Ag^+, Au^+, Cu^+	2	Linear	$Ag(NH_3)_2^+$
Cu^{2+}, Ni^{2+}, **Pd^{2+}**, **Pt^{2+}**	4	Square planar	$Pt(NH_3)_4^{2+}$
Al^{3+}, Au^+, **Cd^{2+}**, Co^{2+}, Cu^+, Ni^{2+}, **Zn^{2+}**	4	Tetrahedral	$Zn(NH_3)_4^{2+}$
Al^{3+}, Co^{2+}, **Co^{3+}**, **Cr^{3+}**, Cu^{2+}, **Fe^{2+}**, **Fe^{3+}**, Ni^{2+}, **Pt^{4+}**	6	Octahedral	$Co(NH_3)_6^{3+}$

*Cations that commonly show only one coordination number are in bold type.

EXAMPLE 19.2

Write formulas (including charges) of all complex ions formed by cobalt(III) with the hydroxide ion and/or ethylenediamine (*en*) molecules as ligands.

STRATEGY

1. See Table 19.2 for the coordination number(s) of Co^{3+}.
2. Recall that coordination number refers to the number of bonds made with the central (metal) atom.
3. Mix *en* molecules and OH^- ions as ligands to arrive at the maximum number of bonds specified by the coordination number.
4. Determine the charge of the complex ion by the relation

   charge = O.N. + charge of ligands

SOLUTION

1. Coordination number	6 = 6 bonds needed
2. Ligands	3 *en* (6 bonds) + 0 OH^- (0 bonds) 2 *en* (4 bonds) + 2 OH^- (2 bonds) 1 *en* (2 bonds) + 4 OH^- (4 bonds) 0 *en* (0 bonds) + 6 OH^- (6 bonds)
3–4. Complex ion with charge	$Co(en)_3$: charge = 3 + 3(0) = 3 ⟶ $Co(en)_3^{3+}$ $Co(en)_2(OH)_2$: charge = 3 + 2(0) + 2(−1) = 1 ⟶ $Co(en)_2(OH)_2^+$ $Co(en)(OH)_4$: charge = 3 + 1(0) + 4(−1) = −1 ⟶ $Co(en)(OH)_4^-$ $Co(OH)_6$: charge = 3 + 6(−1) = −3 ⟶ $Co(OH)_6^{3-}$

END POINT

Notice that moving from left to right, one *en* replaces two OH^- ions. This makes sense: an *en* molecule has two lone pairs that can bond to the metal; OH^- has only one.

19-2 Naming Complex Ions and Coordination Compounds

The nomenclature of compounds containing complex ions is more involved than that of the simple inorganic compounds considered in earlier chapters. We will see first how complex ions are named and then look at the nomenclature of coordination compounds.

Complex Cations and Neutral Complexes

To name a species like $Cu(NH_3)_4^{2+}$ or $Zn(H_2O)_2(OH)_2$, we need to specify

- the number and identity of each ligand (4 NH_3 molecules; 2 H_2O molecules, 2 OH^- ions).
- the oxidation number of the central metal atom: copper(II), zinc(II).

To accomplish this, we follow a set of rules.

1. ***The names of anions that act as ligands are obtained by substituting* -o *for the normal ending.*** Examples include

Cl^-	chlor*o*	SO_4^{2-}	sulfat*o*
OH^-	hydrox*o*	NO_3^-	nitrat*o*
CN^-	cyan*o*	CO_3^{2-}	carbonat*o*

   Ordinarily, the names of molecules are not changed when they become ligands (e.g., ethylenediamine). There are three important exceptions:

H_2O	aqua	NH_3	ammine	CO	carbonyl

2. ***The number of ligands of a particular type is ordinarily indicated by the Greek prefixes* di, tri, tetra, penta, hexa.** Thus we have

$Cu(H_2O)_4^{2+}$	*tetra*aquacopper(II)
$Cr(NH_3)_6^{3+}$	*hexa*amminechromium(III)

   If the name of the ligand is itself complex (e.g., ethylenediamine), the number of such ligands is indicated by the prefixes *bis*, *tris*, *tetrakis*, *pentakis*, *hexakis*. The name of the ligand is enclosed in parentheses.

$Cr(en)_3^{3+}$	*tris*(ethylenediamine)chromium(III)

3. ***When several types of ligand are present, they are named in alphabetical order (without regard to prefixes):***

$Cu(NH_3)_2(H_2O)_2^{2+}$	diamminediaquacopper(II)	ammine comes before aqua
$Cr(NH_3)_5Cl^{2+}$	pentaamminechlororchromium(III)	ammine comes before chloro

4. As you can deduce from the preceding examples, ***the oxidation number of the central metal ion is indicated by a Roman numeral written at the end of the metal's name.***

Complex Anions

If the complex ion is an anion, such as $Zn(OH)_4^{2-}$, ***this is indicated by inserting the suffix* ate *after the name of the metal.***

$Zn(OH)_4^{2-}$	tetrahydroxozinc*ate*(II)

In a few cases, the Latin name of the metal is used in anionic complexes.

$Fe(CN)_6^{3-}$	hexacyano*ferrate*(III)
$Cu(Cl)_4^{2-}$	tetrachloro*cuprate*(II)

Coordination Compounds

Coordination compounds, like simple ionic compounds, are named in a straightforward way. ***The cation is named first, followed by the anion.***

$[Cu(NH_3)_4]Cl_2$	tetraamminecopper(II) chloride
$[Fe(en)_3]PO_4$	tris(ethylenediamine)iron(III) phosphate
$K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III)

The common name of $K_3[Fe(CN)_6]$ is potassium ferricyanide.

EXAMPLE 19.3

Name the following compounds:
$[Cr(NH_3)_4Cl_2]Cl$, $K_2[PtCl_4]$, and $[Co(en)_3](NO_3)_3$

STRATEGY

1. Identify the complex ion (with the help of the brackets) and determine its charge.
2. Find the oxidation number of the metal atom.
3. Write the names of the ligands with their prefixes and assemble in alphabetical order.
4. Identify the anion and cation of the compound. Add the prefix *ate* if the complex ion is the anion.
5. Put all the parts together.

SOLUTION

$[Cr(NH_3)_4Cl_2]Cl$	
1. Complex ion and charge	ion: $Cr(NH_3)_4Cl_2$ charge = +1
2. Oxidation number of Cr	+1 = O.N. + 4(0) + 2(−1); O.N. = +3
3. Ligands with prefix alphabetically	$(NH_3)_4$ = tetraammine; Cl_2 = dichloro tetraamminedichloro
4. Ions	cation: complex ion; anion: chloride
5. Name of compound	tetraamminedichlorochromium(III) chloride
$K_2[PtCl_4]$	
1. Complex ion and charge	ion: $PtCl_4$ charge = −2 since there are two K^+ ions
2. Oxidation number of Pt	−2 = O.N. + 4(−1); O.N. = +2
3. Ligands with prefix	Cl_4 = tetrachloro
4. Ions	cation: potassium; anion: complex ion (end in *ate*)
5. Name of compound	potassium tetrachloroplatinate(II)
$[Co(en)_3](NO_3)_3$	
1. Complex ion and charge	ion: $Co(en)_3$ charge = +3 since there are three NO_3^- ions
2. Oxidation number of Co	−3 = O.N. + 3(0); O.N. = +3
3. Ligands with prefix	$(en)_3$ = tris(ethylenediamine)
4. Ions	cation: complex ion; anion: nitrate
5. Name of compound	tris(ethylenediamine)cobalt(III) nitrate

19-3 Geometry of Complex Ions

The physical and chemical properties of complex ions and of the coordination compounds they form depend on the spatial orientation of ligands around the central metal atom. Here we consider the geometries associated with the coordination numbers 2, 4, and 6. With that background, we then examine the phenomenon of **geometric isomerism,** in which two or more complex ions have the same chemical formula but different properties because of their different geometries.

