

## *Coordination Complexes*

**Coordination compounds**, such as the  $\text{FeCl}_4^-$  ion and  $\text{CrCl}_3 \cdot 6 \text{NH}_3$ , are called such because they contain ions or molecules linked, or coordinated, to a transition metal. They are also known as **complex ions** or **coordination complexes** because they are Lewis acid-base complexes. The ions or molecules that bind to transition-metal ions to form these complexes are called **ligands** (from Latin, "to tie or bind"). The number of ligands bound to the transition metal ion is called the **coordination number**.

Although coordination complexes are particularly important in the chemistry of the transition metals, some main group elements also form complexes. Aluminum, tin, and lead, for example, form complexes such as the  $\text{AlF}_6^{3-}$ ,  $\text{SnCl}_4^{2-}$  and  $\text{PbI}_4^{2-}$  ions.

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### *Werner's Theory of Coordination Complexes*

Alfred Werner developed a model of coordination complexes which explains the following observations.

- At least three different cobalt(III) complexes can be isolated when  $\text{CoCl}_2$  is dissolved in aqueous ammonia and then oxidized by air to the +3 oxidation state. A fourth complex can be made by slightly different techniques. These complexes have different colors and different empirical formulas.

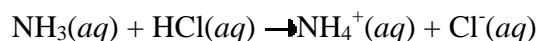
$\text{CoCl}_3 \cdot 6 \text{NH}_3$             orange-yellow

$\text{CoCl}_3 \cdot 5 \text{NH}_3 \cdot \text{H}_2\text{O}$     red

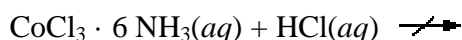
$\text{CoCl}_3 \cdot 5 \text{NH}_3$             purple

$\text{CoCl}_3 \cdot 4 \text{NH}_3$             green

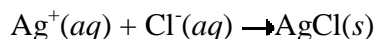
- The reactivity of the ammonia in these complexes has been drastically reduced. By itself, ammonia reacts rapidly with hydrochloric acid to form ammonium chloride.



These complexes don't react with hydrochloric acid, even at  $100^\circ\text{C}$ .



- Solutions of the  $\text{Cl}^-$  ion react with  $\text{Ag}^+$  ion to form a white precipitate of  $\text{AgCl}$ .

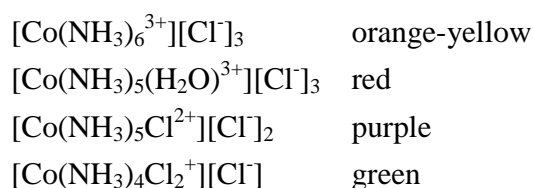


When excess  $\text{Ag}^+$  ion is added to solutions of the  $\text{CoCl}_3 \cdot 6 \text{NH}_3$  and  $\text{CoCl}_3 \cdot 5 \text{NH}_3 \cdot \text{H}_2\text{O}$  complexes, three moles of  $\text{AgCl}$  are formed for each mole of complex in solution, as might be expected. However, only two of the  $\text{Cl}^-$  ions in the  $\text{CoCl}_3 \cdot 5 \text{NH}_3$  complex and only one of the  $\text{Cl}^-$  ions in  $\text{CoCl}_3 \cdot 4 \text{NH}_3$  can be precipitated with  $\text{Ag}^+$  ions.

- Measurements of the conductivity of aqueous solutions of these complexes suggest that the  $\text{CoCl}_3 \cdot 6 \text{NH}_3$  and  $\text{CoCl}_3 \cdot 5 \text{NH}_3 \cdot \text{H}_2\text{O}$  complexes dissociate in water to give a total of four ions.  $\text{CoCl}_3 \cdot 5 \text{NH}_3$  dissociates to give three ions, and  $\text{CoCl}_3 \cdot 4 \text{NH}_3$  dissociates to give only two ions.

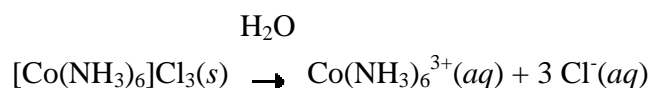
Werner explained these observations by suggesting that transition-metal ions such as the  $\text{Co}^{3+}$  ion have a primary valence and a secondary valence. The *primary valence* is the number of negative ions needed to satisfy the charge on the metal ion. In each of the cobalt(III) complexes previously described, three  $\text{Cl}^-$  ions are needed to satisfy the primary valence of the  $\text{Co}^{3+}$  ion.

The *secondary valence* is the number of ions of molecules that are coordinated to the metal ion. Werner assumed that the secondary valence of the transition metal in these cobalt(III) complexes is six. The formulas of these compounds can therefore be written as follows.

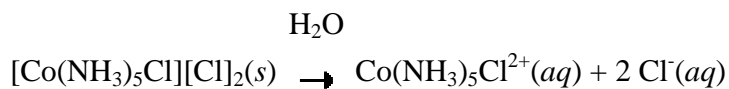


The cobalt ion is coordinated to a total of six ligands in each complex, which satisfies the secondary valence of this ion. Each complex also has a total of three chloride ions that satisfy the primary valence. Some of the  $\text{Cl}^-$  ions are free to dissociate when the complex dissolves in water. Others are bound to the  $\text{Co}^{3+}$  ion and neither dissociate nor react with  $\text{Ag}^+$ .

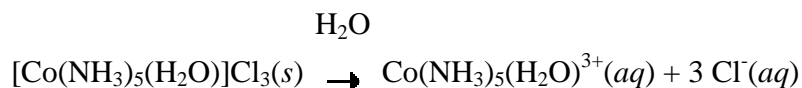
The  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  complex dissociates in water to give a total of four ions, and all three  $\text{Cl}^-$  ions are free to react with  $\text{Ag}^+$  ion.



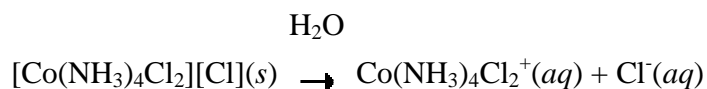
One of the chloride ions is bound to the cobalt in the  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  complex. Only three ions are formed when this compound dissolves in water, and only two  $\text{Cl}^-$  ions are free to precipitate with  $\text{Ag}^+$  ions.



