

22.5: Crystal Field Theory

Learning Objectives

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

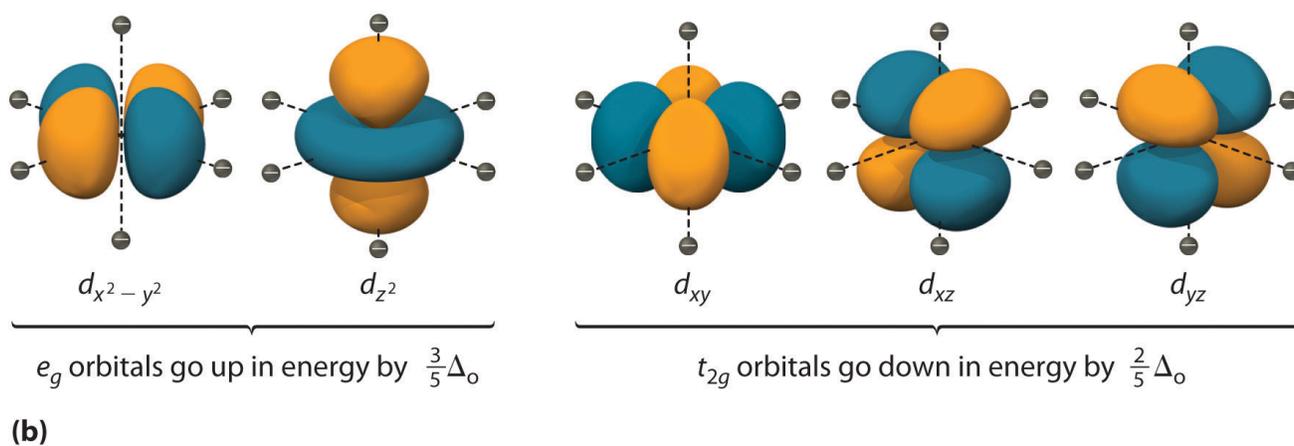
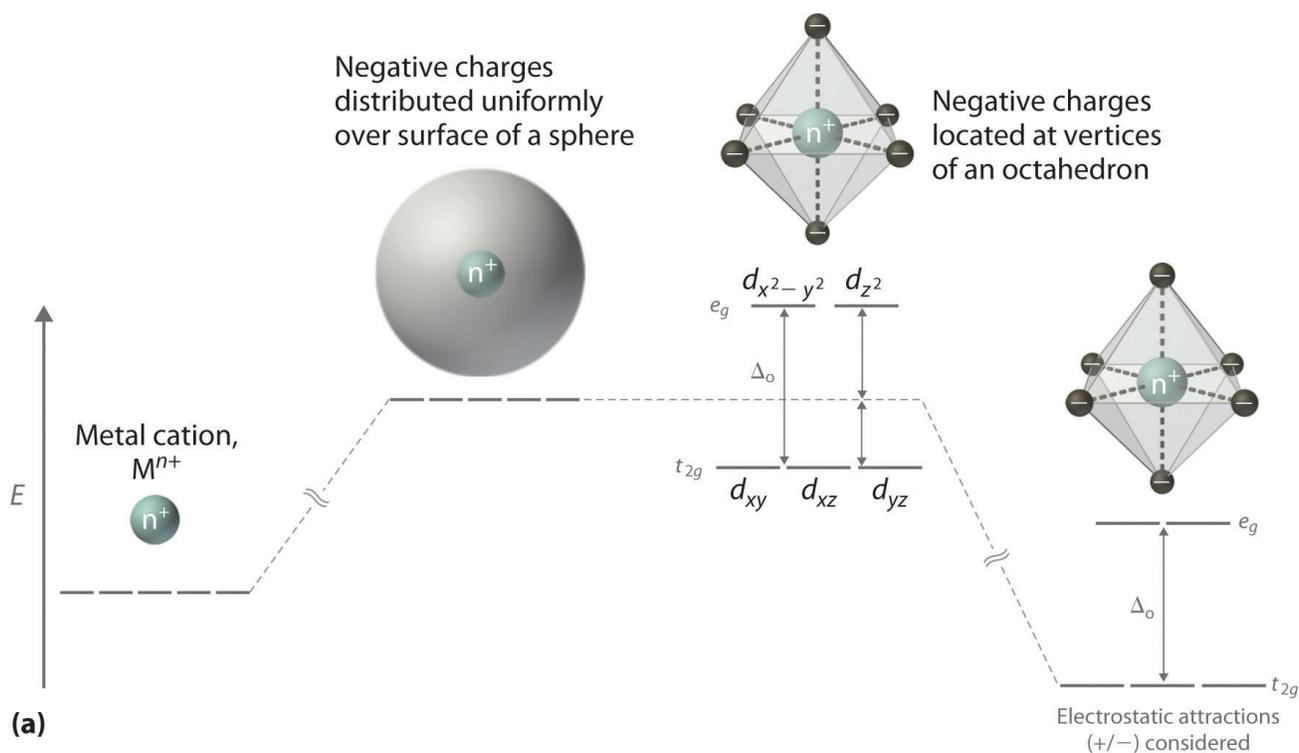
One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit (Figure 23.4 and Figure 23.5). In this section, we describe **crystal field theory (CFT)**, a bonding model that explains many important properties of transition-metal complexes, including 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.