Coordination Number = 2

Complex ions in which the central metal forms only two bonds to ligands are *linear;* that is, the two bonds are directed at a 180° angle. The structures of $CuCl_2^-$, $Ag(NH_3)_2^+$, and $Au(CN)_2^-$ may be represented as

$$(Cl—Cu—Cl)^- \qquad \left[\begin{array}{c} H \\ H—N \\ H \end{array}—Ag—\begin{array}{c} H \\ N—H \\ H \end{array}\right]^+ \qquad (N{\equiv}C—Au—C{\equiv}N)^-$$

Coordination Number = 4

Four-coordinate metal complexes may have either of two different geometries (Figure 19.4). The four bonds from the central metal may be directed toward the corners of a regular **tetrahedron.** This is what we would expect from the VSEPR model (recall Chapter 7). Two common tetrahedral complexes are $Zn(NH_3)_4^{2+}$ and $CoCl_4^{2-}$.

Square planar complexes, in which the four bonds are directed toward the corners of a square, are more common. Certain complexes of copper(II) and nickel(II) show this geometry; it is characteristic of the complexes of Pd^{2+} and Pt^{2+}, including $Pt(NH_3)_4^{2+}$.

Coordination Number = 6

We saw in Chapter 7 that octahedral geometry is characteristic of many molecules (e.g., SF_6) in which a central atom is surrounded by six other atoms. (Remember, an *octa*hedron has eight sides, which is irrelevant here; it has *six* corners, which is important.) All complex ions in which the coordination number is 6 are

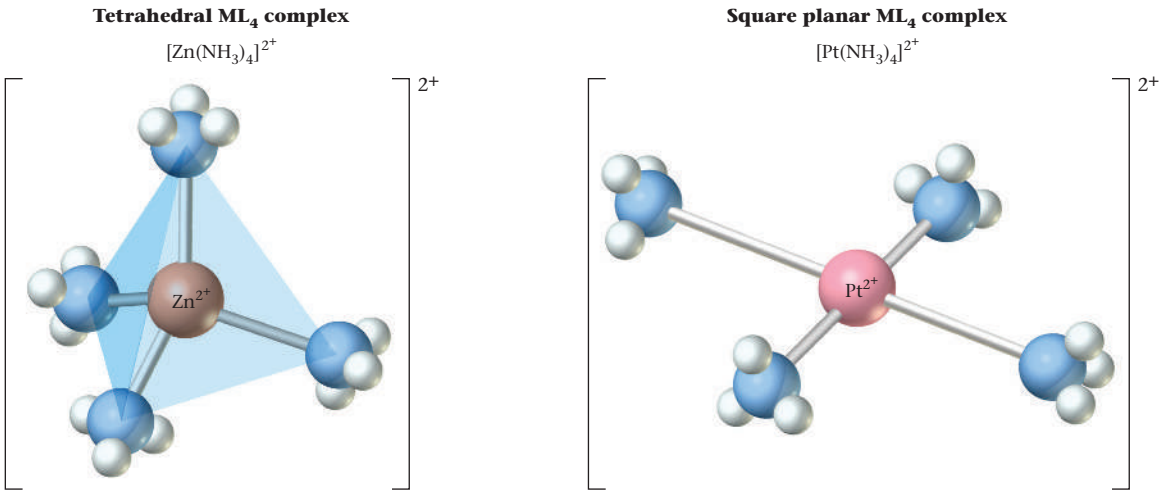


Figure 19.4 Geometry of four-coordinate complexes. Complexes in which the central metal has a coordination number of 4 may be tetrahedral or square planar.

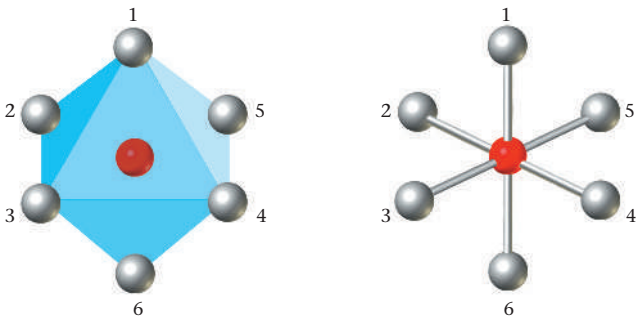


Figure 19.5 An octahedral, six-coordinate complex. The drawing at the left shows six ligands (represented by spheres) at the corners of an octahedron with a metal atom at the center. A simpler way to represent an octahedral complex is shown at the right.

octahedral. The metal ion (or atom) is at the center of the **octahedron;** the six ligands are at the corners. This geometry is shown in Figure 19.5.

The structure is often shown simply as ⇦⇨.

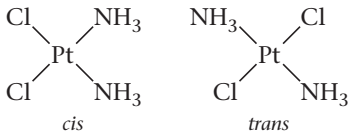
It is important to realize that

- the six ligands can be considered equidistant from the central metal.
- an octahedral complex can be regarded as a derivative of a square planar complex. The two extra ligands are located above and below the square, on a line perpendicular to the square at its center.

Geometric Isomerism

Two or more species with different physical and chemical properties but the same formula are said to be **isomers** of one another. Complex ions can show many different kinds of isomerism, only one of which we will consider. *Geometric isomers* are ones that differ only in the spatial orientation of ligands around the central metal atom. Geometric isomerism is found in square planar and octahedral complexes. It cannot occur in tetrahedral complexes where all four positions are equivalent.

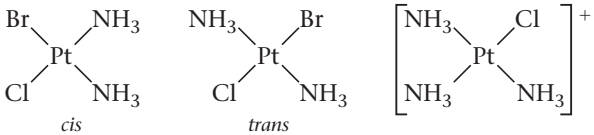
1. ***Square planar.*** There are two compounds with the formula $Pt(NH_3)_2Cl_2$, differing in water solubility, melting point, chemical behavior, and biological activity.* Their structures are



The complex in which the two chloride ions are at adjacent corners of the square, as close to one another as possible, is called the ***cis*** **isomer**. It is made by reacting ammonia with the $PtCl_4^{2-}$ ion. In the ***trans*** **isomer**, made by reacting $Pt(NH_3)_4^{2+}$ with HCl, the two chloride ions are at opposite corners of the square, as far apart as possible.

cis = close together; *trans* = far apart.

Geometric isomerism can occur with any square complex of the type Mabcd, Ma_2bc, or Ma_2b_2, where M refers to the central metal and a, b, c, and d are different ligands. Conversely, geometric isomerism cannot occur with a square complex of the type Ma_4 or Ma_3b. Thus there are two different square complexes with the formula $Pt(NH_3)_2ClBr$ but only one with the formula $Pt(NH_3)_3Cl^+$.



*The *cis* isomer ("cisplatin") is an effective anticancer drug. This reflects the ability of the two Cl atoms to interact with the nitrogen atoms of DNA, a molecule responsible for cell reproduction. The *trans* isomer is ineffective in chemotherapy, presumably because the Cl atoms are too far apart to react with a DNA molecule.