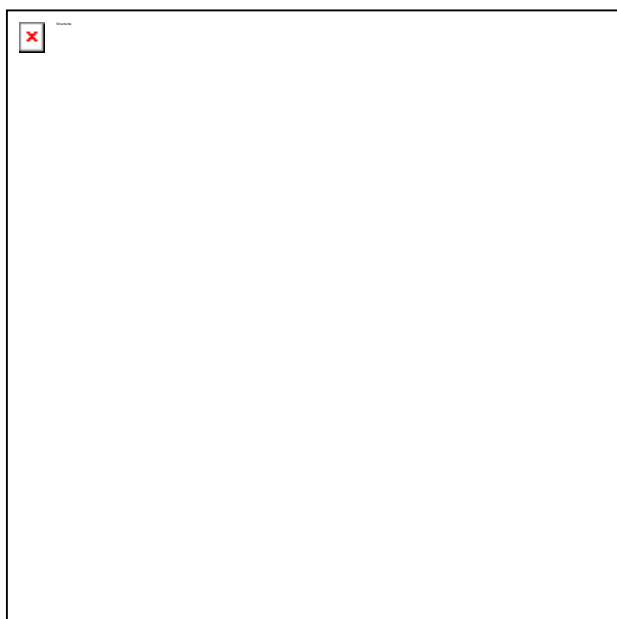
Once again, the three  $\text{Cl}^-$  ions are free to dissociate when  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$  dissolves in water, and they precipitate when  $\text{Ag}^+$  ions are added to the solution.



Two of the chloride ions are bound to the cobalt in  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ . Only two ions are formed when this compound dissolves in water, and only one  $\text{Cl}^-$  ion is free to precipitate with  $\text{Ag}^+$  ions.



Werner assumed that transition-metal complexes had definite shapes. According to his theory, the ligands in six-coordinate cobalt(III) complexes are oriented toward the corners of an octahedron, as shown in the figure below.

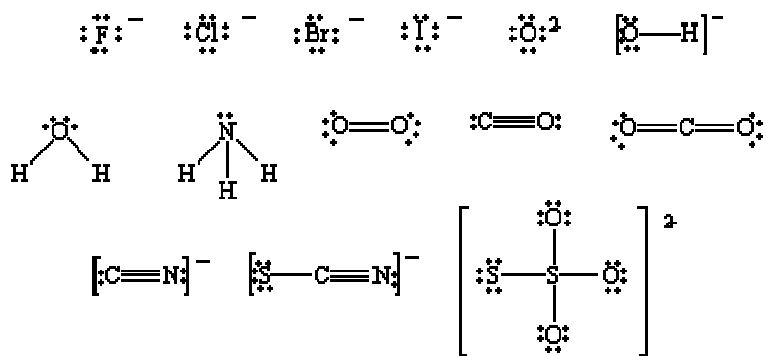


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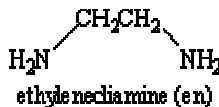
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### Typical Ligands

Any ion or molecule with a pair of nonbonding electrons can be a ligand. Many ligands are described as **monodentate** (literally, "one-toothed") because they "bite" the metal in only one place. Typical monodentate ligands are given in the figure below.



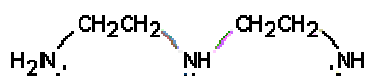
Other ligands can attach to the metal more than once. Ethylenediamine (en) is a typical **bidentate ligand**.



Each end of this molecule contains a pair of nonbonding electrons that can form a covalent bond to a metal ion. Ethylenediamine is also an example of a **chelating ligand**. The term *chelate* comes from a Greek stem meaning "claw." It is used to describe ligands that can grab the metal in two or more places, the way a claw would.

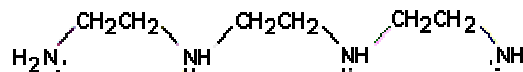
Linking ethylene-diamine fragments gives *tridentate ligands* and *tetradentate ligands*, such as diethylenetriamine (dien) and triethylenetetramine (trien). Adding four  $\text{-CH}_2\text{CO}_2^-$  groups to an ethylenediamine framework gives a *hexadentate ligand*, which can single-handedly satisfy the secondary valence of a transition-metal ion.

Tridentate Ligand:



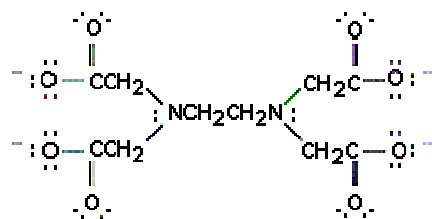
diethylenetriamine (dien)

Tetradentate Ligand:



triethylenetetraamine (trien)

Hexadentate Ligand:



ethylenediaminetetraacetate (EDTA)

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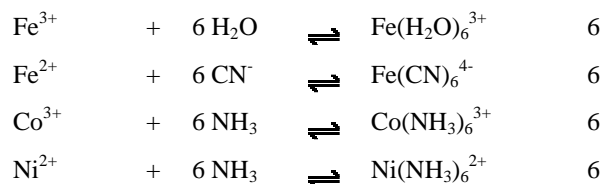
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### Typical Coordination Numbers

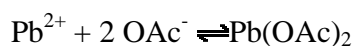
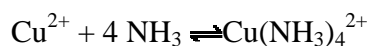
Transition-metal complexes have been characterized with coordination numbers that range from 1 to 12, but the most common coordination numbers are 2, 4, and 6. Examples of complexes with these coordination numbers are given in the table below.

#### Examples of Common Coordination Numbers

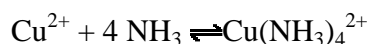
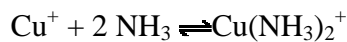
Metal Ion	Ligand	Complex	Coordination Number
$\text{Ag}^+$	+ 2 $\text{NH}_3$	$\text{Ag}(\text{NH}_3)_2^+$	2
$\text{Ag}^+$	+ 2 $\text{S}_2\text{O}_3^{2-}$	$\text{AgCl}_2^-$	2
$\text{Ag}^+$	+ 2 $\text{Cl}^-$	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2
$\text{Pb}^{2+}$	+ 2 $\text{OAc}^-$	$\text{Pb}(\text{OAc})_2$	2
$\text{Cu}^+$	+ 2 $\text{NH}_3$	$\text{Cu}(\text{NH}_3)_2^+$	2
$\text{Cu}^{2+}$	+ 4 $\text{NH}_3$	$\text{Cu}(\text{NH}_3)_4^{2+}$	4
$\text{Zn}^{2+}$	+ 4 $\text{CN}^-$	$\text{Zn}(\text{CN})_4^{2-}$	4
$\text{Hg}^{2+}$	+ 4 $\text{I}^-$	$\text{HgI}_4^{2-}$	4
$\text{Co}^{2+}$	+ 4 $\text{SCN}^-$	$\text{Co}(\text{SCN})_4^{2-}$	4
$\text{Fe}^{2+}$	+ 6 $\text{H}_2\text{O}$	$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	6



Note that the charge on the complex is always the sum of the charges on the ions or molecules that form the complex.

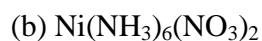


Note also that the coordination number of a complex often increases as the charge on the metal ion becomes larger.