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 in [Chapter 9](#), 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 from [Chapter 6](#) 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 (part (a) in Figure 22.5.1). 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 part (b) in Figure 22.5.1, 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 Figure 22.5.1: 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 negative 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.

The difference in energy between the two sets of d orbitals is called the **crystal field splitting energy** (Δ_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: Δ_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 $2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0$.

Note the Pattern

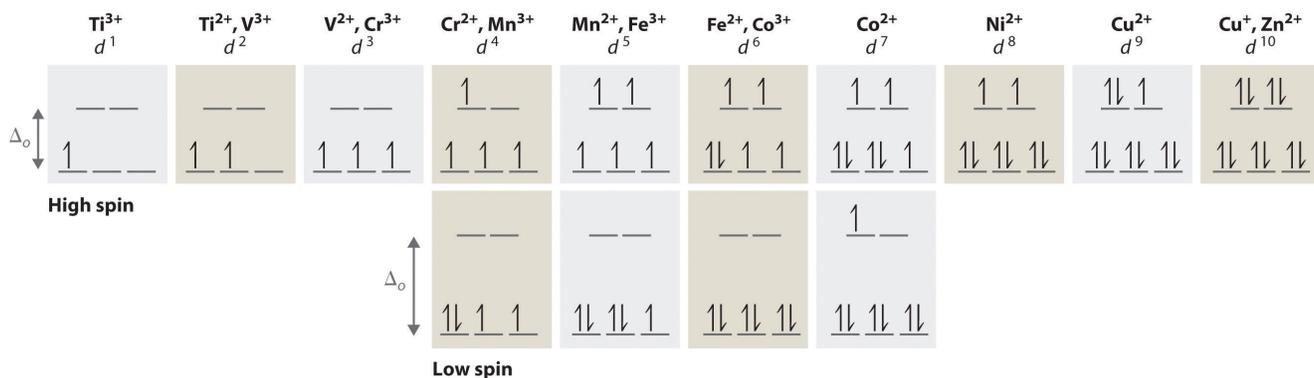
Crystal field splitting does not change the total energy of the d orbitals.

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 part (a) in Figure 22.5.1).

Electronic Structures of Metal Complexes

We can use the d -orbital energy-level diagram in Figure 22.5.1 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 22.5.2 for d^1 – d^3 systems—such as $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, 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 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, 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 22.5.2 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.

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 from Chapter 6 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 $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ 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 $[\text{Mn}(\text{CN})_6]^{3-}$ 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 $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ion is d^{10} with no unpaired electrons.

Note the Pattern

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 Δ_o

The magnitude of Δ_o 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 Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o 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 Δ_o for some representative transition-metal complexes are given in Table 22.5.1.