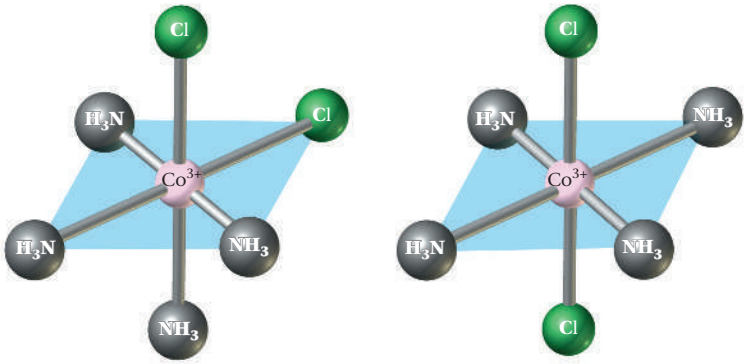


Figure 19.6 ***Cis*** **and** ***trans*** **isomers of** $Co(NH_3)_4Cl_2^+$.

2. *Octahedral.* To understand how geometric isomerism can arise in octahedral complexes, refer back to Figure 19.5. Notice that for any given position of a ligand, four other positions are at the same distance from that ligand, and a fifth is at a greater distance.

It doesn't matter where you start; the octahedron is symmetrical.

Taking position 1 in Figure 19.5 as a point of reference, you can see that groups at 2, 3, 4, and 5 are equidistant from 1; 6 is farther away. In other words, positions 1 and 2, 1 and 3, 1 and 4, 1 and 5 are *cis* to one another; positions 1 and 6 are *trans*. Hence a complex ion like $Co(NH_3)_4Cl_2^+$ (Figure 19.6) can exist in two different isomeric forms. In the *cis* isomer, the two Cl^- ions are at adjacent corners of the octahedron, as close together as possible. In the *trans* isomer they are at opposite corners, as far away from one another as possible.

EXAMPLE 19.4

How many geometric isomers are possible for the neutral complex $[Co(NH_3)_3Cl_3]$?

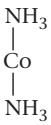
ISOMER I

STRATEGY

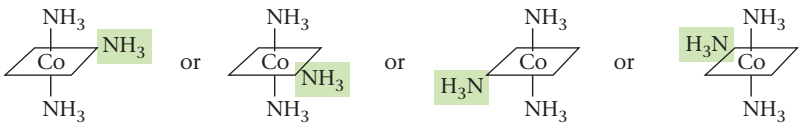
1. Create isomer I by putting two NH_3 molecules *trans* to each other.
2. Check to see how many different isomers you can obtain by placing the third NH_3 molecule at different corners of the octahedron.
3. Put the three chloride ions in the unoccupied corners.

SOLUTION

1. *trans* NH_3



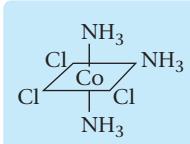
2. Third NH_3



(a) (b) (c) (d)

It does not matter where the third NH_3 molecule (shaded in green) is. It will be *cis* to the NH_3 molecules already in place.

3. Cl ions



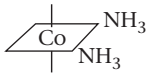
= Isomer I

continued

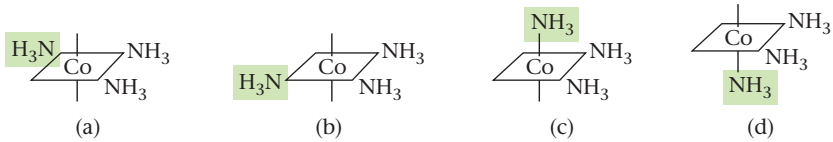
ISOMER II

STRATEGY AND SOLUTION

1. Create the second isomer by placing the two NH_3 molecules *cis* to each other.



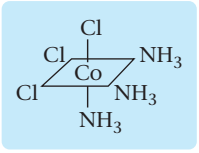
2. Check to see how many different isomers you can obtain by placing the third NH_3 molecule at different corners of the octahedron. (Remember that the symmetry of a regular octagon requires that the distance across the diagonal of a square be the same as that from "top" to "bottom."



Structures (a) and (b) are identical to the first isomer created. There are two NH_3 molecules *cis* to each other and two NH_3 molecules *trans* to each other.

Structures (c) and (d) are identical to each other and different from isomer I. All three NH_3 molecules are *cis* to each other.

3. Choose either structure (c) or (d) and fill in the empty corners with Cl ions.



= Isomer II

Geometric isomerism can also occur in chelated octahedral complexes (Figure 19.7). Notice that an *ethylenediamine molecule*, here and indeed in all complexes, ***can only bridge cis positions.*** It is not long enough to connect to *trans* positions.

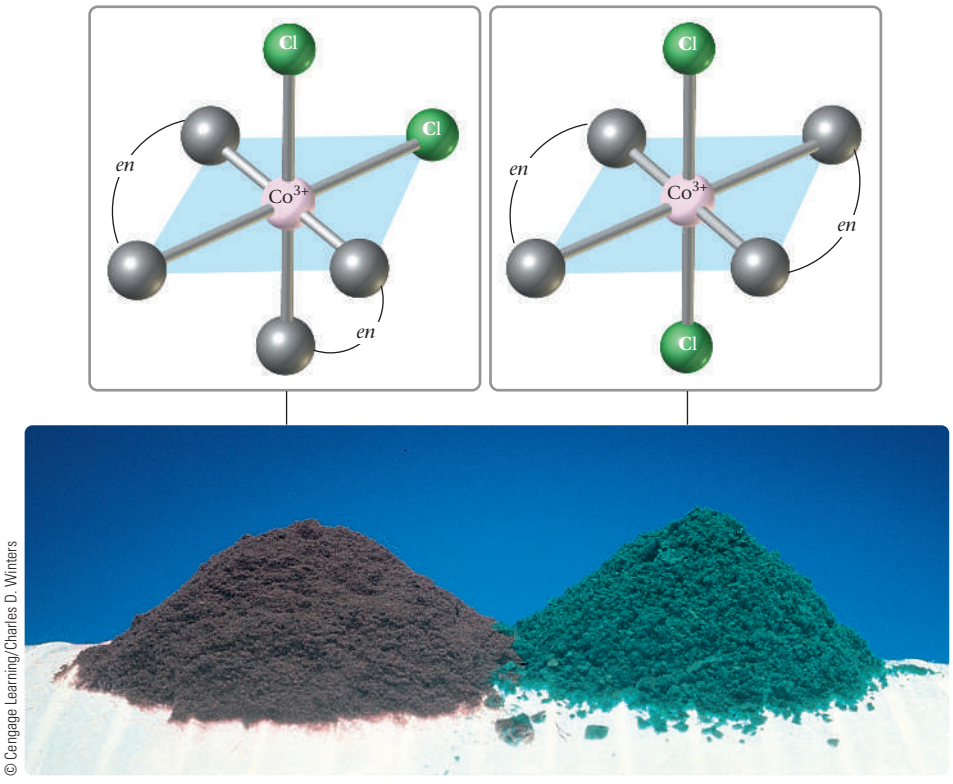


Figure 19.7 ***Cis*** **and** ***trans*** **isomers of** $[Co(en)_2Cl_2]^+$. The ethylenediamine molecule is represented by —*en*—. It forms two bonds per molecule. The *cis* isomer is reddish-purple and the *trans* is dark green.

Marna G. Clarke

Figure 19.8 Brightly colored coordination compounds. Most coordination compounds are brilliantly colored, a property that can be explained by the crystal field model.

19-4 Electronic Structure of Complex Ions

Until about 20 years ago, the *valence bond model* discussed in Chapter 7 was widely used to explain electronic structure and bonding in complex ions. It assumed that lone pairs of electrons were contributed by ligands to form covalent bonds with metal atoms. This model had two major deficiencies. It could not easily explain the magnetic properties of complex ions. More important, it offered no explanation of the most striking characteristic of coordination compounds: their color (Figure 19.8).

We will discuss the **crystal field model** here. It assumes that the bonding between metal ions and ligands is essentially ionic. More specifically, it considers the effect of approaching ligands upon the energies of electronic levels in transition metal cations. We will apply this model to octahedral complexes. Before doing so, it may be helpful to review the electronic structure of uncomplexed transition metal cations, originally covered in Chapter 6.