***Practice Problem 2:***

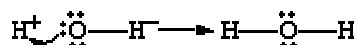
Calculate the charge on the transition-metal ion in the following complexes.



[Click here to check your answer to Practice Problem 2](#)

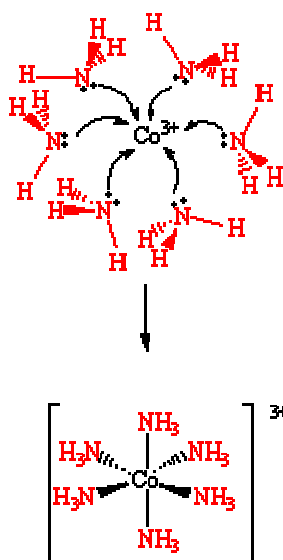
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G. N. Lewis was the first to recognize that the reaction between a transition-metal ion and ligands to form a coordination complex was analogous to the reaction between the  $\text{H}^+$  and  $\text{OH}^-$  ions to form water. The reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions involves the donation of a pair of electrons from the  $\text{OH}^-$  ion to the  $\text{H}^+$  ion to form a covalent bond.

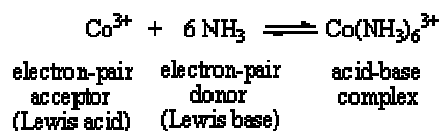


The  $\text{H}^+$  ion can be described as an **electron-pair acceptor**. The  $\text{OH}^-$  ion, on the other hand, is an **electron-pair donor**. Lewis argued that any ion or molecule that behaves like the  $\text{H}^+$  ion should be an acid. Conversely, any ion or molecule that behaves like the  $\text{OH}^-$  ion should be a base. A **Lewis acid** is therefore any ion or molecule that can accept a pair of electrons. A **Lewis base** is an ion or molecule that can donate a pair of electrons.

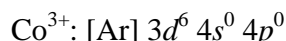
When  $\text{Co}^{3+}$  ions react with ammonia, the  $\text{Co}^{3+}$  ion accepts pairs of nonbonding electrons from six  $\text{NH}_3$  ligands to form covalent cobalt-nitrogen bonds as shown in the figure below.



The metal ion is therefore a Lewis acid, and the ligands coordinated to this metal ion are Lewis bases.



The  $\text{Co}^{3+}$  ion is an electron-pair acceptor, or Lewis acid, because it has empty valence-shell orbitals that can be used to hold pairs of electrons. To emphasize these empty valence orbitals we can write the configuration of the  $\text{Co}^{3+}$  ion as follows.



There is room in the valence shell of this ion for 12 more electrons. (Four electrons can be added to the  $3d$  subshell, two to the  $4s$  orbital, and six to the  $4p$  subshell.) The  $\text{NH}_3$  molecule is an electron-pair donor, or Lewis base, because it has a pair of nonbonding electrons on the nitrogen atom.

According to this model, transition-metal ions form coordination complexes because they have empty valence-shell orbitals that can accept pairs of electrons from a Lewis base. Ligands must therefore be Lewis bases: They must contain at least one pair of nonbonding electrons that can be donated to a metal ion.

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The rules for naming chemical compounds are established by nomenclature committees of the International Union of Pure and Applied Chemistry (IUPAC).

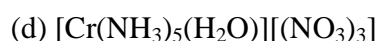
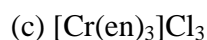
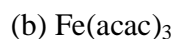
### **RULES FOR NAMING COORDINATION COMPLEXES**

- The name of the positive ion is written before the name of the negative ion.
- The name of the ligand is written before the name of the metal to which it is coordinated.
- The Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on are used to indicate the number of ligands when these ligands are relatively simple. The Greek prefixes *bis-*, *tris-*, and *tetrakis-* are used with more complicated ligands.
- The names of negative ligands always end in *o*, as in *fluoro* ( $\text{F}^-$ ), *chloro* ( $\text{Cl}^-$ ), *bromo* ( $\text{Br}^-$ ), *iodo* ( $\text{I}^-$ ), *oxo* ( $\text{O}^{2-}$ ), *hydroxo* ( $\text{OH}^-$ ), and *cyano* ( $\text{CN}^-$ ).
- A handful of neutral ligands are given common names, such as *aquo* ( $\text{H}_2\text{O}$ ), *ammine* ( $\text{NH}_3$ ), and *carbonyl* ( $\text{CO}$ ).
- Ligands are listed in the following order: negative ions, neutral molecules, and positive ions. Ligands with the same charge are listed in alphabetical order.
- The oxidation number of the metal atom is indicated by a Roman numeral in parentheses after the name of the metal atom.
- The names of complexes with a net negative charge end in *-ate*.  $\text{Co}(\text{SCN})_4^{2-}$ , for example, is the tetrathiocyanatocobaltate(II) ion. When the symbol for the metal is derived from its Latin name, *-ate* is added to the Latin name of the metal. Thus, negatively charged iron complexes are ferrates and negatively charged copper complexes are cuprates.



**Practice Problem 3:**

Name the following coordination complexes.



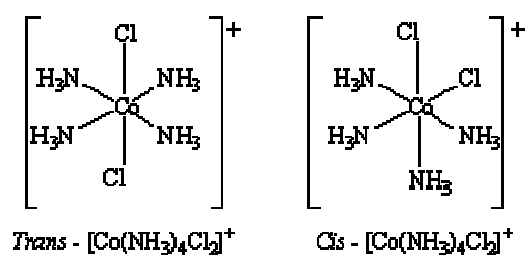
[Click here to check your answer to Practice Problem 3](#)

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***Cis/Trans Isomers***

**Isomers** are compounds with the same chemical formula but different structures. An important test of [Werner's theory](#) of coordination complexes involved the study of coordination complexes that formed isomers (literally, "equal parts").

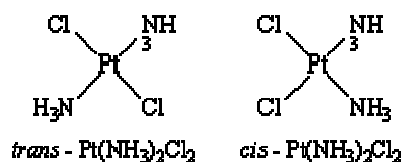
Example: There are two isomers for the  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$  complex ion, as shown in the figure below.



The structures of these isomers differ in the orientation of the two chloride ions around the  $\text{Co}^{3+}$  ion. In the **trans** isomer, the chlorides occupy positions across from one another in the octahedron. In the **cis** isomer, they occupy adjacent positions. The difference between *cis* and *trans* isomers can be remembered by noting that the prefix *trans* is used to describe things that are on opposite sides, as in *transatlantic* or *transcontinental*.

At the time Werner proposed his theory, only one isomer of the  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  complex was known — the green complex. Werner predicted that a second isomer should exist and his discovery in 1907 of a purple compound with the same chemical formula was a key step in convincing scientists who were still critical of his model.