Table 22.5.1 Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	20,300	$[\text{Fe}(\text{CN})_6]^{4-}$	32,800	VCl_4	9010
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12,600	$[\text{Fe}(\text{CN})_6]^{3-}$	35,000	$[\text{CoCl}_4]^{2-}$	3300
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	18,900	$[\text{CoF}_6]^{3-}$	13,000	$[\text{CoBr}_4]^{2-}$	2900
$[\text{CrCl}_6]^{3-}$	13,000	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9300	$[\text{CoI}_4]^{2-}$	2700
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	13,900	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	27,000		
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17,400	$[\text{Co}(\text{NH}_3)_6]^{3+}$	22,900		
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21,500	$[\text{Co}(\text{CN})_6]^{3-}$	34,800		
$[\text{Cr}(\text{CN})_6]^{3-}$	26,600	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8500		
$\text{Cr}(\text{CO})_6$	34,150	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10,800		
$[\text{MnCl}_6]^{4-}$	7500	$[\text{RhCl}_6]^{3-}$	20,400		
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	8500	$[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$	27,000		
$[\text{MnCl}_6]^{3-}$	20,000	$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34,000		
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$	21,000	$[\text{Rh}(\text{CN})_6]^{3-}$	45,500		
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	10,400	$[\text{IrCl}_6]^{3-}$	25,000		
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	14,300	$[\text{Ir}(\text{NH}_3)_6]^{3+}$	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: $1 \text{ cm}^{-1} = 11.96 \text{ J/mol}$.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, *Inorganic Chemistry*, 2nd ed. (New York: W. H. Freeman and Company, 1994).

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 Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[\text{V}(\text{H}_2\text{O})_6]^{2+}$, $\Delta_o = 11,800 \text{ cm}^{-1}$; for $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, $\Delta_o = 17,850 \text{ cm}^{-1}$.

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 Δ_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:



The increase in Δ_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.

The Nature of the Ligands

Experimentally, it is found that the Δ_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 Δ_o decreases as the size of the donor atom increases. For example, Δ_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 NH_3 , results in significantly larger Δ_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 :

$CO \approx CN^-$ → strong-field ligands
 $NO_2^- > en > NH_3 > SCN^- > H_2O > oxalate^{2-}$ → intermediate-field ligands
 $OH^- > F^- > acetate^- > Cl^- > Br^- > I^-$ → weak-field ligands

The values of Δ_o listed in Table 22.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

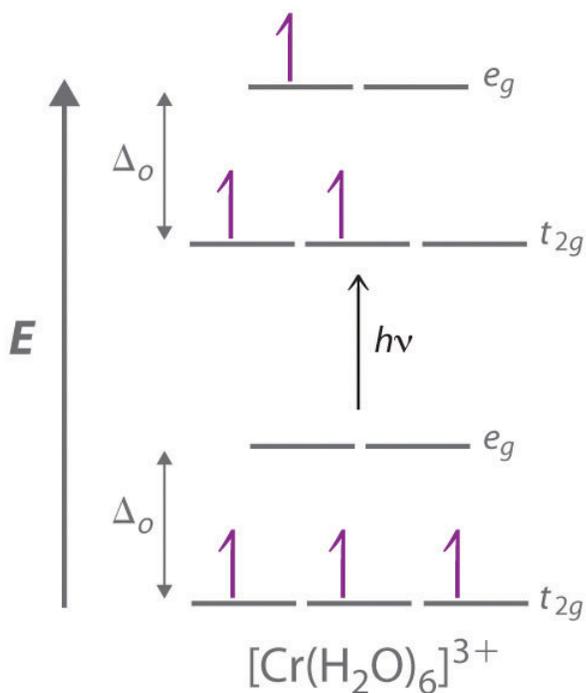
Note the Pattern

The largest Δ_o s 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.

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d – d transition (Figure 22.5.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o .

Figure 22.5.3A d – d Transition



In a $d-d$ transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o , which causes the electron to move to an empty or singly occupied e_g orbital.