"Crystal field" isn't a very descriptive term, but it's part of the jargon.

Transition Metal Cations

Recall (pages 146–147) that in a simple transition metal cation

- there are no outer s electrons. Electrons beyond the preceding noble gas are located in an inner d sublevel (3d for the first transition series).
- electrons are distributed among the five d orbitals in accordance with Hund's rule, giving the maximum number of unpaired electrons.

In transition metal cations, 3d is lower in energy than 4s.

To illustrate these rules, consider the Fe^{2+} ion. Because the atomic number of iron is 26, this +2 ion must contain $26 - 2 = 24e^-$. Of these electrons, the first 18 have the argon structure; the remaining six are located in the 3d sublevel. The abbreviated electron configuration is

$$Fe^{2+} \qquad [Ar]3d^6$$

CHEMISTRY THE **HUMAN** SIDE

The basic ideas concerning the structure and geometry of complex ions presented in this chapter were developed by one of the most gifted individuals in the history of inorganic chemistry, Alfred Werner. His theory of coordination chemistry was published in 1893 when Werner was 26 years old. In his paper Werner made the revolutionary suggestion that metal ions such as Co^{3+} could show two different kinds of valences. For the compound $Co(NH_3)_6Cl_3$, Werner postulated a central Co^{3+} ion joined by "primary valences" (ionic bonds) to three Cl^- ions and by "secondary valences" (coordinate covalent bonds) to six NH_3 molecules. Moreover, he made the inspired guess that the six secondary valences were directed toward the corners of a regular octahedron.

Werner spent the next 20 years obtaining experimental evidence to prove his theory. (At the University of Zürich, there remain several *thousand* samples of coordination compounds prepared by Werner and his students.) He was able to show, for example, that the electrical conductivities in water solution decreased in the order $[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl$ in much the same way as with simple salts, for example, $ScCl_3 > CaCl_2 > NaCl$. Another property he studied was isomerism. In 1907, he was able to isolate a second geometric isomer of $[Co(NH_3)_4Cl_2]Cl$, in complete accord with his theory. Six years later, Werner won the Nobel Prize in Chemistry.

SPL/Science Source

Alfred Werner
(1866–1919)

By all accounts, Werner was a superb lecturer. Sometimes as many as 300 students crowded into a hall with a capacity of 150 to hear him speak. So great was his reputation that students in theology and law came to hear him talk about chemistry. There was, however, a darker side to Werner that few students saw. A young woman badgered by Werner during an oral examination came to see him later to ask whether she had passed; he threw a chair at her. Werner died at age 52 of hardening of the arteries, perhaps caused in part by his addiction to alcohol and strong black cigars.

These six electrons are spread over all five orbitals; the orbital diagram is

$$\begin{array}{cccc} & & & 3d \\ Fe^{2+} & [Ar] & (\uparrow\downarrow)(\uparrow)(\uparrow)(\uparrow)(\uparrow) & \end{array}$$

The Fe^{2+} ion is *paramagnetic*, with four unpaired electrons.

EXAMPLE 19.5

Consider the Co^{3+} ion.

a Derive its abbreviated electron configuration.

STRATEGY AND SOLUTION

1. Find Z (number of protons = number of electrons for a neutral species) for Co in the periodic table.

   $Z = 27$

2. Write the abbreviated electron configuration.

   $[_{18}Ar]4s^2 3d^7$

3. Remove 3 electrons for the charged (+3) atom. Recall that electrons with the highest n are removed first.

   $[_{18}Ar]3d^6$

b How many unpaired electrons are there?

STRATEGY AND SOLUTION

1. Write the abbreviated orbital diagram following Hund's rule.

   $[_{18}Ar]\ (\uparrow\downarrow)\ (\uparrow\ )\ (\uparrow\ )\ (\uparrow\ )\ (\uparrow\ )$

2. Count the number of unpaired electrons.

   There are four unpaired electrons.

The shapes of the five d orbitals are shown in Figure 19.9. These orbitals are given the symbols

$$d_{z^2} \quad d_{x^2-y^2} \quad d_{xy} \quad d_{yz} \quad d_{xz}$$

In the uncomplexed transition metal cation, all of these orbitals have the same energy.

Octahedral Complexes

As six ligands approach a central metal ion to form an octahedral complex, they change the energies of electrons in the d orbitals. The effect (Figure 19.10) is to split the five d orbitals into two groups of different energy.

1. A higher energy pair, the $d_{x^2-y^2}$ and d_{z^2} orbitals
2. A lower energy trio, the d_{xy}, d_{yz}, and d_{xz} orbitals

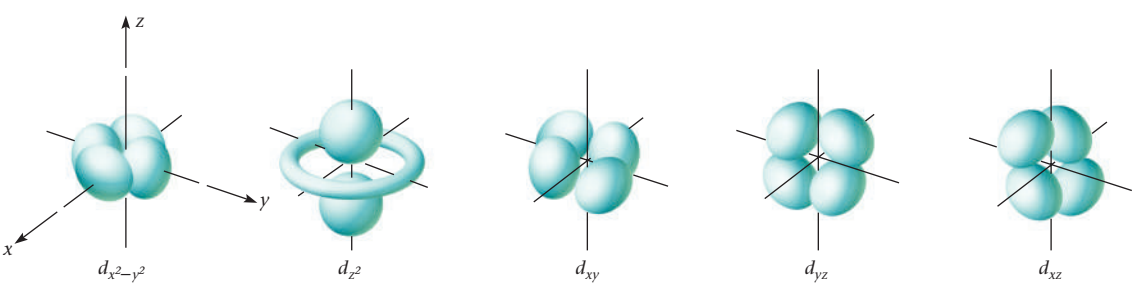


Figure 19.9 **The five d orbitals and their relation to ligands on the *x*-, *y*-, and *z*-axes.**

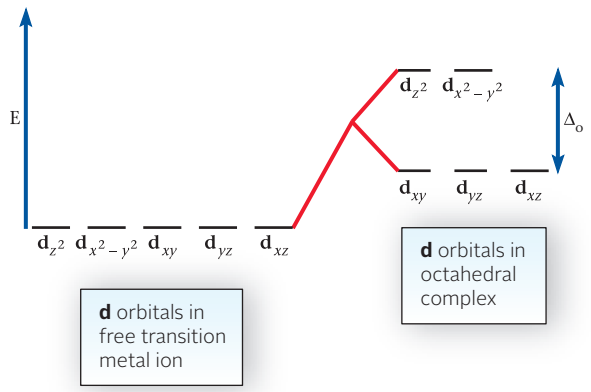


Figure 19.10 Change in the energy levels of d orbitals in complex formation. In a free transition metal ion, all five d orbitals have the same energy. When the ion forms an octahedral complex, two orbitals (d_{z^2}, $d_{x^2-y^2}$) have a higher energy than the other three (d_{xy}, d_{yz}, d_{xz}). The difference in energy between the two d orbital levels in the octahedral complex is known as the *crystal field splitting energy* and has the symbol Δ_o.

The difference in energy between the two groups is called the **crystal field splitting energy** and given the symbol Δ_o (the subscript "o" stands for "octahedral").

To see why this splitting occurs, consider what happens when six ligands (e.g., H_2O, CN^-, NH_3) approach a central metal cation along the *x*-, *y*-, and *z*-axes (Figure 19.9). The unshared electron pairs on these ligands repel the electrons in the d orbitals of the cation. The repulsion is greatest for the $d_{x^2-y^2}$ and d_{z^2} orbitals, which have their maximum electron density directly along the *x*-, *y*-, and *z*-axes, respectively. Electrons in the other three orbitals (d_{xy}, d_{yz}, d_{xz}) are less affected because their densities are concentrated between the axes rather than along them.