*Cis/trans* isomers are also possible in four-coordinate complexes that have a square-planar geometry. The figure below shows the structures of the *cis* and *trans* isomers of dichlorodiammineplatinum(II). The *cis* isomer is used as a drug to treat brain tumors, under the trade name *cisplatin*. This square-planar complex inserts itself into the grooves in the double helix structure of the DNA in cells, which inhibits the replication of DNA. This slows down the rate at which the tumor grows, which allows the body's natural defense mechanisms to act on the tumor.



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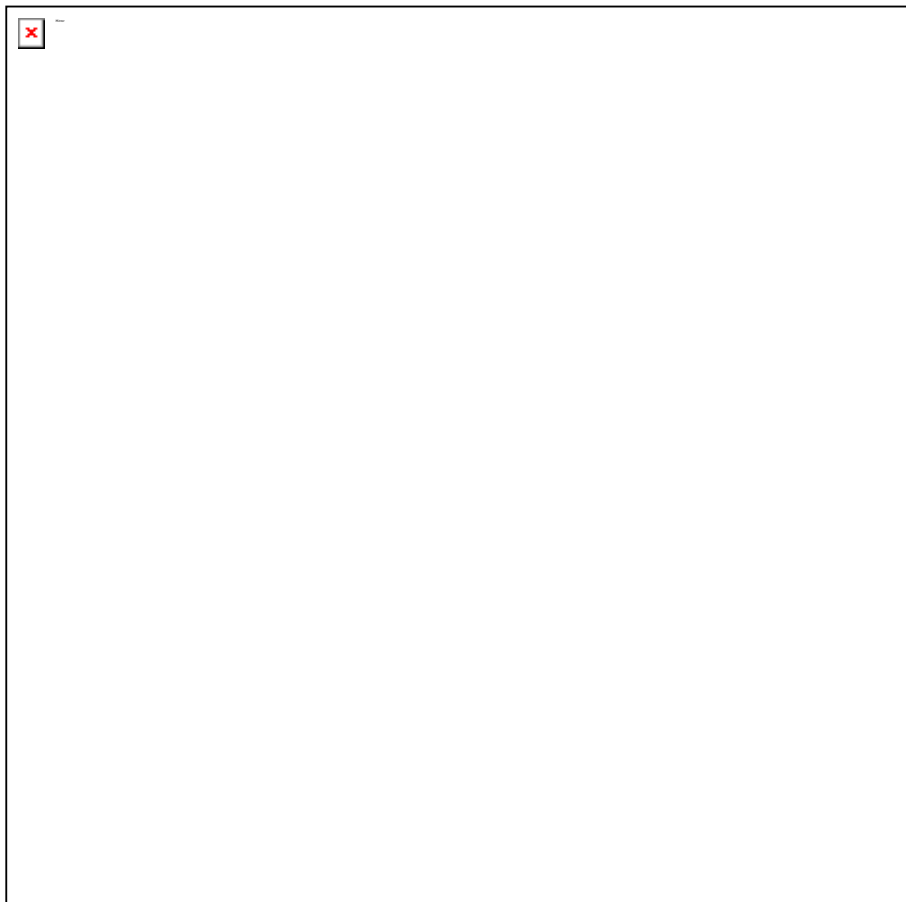
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### *Chiral Isomers*

Another form of isomerism can be understood by considering the difference between gloves and mittens. One glove in each pair fits the left hand, and the other fits the right hand. Mittens usually fit equally well on either hand. To understand why, hold a glove and a mitten in front of a mirror. There is no difference between the mitten shown in the figure below and its mirror image. There is a difference, however, between the glove and its mirror image. The mirror image of the glove that fits the left hand looks like the glove that fits the right hand, and vice versa.



Each member of a pair of gloves is the mirror image of the other the way the right and left hands are mirror images of each other. Gloves therefore have the same property as the hands on which they are placed. As a result, they are said to be **chiral** (from the Greek *cheir*, hand). By definition, any object that has a mirror image that is different from itself is chiral. The  $\text{Co(en)}_3^{3+}$  ion is an example of a chiral molecule, which forms a pair of isomers that are mirror images of each other (see figure below). These isomers have almost identical physical and chemical properties. They have the same melting point, boiling point, density, and color, for example. They differ only in the way they interact with plane-polarized light.



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### *Polarized Light and Optically Active Compounds*

Light consists of electric and magnetic fields that oscillate in all directions perpendicular to the path of the light ray. When light is passed through a polarizer, such as a lens in a pair of polarized sunglasses, these oscillations are confined to a single plane. Compounds that can rotate plane-polarized light are said to be **optically active**. Those that rotate the plane of polarization to the right (clockwise) are said to be **dextrorotatory** (from the Latin *dexter*, "right"). Those that rotate the plane to the left (counterclockwise) are **levorotatory** (from the Latin *laevus*, "left"). All chiral compounds are optically active; one isomer is dextrorotatory and the other is levorotatory.

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# The Valence-Bond Approach to Bonding in Complexes

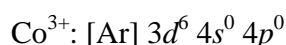
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The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902. It was not until 1927, however, that Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the **valence-bond theory**. The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^3$ , and  $d^2sp^3$  orbitals.

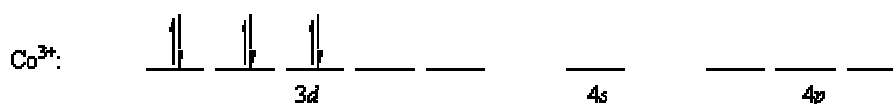
It is easy to apply the valence-bond theory to some coordination complexes, such as the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion. We start with the electron configuration of the transition-metal ion.



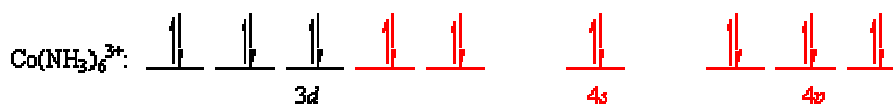
We then look at the valence-shell orbitals and note that the  $4s$  and  $4p$  orbitals are empty.



Concentrating the  $3d$  electrons in the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals in this subshell gives the following electron configuration.



The  $3d_{x^2-y^2}$ ,  $3d_z^2$ ,  $4s$ ,  $4p_x$ ,  $4p_y$  and  $4p_z$  orbitals are then mixed to form a set of empty  $d^2sp^3$  orbitals that point toward the corners of an octahedron. Each of these orbitals can accept a pair of nonbonding electrons from a neutral  $\text{NH}_3$  molecule to form a complex in which the cobalt atom has a filled shell of valence electrons.