Recall from [Chapter 6](#) that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel in End-of-Chapter Application Problem 6 in [Chapter 6](#). Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o , which depends on the structure of the complex. For example, the complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o . Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[\text{Si}_6\text{O}_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o . Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall from [Chapter 9](#) 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 $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. 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 ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 22.5.2 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 22.5.2 CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δ_o)

	High Spin	CFSE (Δ_o)	Low Spin	CFSE (Δ_o)
d^0		0		

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^1	1		0.4			
d^2	1 1		0.8			
d^3	1 1 1		1.2			
d^4	1 1 1	1	0.6	1 ↓ 1 1		1.6
d^5	1 1 1	1 1	0.0	1 ↓ 1 ↓ 1		2.0
d^6	1 ↓ 1 1	1 1	0.4	1 ↓ 1 ↓ 1 ↓		2.4
d^7	1 ↓ 1 ↓ 1	1 1	0.8	1 ↓ 1 ↓ 1 ↓	1	1.8
d^8	1 ↓ 1 ↓ 1 ↓	1 1	1.2			
d^9	1 ↓ 1 ↓ 1 ↓	1 ↓ 1	0.6			
d^{10}	1 ↓ 1 ↓ 1 ↓	1 ↓ 1 ↓	0.0			

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.

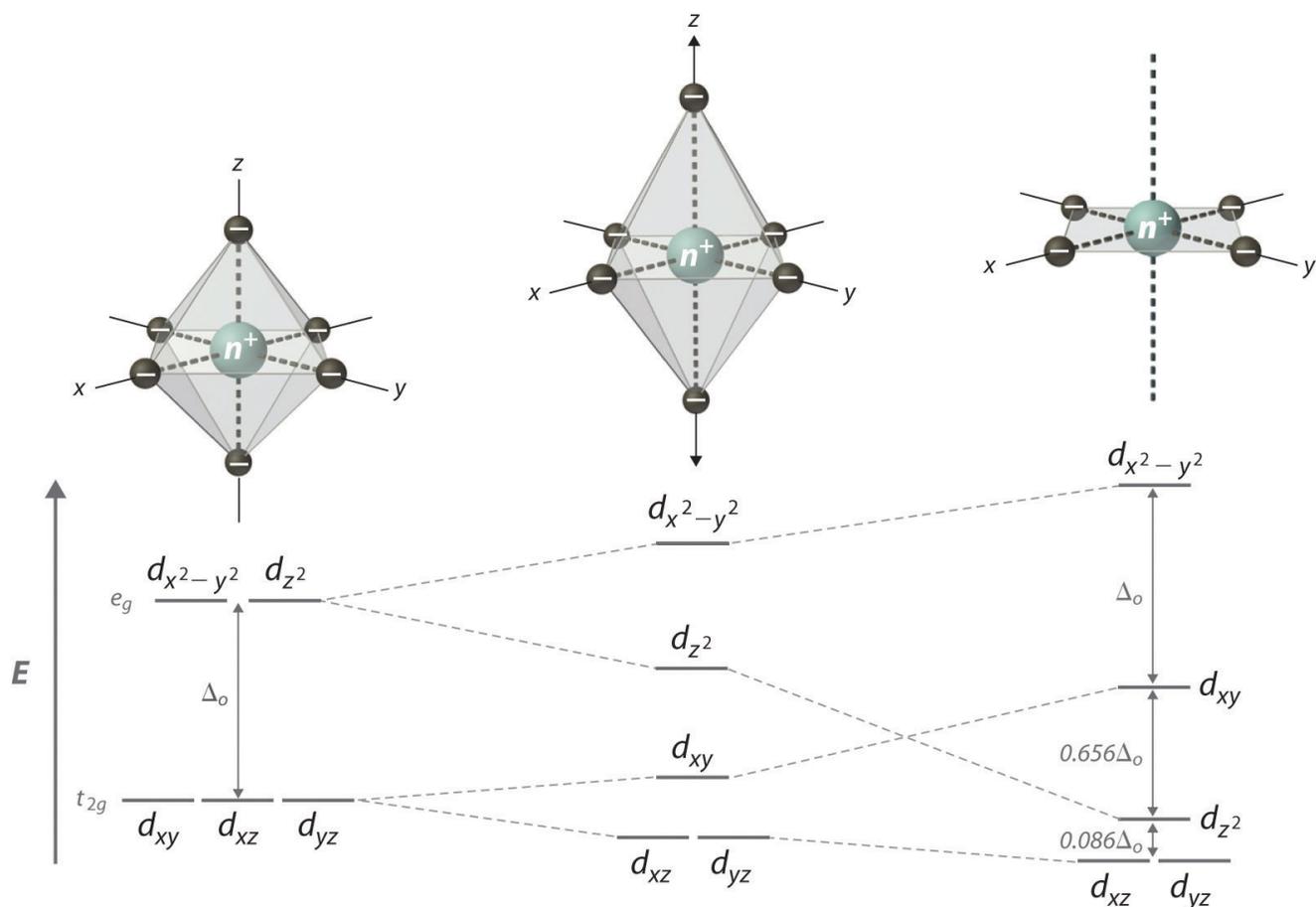
Note the Pattern

Octahedral d^3 and d^8 complexes and low-spin d^6 , d^5 , d^7 , and d^4 complexes exhibit large CFSEs.

Tetragonal and Square Planar Complexes

If two *trans* ligands in an octahedral complex are either chemically different from the other four, as in the *trans*-[Co(NH₃)₄Cl₂]⁺ ion, or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as [Co(NH₃)₆]³⁺ and then slowly remove two *trans* NH₃ molecules by moving them away from the metal along the $\pm z$ axes, as shown in the top half of Figure 22.5.4. As the two axial Co–N distances increase simultaneously, the d orbitals that interact most strongly with the