This gives the d_{xy}, d_{yz}, and d_{xz} orbitals a lower energy.

Depending on the magnitude of Δ_o, a cation may form either of two different kinds of complexes. This is illustrated for the Fe^{2+} ion in the two diagrams in Figure 19.11.

1. In the $Fe(CN)_6^{4-}$ ion shown at the left, Δ_o is so large that the six 3d electrons of the Fe^{2+} ion pair up in the lower energy orbitals. In this way, the Fe^{2+} ion achieves its most stable (lowest energy) electronic structure. The complex is diamagnetic, with no unpaired electrons.
2. In the $Fe(H_2O)_6^{2+}$ ion shown at the right, Δ_o is relatively small, and the six 3d electrons of the Fe^{2+} ion spread out over all the orbitals as expected by Hund's rule. In other words, the electron distribution in the complex is the same as in the Fe^{2+} ion itself (where Δ_o is 0!). The $Fe(H_2O)_6^{2+}$ ion is paramagnetic, with four unpaired electrons.

More generally, it is possible to distinguish between

- **low-spin complexes**, containing the minimum number of unpaired electrons, formed when Δ_o is large; electrons are concentrated in the lower energy orbitals.

When Δ_o is small, the electron distribution is the same as in the simple cation; if Δ_o is large, Hund's rule is not strictly followed.

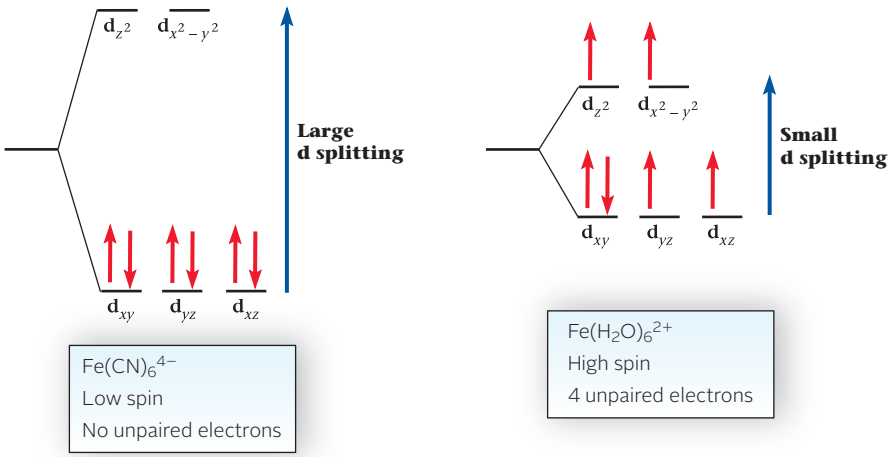


Figure 19.11 Electron distribution in low-spin and high-spin complexes of Fe^{2+}. Depending on the magnitude of Δ_o, either of two different complexes may be formed by Fe^{2+}.

- **high-spin complexes,** containing the maximum number of unpaired electrons, formed when Δ_o is small; electrons are spread out among the d orbitals, exactly as in the uncomplexed transition metal cation.

When Δ_o is small, the electron distribution is the same as in the simple cation; if Δ_o is large, Hund's rule is not strictly followed.

For a given cation,

- the high-spin complex always contains more unpaired electrons than the low-spin complex and so is more strongly paramagnetic.
- the value of Δ_o is determined by the nature of the ligand. So-called "strong-field" ligands (e.g., CN^-), which interact strongly with d-orbital electrons, produce a large Δ_o. Conversely, "weak-field" ligands (e.g., H_2O) interact weakly with d-orbital electrons, producing a small Δ_o.

Remember:
strong-field ligands → large Δ_o → low spin complex
weak-field ligands → small Δ_o → high spin complex

EXAMPLE 19.6

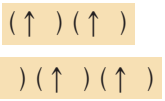
Derive the electron distribution of the Fe^{3+} ion in the low-spin and high-spin octahedral complexes.

STRATEGY

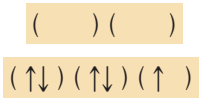
1. Write the abbreviated electron configurations for Fe and then for Fe^{3+}.
2. For the high-spin complex, follow Hund's rule in distributing the electrons to *all* orbitals.
3. For the low-spin complex, follow Hund's rule in distributing the electrons first to the *lower* orbitals. If there are any electrons left, fill the upper orbitals, again following Hund's rule.

SOLUTION

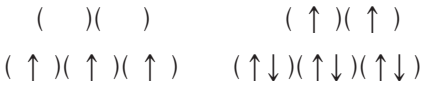
1. Abbreviated electron configurations: Fe: $[_{18}Ar]4s^23d^6$; Fe^{3+}: $[_{18}Ar]3d^5$
2. High-spin complex



3. Low-spin complex



This model of the electronic structure of complex ions explains why high-spin and low-spin complexes occur only with ions that have four to seven electrons (d^4, d^5, d^6, d^7). With three or fewer electrons, only one distribution is possible; the same is true with eight or more electrons.



3 electrons 8 electrons

The color we see is what is left over after certain wavelengths are absorbed.

Color

Most coordination compounds are brightly colored except for those of cations whose d sublevels are completely empty (such as Sc^{3+}) or completely filled (such as Zn^{2+}). These colors are readily explained, at least qualitatively, by the model we have just described. The energy difference between two sets of d orbitals in a complex is ordinarily equal to that of a photon in the visible region. Hence by absorbing visible light, an electron may be able to move from the lower energy set of d orbitals to the higher one. This removes some of the component wavelengths of white light, so that the light reflected or transmitted by the complex is colored (Figure 19.12). The relation between absorbed and transmitted light can be deduced from the color wheel shown in Figure 19.13. For example, a complex that absorbs blue-green light appears orange, and vice versa.

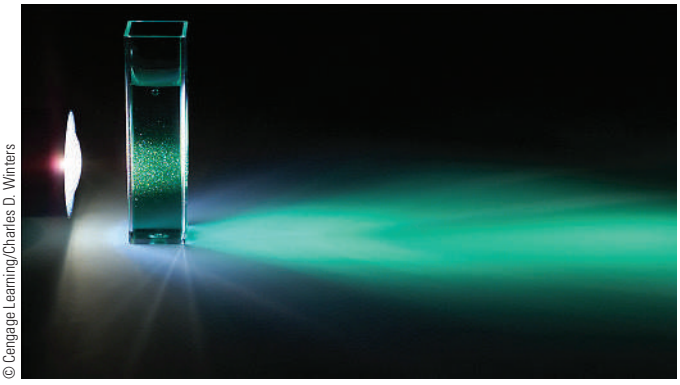


Figure 19.12 Light absorption and color. The color of a solution is due to the color of the light *not* absorbed by the solution. Here a solution of Ni^{2+} ion in water absorbs red and blue light and so appears green.