### Practice Problem 4:

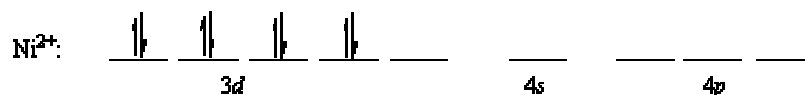
Use valence-bond theory to explain why  $\text{Fe}^{2+}$  ions form the  $\text{Fe}(\text{CN})_6^{4-}$  complex ion.

[Click here to check your answer to Practice Problem 4](#)

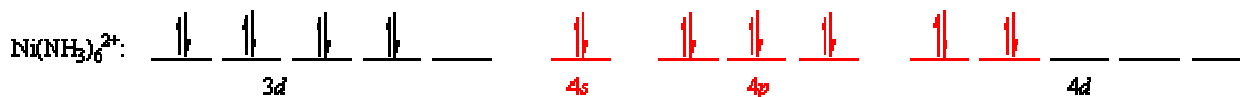
At first glance, complexes such as the  $\text{Ni}(\text{NH}_3)_6^{2+}$  ion seem hard to explain with the valence-bond theory. We start, as always, by writing the configuration of the transition-metal ion.



This configuration creates a problem, because there are eight electrons in the  $3d$  orbitals. Even if we invest the energy necessary to pair the  $3d$  electrons, we can't find two empty  $3d$  orbitals to use to form a set of  $d^2sp^3$  hybrids.



There is a way around this problem. The five  $4d$  orbitals on nickel are empty, so we can form a set of empty  $sp^3d^2$  hybrid orbitals by mixing the  $4d_{x^2-y^2}$ ,  $4d_z^2$ ,  $4s$ ,  $4p_x$ ,  $4p_y$  and  $4p_z$  orbitals. These hybrid orbitals then accept pairs of nonbonding electrons from six ammonia molecules to form a complex ion.



The valence-bond theory therefore formally distinguishes between "inner-shell" complexes, which use  $3d$ ,  $4s$  and  $4p$  orbitals to form a set of  $d^2sp^3$  hybrids, and "outer-shell" complexes, which use  $4s$ ,  $4p$  and  $4d$  orbitals to form  $sp^3d^2$  hybrid orbitals.

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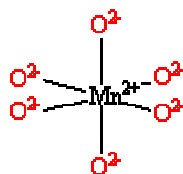
## Crystal Field Theory

<a href="#">Octahedral Crystal Fields</a>	<a href="#">Tetrahedral Crystal Fields</a>	<a href="#">Square Planar Complexes</a>
<a href="#">The Spectrochemical Series</a>	<a href="#">High-Spin Versus Low-Spin Octahedral Complexes</a>	

At almost exactly the same time that chemists were developing the valence-bond model for coordination complexes, physicists such as Hans Bethe, John Van Vleck, and Leslie Orgel were developing an alternative known as **crystal field theory**. This theory tried to describe the effect of the electrical field of neighboring ions on the energies of the valence orbitals of an ion in a crystal. Crystal field theory was developed by considering two compounds: manganese(II) oxide, MnO, and copper(I) chloride, CuCl.

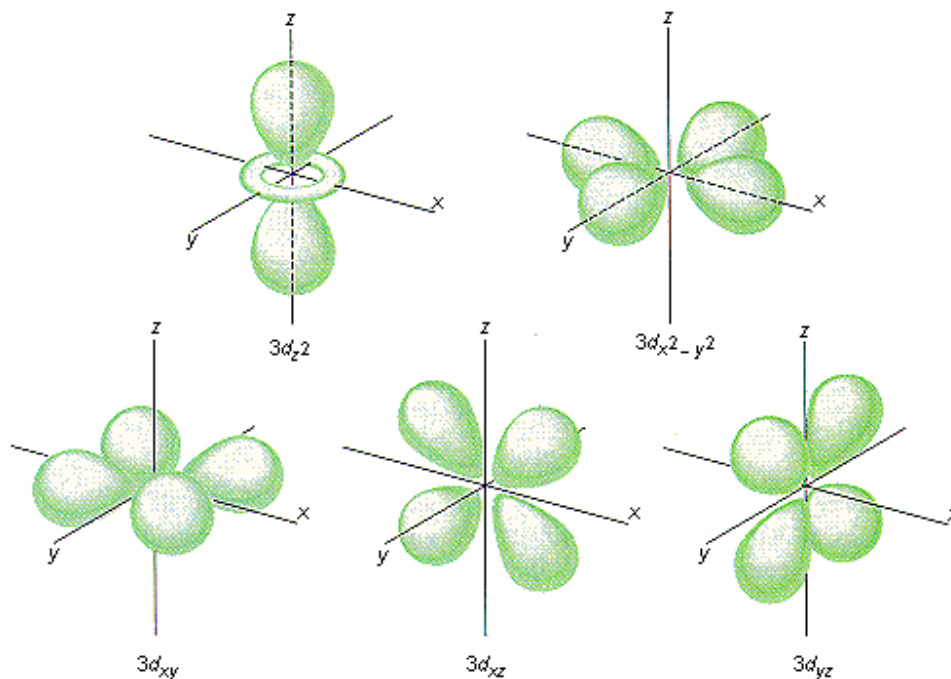
### *Octahedral Crystal Fields*

Each  $\text{Mn}^{2+}$  ion in manganese(II) oxide is surrounded by six  $\text{O}^{2-}$  ions arranged toward the corners of an octahedron, as shown in the figure below. MnO is therefore a model for an *octahedral* complex in which a transition-metal ion is coordinated to six ligands.

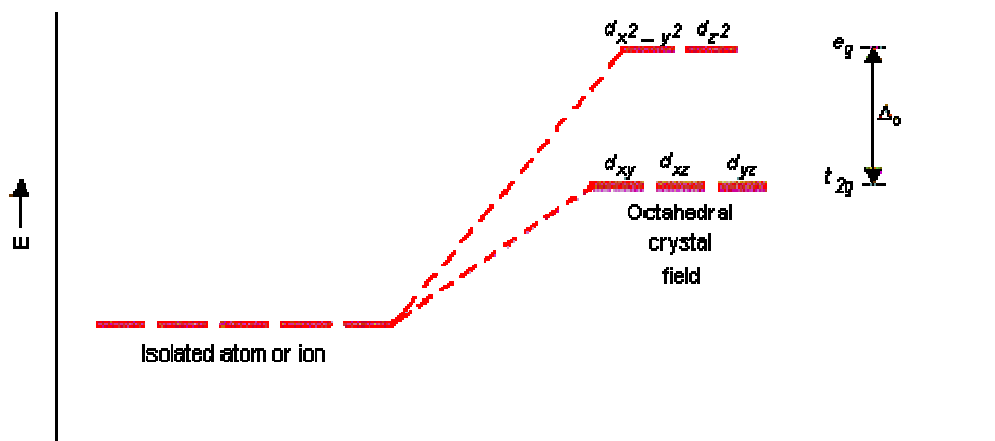


What happens to the energies of the  $4s$  and  $4p$  orbitals on an  $\text{Mn}^{2+}$  ion when this ion is buried in an MnO crystal? Repulsion between electrons that might be added to these orbitals and the electrons on the six  $\text{O}^{2-}$  ions that surround the metal ion in MnO increase the energies of these orbitals. The three  $4p$  orbitals are still degenerate, however. These orbitals still have the same energy because each  $4p$  orbital points toward two  $\text{O}^{2-}$  ions at the corners of the octahedron.

