Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

**d-Orbital Splittings**

CFT focuses on the interaction of the five \((n - 1)d\) orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure ⟨\PageIndex{1a}\⟩). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure ⟨\PageIndex{1b}\⟩, the \(d_{z^2}\) and \(d_{x^2−y^2}\) orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the \(e_g\) orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (\(d_{xy}\), \(d_{xz}\), and \(d_{yz}\), collectively called the \(t_{2g}\) orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.
Figure 1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals increase in energy, while the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two $e_g$ orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of charge. In contrast, the three $t_{2g}$ orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge. (CC BY-SA-NC; anonymous by request)

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy ($\Delta_o$), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: $\Delta_t$.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two $e_g$ orbitals increase in energy by $0.6\Delta_o$, whereas the three $t_{2g}$ orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$[2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.]$$

Crystal field splitting does not change the total energy of the d orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 1).

The crystal field splitting energy also applies to tetrahedral complexes: $\Delta_t$. It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two $e_g$ orbitals increase in energy by $0.6\Delta_o$, whereas the three $t_{2g}$ orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$[2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.]$$

Crystal field splitting does not change the total energy of the d orbitals.
Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure \( \PageIndex{1} \) to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti\(^{3+} \) ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund’s rule. As shown in Figure 24.6.2, for d\(^1–d^3 \) systems—such as [Ti(H\(_2\)O)\(_6\)]\(^{3+} \), [V(H\(_2\)O)\(_6\)]\(^{3+} \), and [Cr(H\(_2\)O)\(_6\)]\(^{3+} \), respectively—the electrons successively occupy the three degenerate t\(_{2g} \) orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex [Cr(H\(_2\)O)\(_6\)]\(^{3+} \), for example, by saying that the chromium ion has a d\(^3 \) electron configuration or, more succinctly, Cr\(^{3+} \) is a d\(^3 \) ion.

![Figure](\( \PageIndex{2} \)): The Possible Electron Configurations for Octahedral d\(^n \) Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d\(^4 \), d\(^5 \), d\(^6 \), and d\(^7 \) configurations; the magnitude of Δ\(_o \) determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

When we reach the d\(^4 \) configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e\(_g \) orbitals or one of the singly occupied t\(_{2g} \) orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ\(_o \) is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e\(_g \) orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the [Cr(H\(_2\)O)\(_6\)]\(^{2+} \) ion, is called a high-spin complex. Conversely, if Δ\(_o \) is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t\(_{2g} \) orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the [Mn(CN)\(_6\)]\(^{3–} \) ion, is called a low-spin complex. Similarly, metal ions with the d\(^5 \), d\(^6 \), or d\(^7 \) electron configurations can be either high spin or low spin, depending on the magnitude of Δ\(_o \).

In contrast, only one arrangement of d electrons is possible for metal ions with d\(^8 \)–d\(^{10} \) electron configurations. For example, the [Ni(H\(_2\)O)\(_6\)]\(^{2+} \) ion is d\(^8 \) with two unpaired electrons, the [Cu(H\(_2\)O)\(_6\)]\(^{2+} \) ion is d\(^9 \) with one unpaired electron, and the [Zn(H\(_2\)O)\(_6\)]\(^{2+} \) ion is d\(^{10} \) with no unpaired electrons.

If Δ\(_o \) is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ\(_o \) is greater, a low-spin configuration forms.
Factors That Affect the Magnitude of $\Delta_0$

The magnitude of $\Delta_0$ dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of $\Delta_0$ (i.e., $\Delta_0 > P$) yield a low-spin complex, whereas small values of $\Delta_0$ (i.e., $\Delta_0 < P$) produce a high-spin complex. As we noted, the magnitude of $\Delta_0$ depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of $\Delta_0$ for some representative transition-metal complexes are given in Table 1.