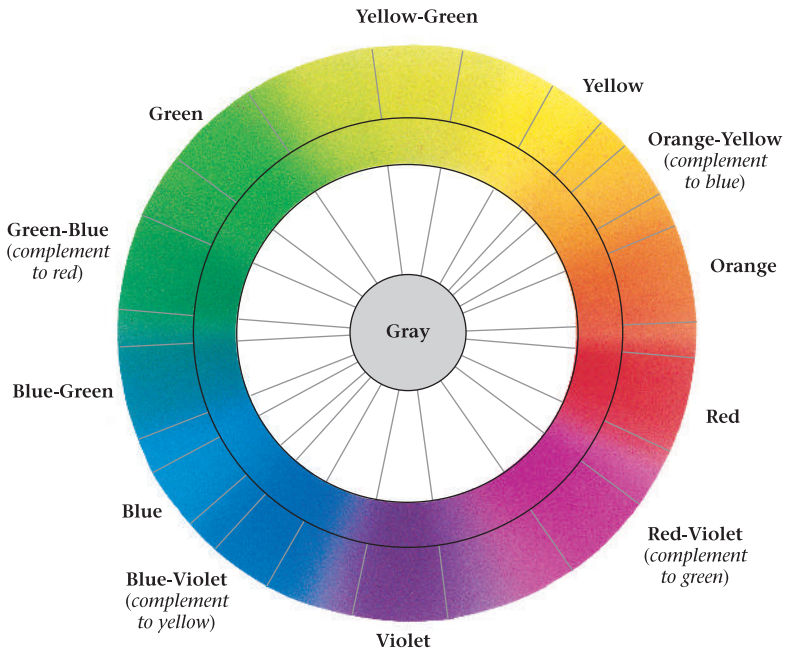


Figure 19.13 The color wheel. The color of a complex is complementary to (180° across from) the color of the light absorbed.

From the color (absorption spectrum) of a complex ion, it is sometimes possible to deduce the value of Δ_o, the crystal field splitting energy. The situation is particularly simple in $_{22}Ti^{3+}$, which contains only one 3d electron. Consider, for example, the $Ti(H_2O)_6^{3+}$ ion, which has an intense purple color. This ion absorbs at 510 nm, in the green region. The purple (red-violet) color of a solution of $Ti(H_2O)_6^{3+}$ is what is left over when the green component is subtracted from the visible spectrum. Using the equation relating energy to wavelength (Chapter 6), it is possible to calculate the energy of a photon with a wavelength of 510 nm:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(2.998 \times 10^{8}\ \text{m/s})}{510 \times 10^{-9}\ \text{m}} = 3.90 \times 10^{-19}\ \text{J}$$

The energy in kilojoules per mole is

$$E = 3.90 \times 10^{-19}\ \text{J} \times \frac{1\ \text{kJ}}{10^{3}\ \text{J}} \times \frac{6.022 \times 10^{23}}{1\ \text{mol}} = 2.35 \times 10^{2}\ \text{kJ/mol}$$

This is the energy absorbed in raising the 3d electron from a lower to a higher orbital. In other words, in the $Ti(H_2O)_6^{3+}$ ion, the two sets of d orbitals are separated by this amount of energy. The splitting energy, Δ_o, is 235 kJ/mol.

The smaller the value of Δ_o, the longer the wavelength of the light absorbed. This effect is shown in Table 19.3 and Figure 19.14. When weak-field ligands such

Table 19.3 Colors of Complex Ions of Co^{3+}

Complex	Color Observed	Color Absorbed	Approximate Wavelength (nm) Absorbed
$Co(NH_3)_6^{3+}$	Yellow	Violet	430
$Co(NH_3)_5NCS^{2+}$	Orange	Blue-green	470
$Co(NH_3)_5H_2O^{3+}$	Red	Green-blue	500
$Co(NH_3)_5Cl^{2+}$	Purple	Yellow-green	530
trans-$Co(NH_3)_4Cl_2^{+}$	Green	Red	680

Ray Boyington/S. Ruven Smith

Figure 19.14 A spectrochemical series. The five cations listed in Table 19.3 vary in color from yellow $[Co(NH_3)_6]Cl_3$ to green $[trans\text{-}Co(NH_3)_4Cl_2]Cl$. ◂ *i*

i This series is based on experiment, not theory.

as NCS^-, H_2O, or Cl^- are substituted for NH_3, the light absorbed shifts to longer wavelengths (lower energies). On the basis of observations like these, ligands can be arranged in order of decreasing tendency to split the d orbitals. A short version of such a *spectrochemical series* is

$$CN^- > NO_2^- > en > NH_3 > NCS^- > H_2O > F^- > Cl^-$$

strong field → decreasing Δ_o → weak field

CHEMISTRY **BEYOND** THE CLASSROOM

Chelates: Natural and Synthetic

Chelating agents, capable of bonding to metal atoms at more than one position, are abundant in nature. Certain species of soybeans synthesize and secrete organic chelating agents that extract iron from insoluble compounds in the soil, thereby making it available to the plant. Mosses and lichens growing on boulders use a similar process to obtain the metal ions they need for growth.

Many important natural products are chelates in which a central metal atom is bonded into a large organic molecule. In chlorophyll, the green coloring matter of plants, the central atom is magnesium; in the essential vitamin B_{12}, it is cobalt. The structure of heme, the pigment responsible for the red color of blood, is shown in Figure A. There is an Fe^{2+} ion at the center of the complex surrounded by four nitrogen atoms at the corners of a square. A fifth coordination position around the iron is occupied by the molecule globin, which in combination with heme, gives the protein referred to as hemoglobin.

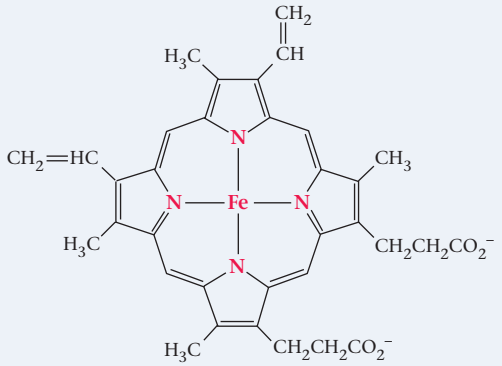


Figure A Structure of heme. In the hemoglobin molecule, the Fe^{2+} ion is at the center of an octahedron, surrounded by four nitrogen atoms, a globin molecule, and a water molecule.

The sixth coordination position of Fe^{2+} in heme is occupied by a water molecule that can be replaced reversibly by oxygen to give a derivative known as oxyhemoglobin, which has the bright red color characteristic of arterial blood.

$$\text{hemoglobin} + O_2 \rightleftharpoons \text{oxyhemoglobin} + H_2O$$

The position of this equilibrium is sensitive to the pressure of oxygen. In the lungs, where the blood is saturated with air ($P_{O_2} = 0.2$ atm), the hemoglobin is almost completely converted to oxyhemoglobin. In the tissues, the partial pressure of oxygen drops, and the oxyhemoglobin breaks down to release O_2 essential for metabolism. In this way, hemoglobin acts as an oxygen carrier, absorbing oxygen in the lungs and liberating it to the tissues.

Unfortunately, hemoglobin forms a complex with carbon monoxide that is considerably more stable than oxyhemoglobin. The equilibrium constant for the reaction

$$\text{hemoglobin} \cdot O_2(aq) + CO(g) \rightleftharpoons \text{hemoglobin} \cdot CO(aq) + O_2(g)$$

is about 200 at body temperature. Consequently, the carbon monoxide complex is formed preferentially in the lungs even at CO concentrations as low as one part per thousand. When this happens, the flow of oxygen to the tissues is cut off, resulting eventually in muscular paralysis and death.

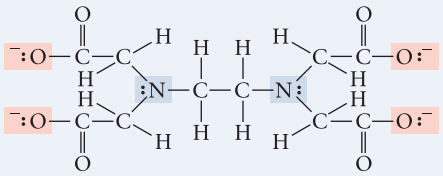


Figure B Structure of the EDTA ion; the chelating atoms, six in all, have color screens.

Many chelating agents have been synthesized in the laboratory to take advantage of their ability to tie up *(sequester)* metal cations. Perhaps the best known synthetic chelating agent is the ethylenediaminetetraacetate (EDTA) ion shown in Figure B. EDTA can bond at as many as six positions, thereby occupying all the octahedral sites surrounding a central metal cation.