Repulsion between electrons on the  $\text{O}^{2-}$  ions and electrons in the  $3d$  orbitals on the metal ion in MnO also increases the energy of these orbitals. But the five  $3d$  orbitals on the  $\text{Mn}^{2+}$  ion are no longer degenerate. Let's assume that the six  $\text{O}^{2-}$  ions that surround each  $\text{Mn}^{2+}$  ion define an  $XYZ$  coordinate system. Two of the  $3d$  orbitals ( $3d_{x^2-y^2}$  and  $3d_z^2$ ) on the  $\text{Mn}^{2+}$  ion point directly toward the six  $\text{O}^{2-}$  ions, as shown in the figure below. The other three orbitals ( $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$ ) lie between the  $\text{O}^{2-}$  ions.



The energy of the five  $3d$  orbitals increases when the six  $O^{2-}$  ions are brought close to the  $Mn^{2+}$  ion. However, the energy of two of these orbitals ( $3d_{x^2-y^2}$  and  $3d_z^2$ ) increases much more than the energy of the other three ( $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$ ), as shown in the figure below. The crystal field of the six  $O^{2-}$  ions in  $MnO$  therefore splits the degeneracy of the five  $3d$  orbitals. Three of these orbitals are now lower in energy than the other two.



By convention, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals in an octahedral complex are called the  $t_{2g}$  orbitals. The  $d_{x^2-y^2}$  and  $d_z^2$  orbitals, on the other hand, are called the  $e_g$  orbitals.



The easiest way to remember this convention is to note that there are three orbitals in the  $t_{2g}$  set.

$$t_{2g}: d_{xy}, d_{xz}, \text{ and } d_{yz} \quad e_g: d_{x^2-y^2} \text{ and } d_z^2$$

The difference between the energies of the  $t_{2g}$  and  $e_g$  orbitals in an octahedral complex is represented by the symbol  $\Delta_o$ . This splitting of the energy of the  $d$  orbitals is not trivial;  $\Delta_o$  for the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion, for example, is 242 kJ/mol.

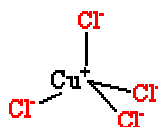
The magnitude of the splitting of the  $t_{2g}$  and  $e_g$  orbitals changes from one octahedral complex to another. It depends on the identity of the metal ion, the charge on this ion, and the nature of the ligands coordinated to the metal ion.

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### *Tetrahedral Crystal Fields*

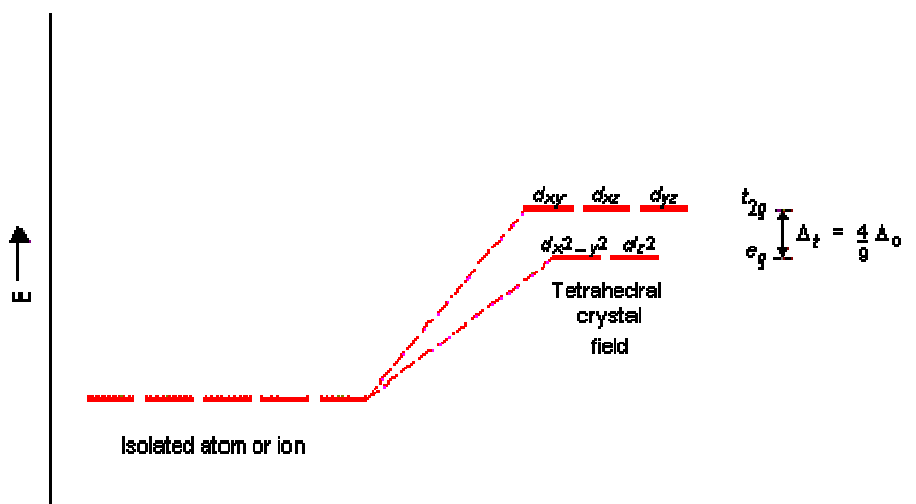
Each  $\text{Cu}^+$  ion in copper(I) chloride is surrounded by four  $\text{Cl}^-$  ions arranged toward the corners of a tetrahedron, as shown in the figure below.  $\text{CuCl}$  is therefore a model for a *tetrahedral* complex in which a transition-metal ion is coordinated to four ligands.



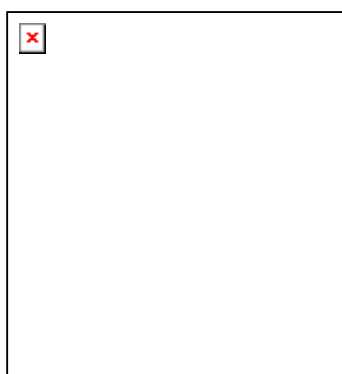
Once again, the negative ions in the crystal split the energy of the  $d$  atomic orbitals on the transition-metal ion. The tetrahedral crystal field splits these orbitals into the same  $t_{2g}$  and  $e_g$  sets of orbitals as does the octahedral crystal field.

$$t_{2g}: d_{xy}, d_{xz}, \text{ and } d_{yz} \quad e_g: d_{x^2-y^2} \text{ and } d_z^2$$

But the two orbitals in the  $e_g$  set are now lower in energy than the three orbitals in the  $t_{2g}$  set, as shown in the figure below.



To understand the splitting of  $d$  orbitals in a tetrahedral crystal field, imagine four ligands lying at alternating corners of a cube to form a tetrahedral geometry, as shown in the figure below. The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals on the metal ion at the center of the cube lie between the ligands, and the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals point toward the ligands. As a result, the splitting observed in a tetrahedral crystal field is the opposite of the splitting in an octahedral complex.