two axial ligands will *decrease* in energy due to a decrease in electrostatic repulsions between electrons in these orbitals and the negative ends of the ligand dipoles. The affected d orbitals are those with a component along the $\pm z$ axes—namely, d_{z^2} , d_{xz} , and d_{yz} . They will not be affected equally, however. Because the d_{z^2} orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the energy of the other two, as shown in the bottom half of Figure 22.5.4. In addition, the positive charge on the metal will increase somewhat as the axial ligands are removed, causing the four remaining in-plane ligands to be more strongly attracted to the metal. This will increase their interactions with the other two d orbitals and increase their energy. Again, the two d orbitals will not be affected equally. Because the $d_{x^2-y^2}$ orbital points directly at the four in-plane ligands, its energy will increase more rapidly than the energy of the d_{xy} orbital, which points between the in-plane ligands. If we remove the two axial ligands to an infinite distance, we obtain a square planar complex. The energies of the d_{z^2} and d_{xy} orbitals actually cross as the axial ligands are removed, and the largest orbital splitting in a square planar complex is identical in magnitude to Δ_o .

Figure 22.5.4 d -Orbital Splittings for Tetragonal and Square Planar Complexes

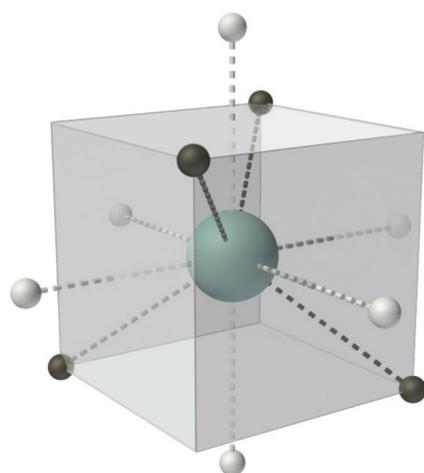


Moving the two axial ligands away from the metal ion along the z axis initially gives an elongated octahedral complex (center) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the d_{z^2} , d_{xz} and d_{yz} orbitals to decrease in energy and the $d_{x^2-y^2}$ and d_{xy} orbitals to increase in energy. As explained in the text, the change in energy is not the same for all five d orbitals. Removing the two axial ligands completely causes the energy of the d_{z^2} orbital to decrease so much that the order of the d_{z^2} and d_{xy} orbitals is reversed.