EDTA forms 1:1 complexes with a large number of cations, including those of some of the main-group metals. The complex formed by calcium with EDTA is used to treat lead poisoning. When a solution containing the Ca-EDTA complex is given by injection, the calcium is displaced by lead. The more stable Pb-EDTA complex is eliminated in the urine. EDTA has also been used to remove radioactive isotopes of metals, notably plutonium, from body tissues.

You may have noticed Ca-EDTA on the list of ingredients of many prepared foods, ranging from beer to mayonnaise. EDTA acts as a scavenger to pick up traces of metal ions that catalyze the chemical reactions responsible for flavor deterioration, loss of color, or rancidity. Typically, Ca-EDTA is added at a level of 30 to 800 ppm.

Still another use of EDTA is in the field of art restoration. Figure C shows "before and after" photographs of Rodin's bronze sculpture "The Thinker." This stood in front of the Rodin Museum in Philadelphia for about 60 years prior to its restoration in 1992. Over time the sculpture had picked up a thick coating of insoluble $CuSO_4 \cdot 3Cu(OH)_2(s)$. Application of a wet paste containing EDTA dissolved the coating by forming the soluble $Cu(EDTA)^{2-}$ complex.

$$CuSO_4 \cdot 3Cu(OH)_2(s) + 4EDTA^{4-}(aq) \longrightarrow 4Cu(EDTA)^{2-}(aq) + SO_4^{2-}(aq) + 6OH^-(aq)$$

The Thinker, 1880, Auguste Rodin. The Rodin Museum, Philadelphia, Gift of Jules E. Mastbaum, 1929. Photography by Joe Mikuliak

The Thinker, 1880, Auguste Rodin. The Rodin Museum, Philadelphia, Gift of Jules E. Mastbaum, 1929. Photography by Joe Mikuliak

Figure C *The Thinker* by Rodin, before (*left*) and after (*right*).

Key Concepts

1. Relate the composition of a complex ion to its charge, coordination number, and the oxidation number of the central metal.
   (Examples 19.1 and 19.2; Problems 1–12)
2. Write the name of complex ions and coordination compounds.
   (Example 19.3; Problems 17–22)

3. Sketch the geometry of a complex ion and identify geometric isomers.
   (Example 19.4; Problems 23–30)
4. Give the electron configuration and/or orbital diagram of a transition metal cation.
   (Example 19.5; Problems 31–34)
5. Derive orbital diagrams for high-spin and low-spin complexes.
   (Example 19.6; Problems 35–46)

Key Terms

central atom
chelates
cis isomer
complex ion
coordination compounds
coordination number
crystal field model
crystal field splitting energy
geometric isomerism
high-spin complexes
isomers
ligands
low-spin complexes
octahedron
square planar
tetrahedron
trans isomer

Summary Problem

Consider the complex $[Pt(NH_3)_2(CN)_4]$.

(a) Identify the ligands and their charges.

(b) What is the oxidation number of platinum?

(c) Suppose the ammonia molecules were replaced by OH^- ions. Write the formula of the resulting complex.

(d) What is the coordination number of platinum in the compound?

(e) Describe the geometry of the complex.

(f) How many possible geometric isomers are there?

(g) Write the abbreviated electron configuration for the platinum(IV) ion.

(h) Cyanide ligands are ligands with the strongest crystal field (large Δ_o). Show the electron distribution for platinum in this compound. Is this a high-spin or low-spin complex?

(i) Is the complex paramagnetic or diamagnetic?

Answers

(a) $NH_3 = 0$; $CN^- = -1$
(b) $+4$
(c) $[Pt(OH)_2(CN)_4^{2-}]$
(d) 6
(e) octahedral
(f) two
(g) $[Xe]\ 4f^{14}5d^6$
(h) low spin ( )( )
(↑↓)(↑↓) (↑↓)
(i) diamagnetic

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

19-1 Composition of Complex Ions

1. Consider the complex ion $[Fe(C_2O_4)_2(NH_3)Cl^{3-}]$.
(a) Identify the ligands and their charges.
(b) What is the oxidation number of nickel?
(c) What is the formula for the potassium salt of this ion?

2. Consider the complex ion $[Cd(en)(SCN)_2(OH)_2^-]$.
(a) Identify the ligands and their charges.
(b) What is the oxidation number of cadmium?
(c) What is the formula for the magnesium salt of this ion?

3. Nickel(III) forms many complexes, among them those with the following ligands. Give the formula and charge of each nickel complex described below.
(a) four carbonyl molecules (CO) and two chloride ions
(b) two ethylenediamine molecules
(c) two thiocyanate molecules (SCN^-), two hydroxide ions, and two ammonia molecules

4. Platinum(II) forms many complexes, among them those with the following ligands. Give the formula and charge of each complex.
(a) two ammonia molecules and one oxalate ion ($C_2O_4^{2-}$)
(b) two ammonia molecules, one thiocyanate ion (SCN^-), and one bromide ion
(c) one ethylenediamine molecule and two nitrite ions

5. What is the coordination number of the metal in the following complexes?
(a) $[Co(en)_2(SCN)Cl^+]$ **(b)** $[Ni(CN)_4^{2-}]$
(c) $[Zn(C_2O_4)_2^{2-}]$ **(d)** $[Ag(NH_3)Cl]$

6. What is the coordination number of the central metal atom in the following complexes?
(a) $[Fe(H_2O)_6^{3+}]$ **(b)** $[Pt(NH_3)Br_3^-]$
(c) $[V(en)Cl_4^{2-}]$ **(d)** $[Au(CN)_2^+]$

7. What is the oxidation number of the metal atom in the complex ions in Question 5?

8. What is the oxidation number of the metal atom in the complex ions in Question 6?

9. Write the formula for the carbonate salt (if the complex ion is a cation) or the barium salt (if the complex ion is an anion) for the ions in Question 5.

10. Follow the directions for Question 9 for the complex ions in Question 6.

11. Refer to Table 19.2 to predict the formula of the complex formed by

(a) Cu^+ with NH_3
(b) Pt^{2+} with the oxalate ion
(c) Cadmium(II) with water molecules
(d) Fe^{3+} with CN^-

12. Refer to Table 19.2 to predict the formula of the complex formed by

(a) Pt^{4+} with NH_3 **(b)** Ag^+ with CN^-
(c) Zn^{2+} with $C_2O_4^{2-}$ **(d)** Cd^{2+} with CN^-

13. What is the mass percent of sulfur in the $[Ag(SCN)_2^-]$ complex ion?

14. What is the mass percent of Cl in the sulfate salt of $[Ni(H_2O)_4Cl_2^+]$?

15. There are four iron atoms in each hemoglobin molecule. The mass percent of iron in a hemoglobin molecule is 0.35%. Estimate the molar mass of hemoglobin.

16. Vitamin B_{12} is a coordination compound with cobalt as its central atom. It contains 4.4% cobalt by mass and has a molar mass of 1.3×10^3 g/mol. How many cobalt atoms are in a molecule of vitamin B_{12}?