Table 1: Crystal Field Splitting Energies for Some Octahedral ($\Delta_0$) and Tetrahedral ($\Delta_t$) Transition-Metal Complexes

<table>
<thead>
<tr>
<th>Octahedral Complexes</th>
<th>$\Delta_0$ (cm$^{-1}$)</th>
<th>Octahedral Complexes</th>
<th>$\Delta_0$ (cm$^{-1}$)</th>
<th>Tetrahedral Complexes</th>
<th>$\Delta_t$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti(H$_2$O)$_6$]$^{3+}$</td>
<td>20,300</td>
<td>[Fe(CN)$_6$]$^{4-}$</td>
<td>32,800</td>
<td>VCl$_4$</td>
<td>9010</td>
</tr>
<tr>
<td>[V(H$_2$O)$_6$]$^{2+}$</td>
<td>12,600</td>
<td>[Fe(CN)$_6$]$^{3-}$</td>
<td>35,000</td>
<td>[CoCl$_4$]$^{2-}$</td>
<td>3300</td>
</tr>
<tr>
<td>[V(H$_2$O)$_6$]$^{3+}$</td>
<td>18,900</td>
<td>[CoF$_6$]$^{3-}$</td>
<td>13,000</td>
<td>[CoBr$_4$]$^{2-}$</td>
<td>2900</td>
</tr>
<tr>
<td>[CrCl$_6$]$^{3-}$</td>
<td>13,000</td>
<td>[Co(H$_2$O)$_6$]$^{2+}$</td>
<td>9300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(H$_2$O)$_6$]$^{2+}$</td>
<td>13,900</td>
<td>[Co(H$_2$O)$_6$]$^{3+}$</td>
<td>27,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(H$_2$O)$_6$]$^{3+}$</td>
<td>17,400</td>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>22,900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_6$]$^{3+}$</td>
<td>21,500</td>
<td>[Co(CN)$_6$]$^{3-}$</td>
<td>34,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(CN)$_6$]$^{3-}$</td>
<td>26,600</td>
<td>[Ni(H$_2$O)$_6$]$^{2+}$</td>
<td>8500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>34,150</td>
<td>[Ni(NH$_3$)$_6$]$^{2+}$</td>
<td>10,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnCl$_6$]$^{4-}$</td>
<td>7500</td>
<td>[RhCl$_6$]$^{3-}$</td>
<td>20,400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(H$_2$O)$_6$]$^{2+}$</td>
<td>8500</td>
<td>[Rh(H$_2$O)$_6$]$^{3+}$</td>
<td>27,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnCl$_6$]$^{3-}$</td>
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<td>[Rh(NH$_3$)$_6$]$^{3+}$</td>
<td>34,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(H$_2$O)$_6$]$^{3+}$</td>
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<td>[Rh(CN)$_6$]$^{3-}$</td>
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<tr>
<td>[Fe(H$_2$O)$_6$]$^{2+}$</td>
<td>10,400</td>
<td>[IrCl$_6$]$^{3-}$</td>
<td>25,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm$^{-1}$); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm$^{-1} = 11.96$ J/mol.
Octahedral Complexes \( \Delta_o \) (cm\(^{-1}\)) Octahedral Complexes \( \Delta_o \) (cm\(^{-1}\)) Tetrahedral Complexes \( \Delta_t \) (cm\(^{-1}\))

\[ \text{[Fe(H}_2\text{O)}_6]^{3+} \] 14,300 \[ \text{[Ir(NH}_3\text{)}_6]^{3+} \] 41,000

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm\(^{-1}\)); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm\(^{-1}\) = 11.96 J/mol.


**Factor 1: Charge on the Metal Ion**

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of \( \Delta_o \) increases as the charge on the metal ion increases. Typically, \( \Delta_o \) for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for \([V(H}_2\text{O)}_6]^{2+}\), \( \Delta_o = 11,800 \text{ cm}^{-1}\); for \([V(H}_2\text{O)}_6]^{3+}\), \( \Delta_o = 17,850 \text{ cm}^{-1}\).