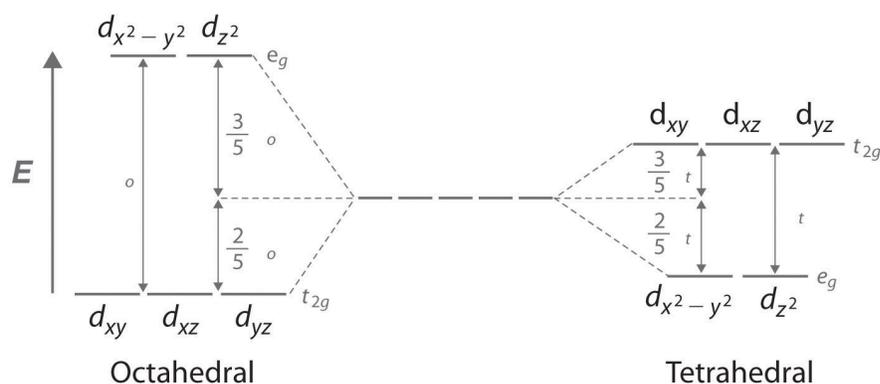
Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (part (a) in Figure 22.5.5); consequently, none of the five d orbitals points directly at the ligands. Nonetheless, the d_{xy} , d_{xz} , and d_{yz} orbitals interact more strongly with the ligands than do $d_{x^2-y^2}$ and d_{z^2} again resulting in a splitting of the five d orbitals into two sets. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for Δ_o , however, for two reasons. First, the d orbitals interact less strongly with the ligands in a tetrahedral arrangement. Second, there are only four negative charges rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that, for complexes of the same metal ion with the same charge, the same ligands, and the same M-L distance, $\Delta_t = \frac{4}{9}\Delta_o$. The relationship between the splitting of the five d orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure 22.5.5

Figure 22.5.5d-Orbital Splittings for a Tetrahedral Complex



(a)



(b)

(a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the d_{xy} , d_{xz} , and d_{yz} orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex.

Note the Pattern

$\Delta_t < \Delta_o$ because of weaker d -orbital–ligand interactions and decreased electrostatic interactions.

Because Δ_o is so large for the second- and third-row transition metals, *all* four-coordinate complexes of these metals are square planar due to the much higher CFSE for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+} , which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral. The former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[\text{Ni}(\text{CN})_4]^{2-}$ ion is square planar, while the $[\text{NiCl}_4]^{2-}$ ion is tetrahedral.

✓ Example 22.5.1

1. $[\text{CoF}_6]^{3-}$
2. $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$

Given: complexes

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

Solution

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:

1. **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.

2. **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^8 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_{z^2} , d_{xz} (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 22.5.1

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

1. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
2. $[\text{PtCl}_4]^{2-}$

Answer

octahedral; high spin;

square planar; low spin; no unpaired electrons

Consequences of d -Orbital Splitting

The splitting of the d orbitals because of their interaction with the ligands in a complex has important consequences for the chemistry of transition-metal complexes; they can be divided into structural effects and thermodynamic effects. Although the two kinds of effects are interrelated, we will consider them separately.