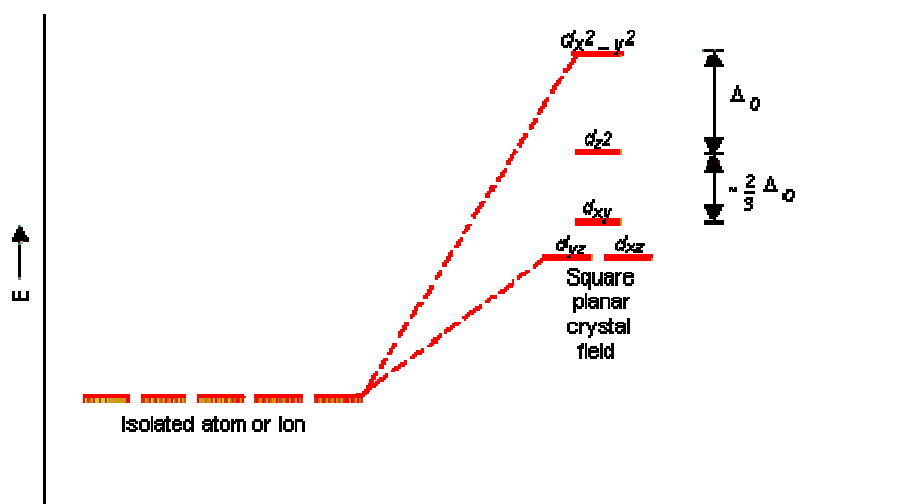
Because a tetrahedral complex has fewer ligands, the magnitude of the splitting is smaller. The difference between the energies of the  $t_{2g}$  and  $e_g$  orbitals in a tetrahedral complex ( $\Delta_t$ ) is slightly less than half as large as the splitting in analogous octahedral complexes ( $\Delta_o$ ).

$$\Delta_t = \frac{4}{9} \Delta_o$$

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### Square-Planar Complexes

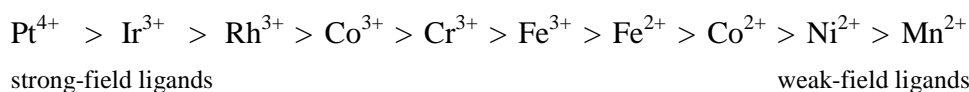
The crystal field theory can be extended to square-planar complexes, such as  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ . The splitting of the  $d$  orbitals in these compounds is shown in the figure below.



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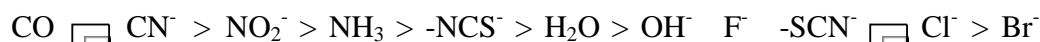
### The Spectrochemical Series

The splitting of  $d$  orbitals in the crystal field model not only depends on the geometry of the complex, it also depends on the nature of the metal ion, the charge on this ion, and the ligands that surround the metal. When the geometry and the ligands are held constant, this splitting decreases in the following order.



Metal ions at one end of this continuum are called *strong-field ions*, because the splitting due to the crystal field is unusually strong. Ions at the other end are known as *weak-field ions*.

When the geometry and the metal are held constant, the splitting of the  $d$  orbitals decreases in the following order.



strong-field ligands

weak-field ligands

Ligands that give rise to large differences between the energies of the  $t_{2g}$  and  $e_g$  orbitals are called *strong-field ligands*. Those at the opposite extreme are known as *weak-field ligands*.

Because they result from studies of the absorption spectra of transition-metal complexes, these generalizations are known as the **spectrochemical series**. The range of values of  $\Delta$  for a given geometry is remarkably large. The value of  $\Delta_o$  is 100 kJ/mol in the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  ion, for example, and 520 kJ/mol in the  $\text{Rh}(\text{CN})_6^{3-}$  ion.

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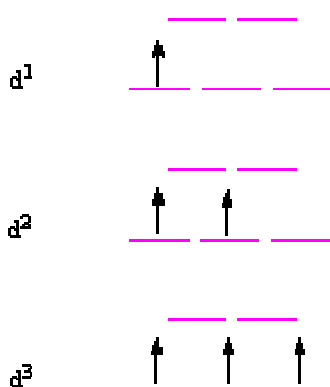
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### *High-Spin Versus Low-Spin Octahedral Complexes*

Once we know the relative energies of the  $d$  orbitals in a transition-metal complex, we have to worry about how these orbitals are filled. Degenerate orbitals are filled according to Hund's rules.

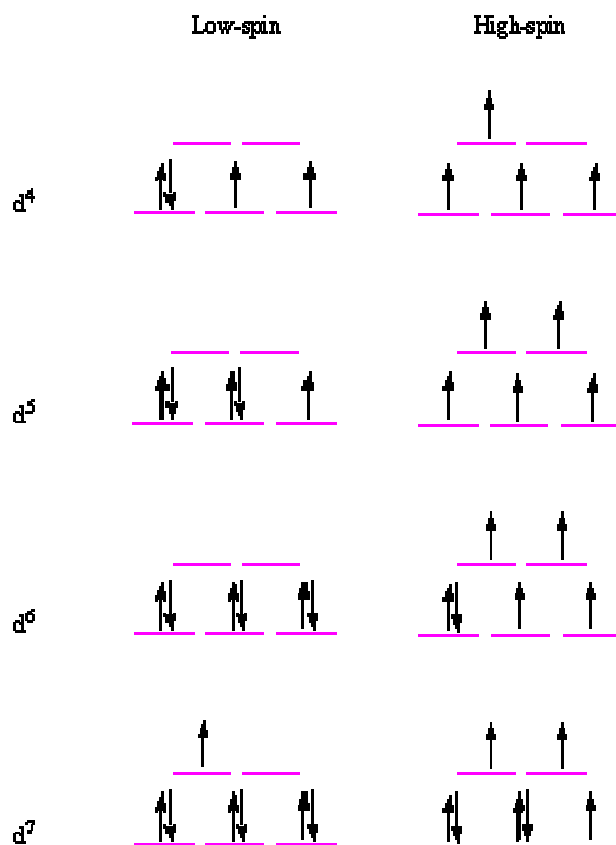
- One electron is added to each of the degenerate orbitals in a subshell before a second electron is added to any orbital in the subshell.
- Electrons are added to a subshell with the same value of the spin quantum number until each orbital in the subshell has at least one electron.

Octahedral transition-metal ions with  $d^1$ ,  $d^2$ , or  $d^3$  configurations can therefore be described by the following diagrams.

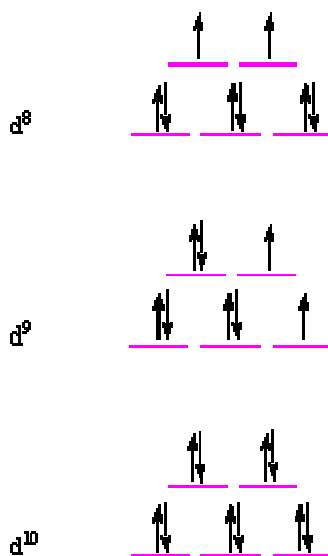


When we try to add a fourth electron, we are faced with a problem. This electron could be used to pair one of the electrons in the lower energy ( $t_{2g}$ ) set of orbitals or it could be placed in one of the higher energy ( $e_g$ ) orbitals. One of these configurations is called **high-spin**

because it contains four unpaired electrons with the same spin. The other is called **low-spin** because it contains only two unpaired electrons. The same problem occurs with octahedral  $d^5$ ,  $d^6$ , and  $d^7$  complexes.