**Factor 2: Principal Quantum Number of the Metal**

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of \( \Delta_o \) increases with increasing principal quantum number: \( \Delta_o \) (3d) < \( \Delta_o \) (4d) < \( \Delta_o \) (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

\[
\begin{align*}
\text{[Co(NH}_3\text{)}_6]^{3+}: \ & \Delta_o = 22,900 \text{ cm}^{-1} \\
\text{[Rh(NH}_3\text{)}_6]^{3+}: \ & \Delta_o = 34,100 \text{ cm}^{-1} \\
\text{[Ir(NH}_3\text{)}_6]^{3+}: \ & \Delta_o = 40,000 \text{ cm}^{-1}
\end{align*}
\]

The increase in \( \Delta_o \) with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

**Factor 3: The Nature of the Ligands**

Experimentally, it is found that the \( \Delta_o \) observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of \( \Delta_o \) decreases as the size of the donor atom increases. For example, \( \Delta_o \) values for halide complexes generally decrease in the order \( F^- > Cl^- > Br^- > I^- \) because smaller, more localized charges, such as we see for \( F^- \), interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as \( \text{NH}_3 \), results in significantly larger \( \Delta_o \) values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as \( F^- \). The experimentally observed order of the crystal field splitting energies
produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

\[
\text{strong-field ligands} \quad \{\text{CO} \approx \text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{intermediate-field ligands} \quad \{\text{SCN}^- > \text{H}_2\text{O} > \text{oxalate}^{2-} > \text{OH}^- > \text{F} > \text{acetate}^- > \text{weak-field ligands} \quad \{\text{Cl}^- > \text{Br}^- > \text{I}^-\}\}
\]

The values of Δ_o listed in Table \ref{Table1} illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.

Example \ref{Example1}:

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. \([\text{CoF}_6]^{3-}\)

b. \([\text{Rh(CO)}_2\text{Cl}_2]^-\)

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.

b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.

c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.

d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

SOLUTION

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^6 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order d_{xz}^2,d_{yz}, and d_{x^2-y^2} (these are
degenerate); $d_{xy}$; and $d_{x^2−y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2−y^2}$ orbital empty. Thus there are no unpaired electrons.

Exercise \(\PageIndex{1}\)

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. \([\text{Mn(H}_2\text{O)}_6]^{2+}\)
b. \([\text{PtCl}_4]^{2−}\)

**Answer a**

octahedral; high spin; five

**Answer b**

square planar; low spin; no unpaired electrons

---

**Crystal Field Stabilization Energies**

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of $d$ orbitals (the $t_{2g}$ orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single $d$ electron in a $d^1$ complex such as \([\text{Ti(H}_2\text{O)}_6]^{3+}\) is located in one of the $t_{2g}$ orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_0$. The additional stabilization of a metal complex by selective population of the lower-energy $d$ orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in $t_{2g}$ orbitals by the energy of those orbitals ($−0.4\Delta_0$), multiplying the number of electrons in $e_g$ orbitals by the energy of those orbitals ($+0.6\Delta_0$), and summing the two. Table \(\PageIndex{2}\) gives CFSE values for octahedral complexes with different $d$ electron configurations. The CFSE is highest for low-spin $d^6$ complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the $d^3$ configuration.

**Table \(\PageIndex{2}\): CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of \(\Delta_0\))**

<table>
<thead>
<tr>
<th></th>
<th>High Spin</th>
<th>CFSE ($\Delta_0$)</th>
<th>Low Spin</th>
<th>CFSE ($\Delta_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_{2g}$</td>
<td>$e_g$</td>
<td>$t_{2g}$</td>
<td>$e_g$</td>
</tr>
<tr>
<td>$d^0$</td>
<td>$d^0$</td>
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<td></td>
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### CFSEs and Spin Multiplicity

<table>
<thead>
<tr>
<th>High Spin</th>
<th>CFSE ($\Delta_0$)</th>
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<th>CFSE ($\Delta_0$)</th>
</tr>
</thead>
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<tr>
<td>$d^1$</td>
<td>1</td>
<td></td>
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<td>1</td>
<td></td>
<td>0.8</td>
</tr>
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<tr>
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<td>1 1</td>
<td>1</td>
<td>0.6 1 1</td>
</tr>
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<td>1 1</td>
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<td>1 1</td>
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</tbody>
</table>

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

Octahedral $d^3$ and $d^8$ complexes and low-spin $d^6$, $d^7$, and $d^4$ complexes exhibit large CFSEs.

### Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using classical bonding theory.
valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy ($\Delta_o$), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the $\Delta_o$ is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the $\Delta_o$ is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large $\Delta_o$, whereas weak-field ligands interact more weakly and give a smaller $\Delta_o$. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.