19-2 Naming Complex Ions and Coordination Compounds

17. Write formulas for the following ions or compounds:

(a) zinchexachloroplatinate(IV)
(b) dichlorobis(ethylenediamine)nickel(II)
(c) diamminetriaquahydroxochromium(III) nitrate
(d) ammonium pentachlorohydroxoferrate(III)

18. Write formulas for the following ions or compounds.

(a) diamminetetraquachromium(II) chloride
(b) tetrachlorosulfatocadmium(III)
(c) sodium tetrahydroxonickelate(II)
(d) dibromo*bis*(ethylenediamine)iron(III)

19. Name the following ions or compounds:

(a) $[Ru(NH_3)_5Cl^{2+}]$ **(b)** $[Mn(NH_2CH_2CH_2NH_2)_3^{2+}]$
(c) $K_2[PtCl_4]$ **(d)** $[Cr(NH_3)_5I]I_2$

20. Name the following ions or compounds:

(a) $Na[Al(OH)_4]$ **(b)** $[Co(C_2O_4)_2(H_2O_2)^-]$
(c) $[Ir(NH_3)_3Cl_3]$ **(d)** $[Cr(en)(NH_3)_2Br_2]_2SO_4$

21. Name the compounds or ions in Question 5.

22. Name the compounds or ions in Question 6.

19-3 Geometry of Complex Ions

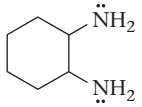
23. Sketch the geometry of

(a) $[Zn(NH_3)_2Cl_2]$ (tetrahedral)
(b) *cis*-$[Co(H_2O)_4Cl_2]^+$
(c) *trans*-$[Pt(NH_3)_2Br_2]^{2+}$
(d) *trans*-$[Ni(ox)_2(OH)_2]^{3-}$
(e) $[Au(CN)Br]^+$

24. Sketch the geometry of

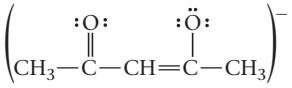
(a) *trans*-$[Cu(Br)_2(H_2O)_4]$
(b) $[Zn(OH)_2I_2^{2-}]$ (tetrahedral)
(c) $[Pt(NH_3)_4^{2+}]$ (square planar)
(d) *cis*-$[Ni(H_2O)_2(C_2O_4)_2^{2-}]$
(e) $[Au(CN)(NH_3)]$

25. The compound 1,2-diaminocyclohexane



(abbreviated "dech") is a ligand in the promising anticancer complex *cis*-$Pd(H_2O)_2(dech)^{2+}$. Sketch the geometry of this complex.

26. The acetylacetonate ion ($acac^-$)



forms complexes with many metal ions. Sketch the geometry of $Fe(acac)_3$.

27. Which of the following octahedral complexes show geometric isomerism? If geometric isomers are possible, draw their structures.

(a) $[Co(en)Cl_4^-]$
(b) $[Ni(C_2O_4)_2ClBr^{4-}]$
(c) $[Cd(NH_3)_2Cl_4^{2-}]$

28. Follow the directions of Question 27 for the following:

(a) $[Mn(H_2O)_2(NO_2)_4^{2-}]$
(b) $[Pt(NH_3)_3(Cl_3)^+]$
(c) $[Al(C_2O_4)(CO)_2(Br)_2^-]$

29. Draw all the structural formulas for the octahedral complexes of Co^{3+} with only *ox* and/or NH_3 as ligands.

30. Draw all the structural formulas for the octahedral complexes of $[Ni(H_2O)_3(OH)_2Cl]$.

19-4 Electronic Structure of Complex Ions

Electronic Structure of Metal Ions

31. Give the abbreviated electron configuration of the following metal ions:

(a) Cr^{3+} **(b)** Pd^{2+} **(c)** V^{3+}
(d) Ir^{3+} **(e)** Ru^{2+}

32. Give the electronic configuration for

(a) Cd^{2+} **(b)** Fe^{2+} **(c)** Pt^{2+}
(d) Mn^{2+} **(e)** Ni^{3+}

33. Write an abbreviated orbital diagram and determine the number of unpaired electrons in each species in Question 31.

34. Write an abbreviated orbital diagram and determine the number of unpaired electrons in each species in Question 32.

Electron Distributions and Crystal Field Energy

35. Give the electron distribution in low-spin and/or high-spin complexes of

(a) Ru^{4+} **(b)** Pt^{2+}

36. Follow the directions of Question 35 for

(a) Zn^{2+} **(b)** Ni^{3+}

37. For complexes of V^{3+}, only one distribution of electrons is possible. Explain.

38. Explain why Mn^{3+} forms high-spin and low-spin octahedral complexes but Mn^{4+} does not.

39. $[Cr(CN)_6^{4-}]$ is less paramagnetic than $[Cr(H_2O)_6^{2+}]$. Explain.

40. Why is $[Co(NH_3)_6^{3+}]$ diamagnetic while $[CoF_6^{3-}]$ is paramagnetic?

41. Give the number of unpaired electrons in octahedral complexes with strong-field ligands for

(**a**) Rh^{3+} (**b**) Mn^{3+} (**c**) Ag^{+}
(**d**) Pt^{4+} (**e**) Au^{3+}

42. For the species in Question 41, indicate the number of unpaired electrons with weak-field ligands.

43. $Ti(NH_3)_6^{3+}$ has a d-orbital electron transition at 399 nm. Find Δ_o at this wavelength.

44. MnF_6^{2-} has a crystal field splitting energy, Δ_o, of 2.60×10^2 kJ/mol. What is the wavelength responsible for this energy?

45. The wavelength of maximum absorption of $[Cu(NH_3)_4^{2+}]$ is 580 nm (orange-yellow). What color is a solution of $[Cu(NH_3)_4^{2+}]$?

46. A solution of $[Fe(CN)_6^{3-}]$ appears red. Using Figure 19.13, estimate the wavelength of maximum absorption.

Unclassified

47. A chemist synthesizes two coordination compounds. One compound decomposes at 280°C, the other at 240°C. Analysis of the compounds gives the same mass percent data: 52.6% Pt, 7.6% N, 1.63% H, and 38.2% Cl. Both compounds contain a +4 central ion.

(**a**) What is the simplest formula of the compounds?
(**b**) Draw structural formulas for the complexes present.

48. Analysis of a coordination compound gives the following results: 22.0% Co, 31.4% N, 6.78% H, and 39.8% Cl. One mole of the compound dissociates in water to form four moles of ions.

(**a**) What is the simplest formula of the compound?
(**b**) Write an equation for its dissociation in water.

Conceptual Problems

49. Explain why

(**a**) oxalic acid removes rust stains.
(**b**) there are no geometric isomers of tetrahedral complexes.
(**c**) cations such as Co^{2+} act as Lewis acids.
(**d**) $C_2O_4^{2-}$ is a chelating agent.
(**e**) NH_3 can be a ligand but NH_4^{+} is not.

50. Indicate whether each of the following is true or false. If the statement is false, correct it.

(**a**) The coordination number of iron(III) in $[Fe(NH_3)_4(en)^{3+}]$ is 5.
(**b**) $[Ni(CN)_6^{4-}]$ is expected to absorb at a longer wavelength than $[Ni(NH_3)_6^{2+}]$.
(**c**) Complexes of Cr^{3+} are brightly colored, and those of Zn^{2+} are colorless.
(**d**) Ions with seven or more d electrons cannot form both high- and low-spin octahedral complexes.

Challenge Problems

51. A child eats 10.0 g of paint containing 5.0% Pb. How many grams of the sodium salt of EDTA, $Na_4(EDTA)$, should he receive to bring the lead into solution as Pb · EDTA?

52. A certain coordination compound has the simplest formula $PtN_2H_6Cl_2$. It has a molar mass of about 600 g/mol and contains both a complex cation and a complex anion. What is its structure?

53. Two coordination compounds decompose at different temperatures but have the same mass percent analysis data: 20.25% Cu, 15.29% C, 7.07% H, 26.86% N, 10.23% S, and 20.39% O. Each contains Cu^{2+}.

(**a**) Determine the simplest formula of the compounds.
(**b**) Draw the structural formulas of the complex ion in each case.

54. In the $[Ti(H_2O)_6^{3+}]$ ion, the splitting between the d levels, Δ_o, is 55 kcal/mol. What is the color of this ion? Assume that the color results from a transition between upper and lower d levels.