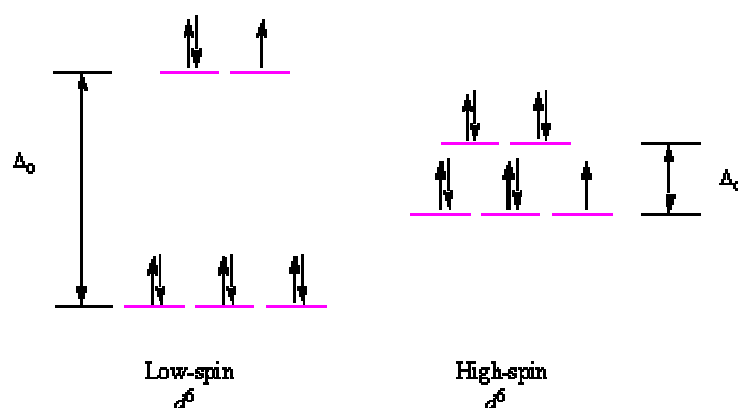
For octahedral  $d^8$ ,  $d^9$ , and  $d^{10}$  complexes, there is only one way to write satisfactory configurations.



As a result, we have to worry about high-spin versus low-spin octahedral complexes only when there are four, five, six, or seven electrons in the  $d$  orbitals.

The choice between high-spin and low-spin configurations for octahedral  $d^4$ ,  $d^5$ ,  $d^6$ , or  $d^7$  complexes is easy. All we have to do is compare the energy it takes to pair electrons with the energy it takes to excite an electron to the higher energy ( $e_g$ ) orbitals. If it takes less energy to pair the electrons, the complex is low-spin. If it takes less energy to excite the electron, the complex is high-spin.

The amount of energy required to pair electrons in the  $t_{2g}$  orbitals of an octahedral complex is more or less constant. The amount of energy needed to excite an electron into the higher energy ( $e_g$ ) orbitals, however, depends on the value of  $\Delta_o$  for the complex. As a result, we expect to find low-spin complexes among metal ions and ligands that lie toward the high-field end of the spectrochemical series. High-spin complexes are expected among metal ions and ligands that lie toward the low-field end of these series.



Compounds in which all of the electrons are paired are **diamagnetic** — they are repelled by both poles of a magnet. Compounds that contain one or more unpaired electrons are **paramagnetic** — they are attracted to the poles of a magnet. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of unpaired electrons in the complex. We can therefore determine whether a complex is high-spin or low-spin by measuring the strength of the interaction between the complex and a magnetic field.

**Practice Problem 5:**

Explain why the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion is a diamagnetic, low-spin complex, whereas the  $\text{CoF}_6^{3-}$  ion is a paramagnetic, high-spin complex.

[Click here to check your answer to Practice Problem 5](#)

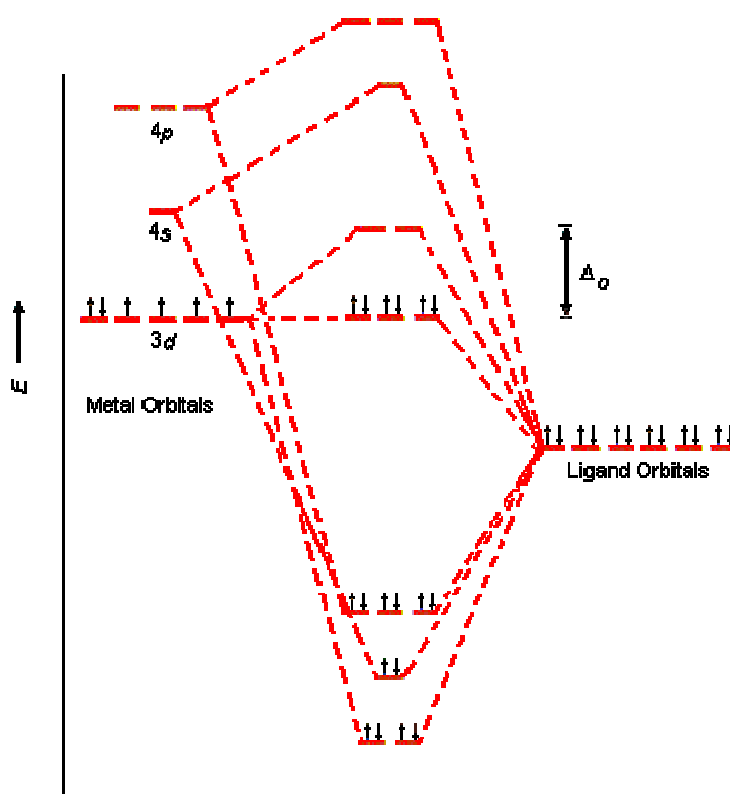
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## Ligand-Field Theory

The [valence-bond model](#) and the [crystal field theory](#) explain some aspects of the chemistry of the transition metals, but neither model is good at predicting all of the properties of transition-metal complexes. A third model, based on molecular orbital theory, was therefore

developed that is known as **ligand-field theory**. Ligand-field theory is more powerful than either the valence-bond or crystal-field theories. Unfortunately it is also more abstract.

The ligand-field model for an octahedral transition-metal complex such as the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion assumes that the  $3d$ ,  $4s$ , and  $4p$  orbitals on the metal overlap with one orbital on each of the six ligands to form a total of 15 molecular orbitals, as shown in the figure below.



Six of these orbitals are *bonding molecular orbitals*, whose energies are much lower than those of the original atomic orbitals. Another six are *antibonding molecular orbitals*, whose energies are higher than those of the original atomic orbitals. Three are best described as *nonbonding molecular orbitals*, because they have essentially the same energy as the  $3d$  atomic orbitals on the metal.

Ligand-field theory enables the  $3d$ ,  $4s$ , and  $4p$  orbitals on the metal to overlap with orbitals on the ligand to form the octahedral covalent bond skeleton that holds this complex together. At the same time, this model generates a set of five orbitals in the center of the diagram that are split into  $t_{2g}$  and  $e_g$  subshells, as predicted by the crystal-field theory. As a result, we don't have to worry about "inner-shell" versus "outer-shell" metal complexes. In effect, we can use the  $3d$  orbitals in two different ways. We can use them to form the covalent bond skeleton and then use them again to form the orbitals that hold the electrons that were originally in the  $3d$  orbitals of the transition metal.