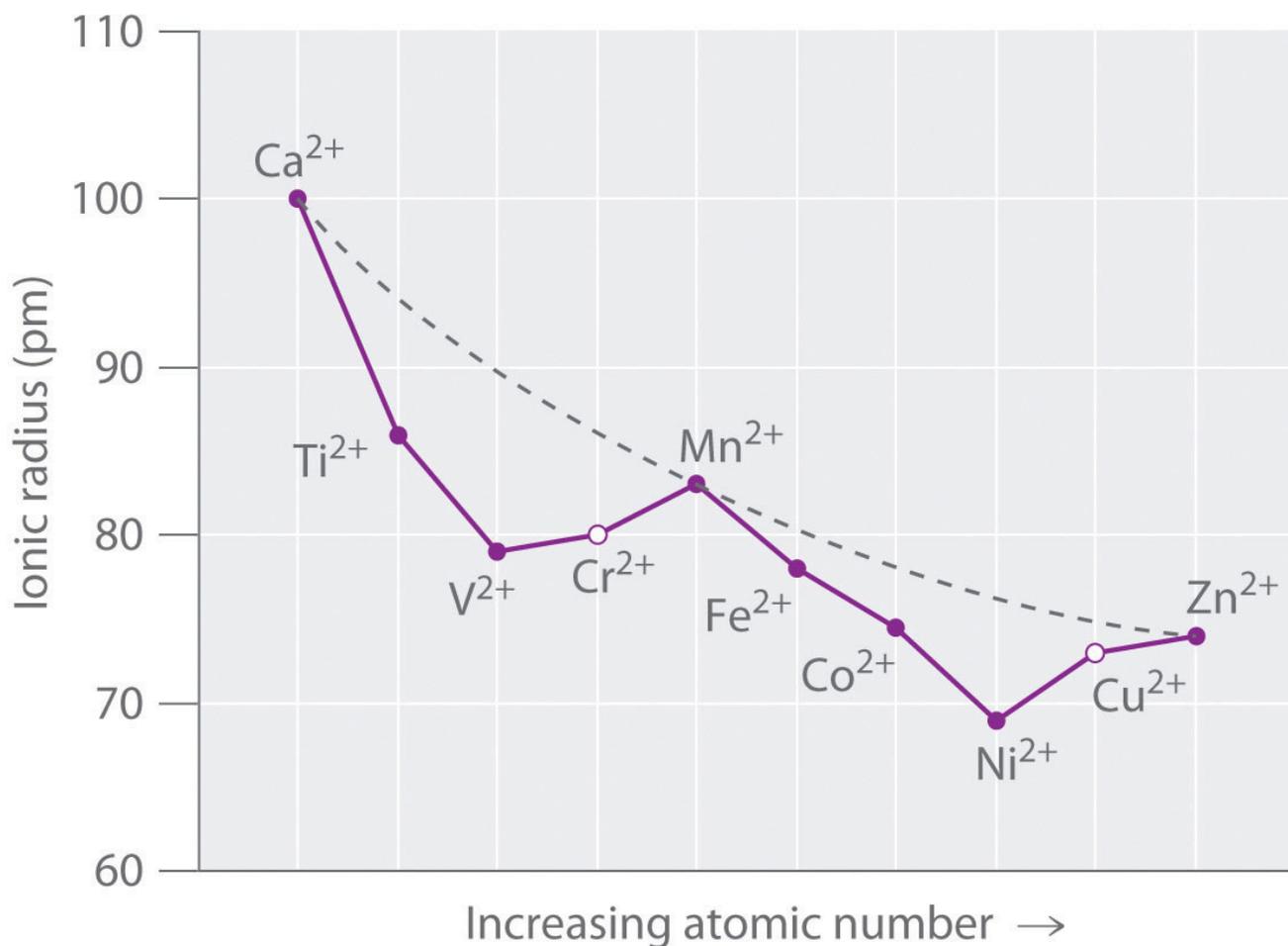
Structural Effects

There are two major kinds of structural effects: effects on the ionic radius of metal ions with regular octahedral or tetrahedral geometries, and structural distortions that are observed for specific electron configurations.

Ionic Radii

Figure 22.5.6 is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. Only Ca^{2+} (d^0), Mn^{2+} (high-spin d^5), and Zn^{2+} (d^{10}) fall on the smooth curve calculated based on the effective nuclear charge (Z_{eff}), which assumes that the distribution of d electrons is spherically symmetrical. *All the other divalent ions fall below this curve because they have asymmetrical distributions of d electrons.* (The points shown for Cr^{2+} and Cu^{2+} are only estimated values; as you will learn shortly, these two ions do not form any truly octahedral complexes.) To see why an asymmetrical distribution of d electrons makes a metal ion smaller than expected, consider the Ti^{2+} ion, which has a d^2 configuration with both electrons in the t_{2g} orbitals. Because the t_{2g} orbitals are directed *between the ligands*, the two d electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than expected, the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five d orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving a larger ionic radius.

Figure 22.5.6 *The Effect of d -Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals*



Because these radii are based on the structures of octahedral complexes and Cr^{2+} and Cu^{2+} do not form truly octahedral complexes, the points for these ions are shown as open circles. The dashed line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge (Z_{eff}), assuming a spherical distribution of the 3d electrons.

A similar effect is observed for the V^{2+} ion, which has a d^3 configuration. Because the three electrons in the t_{2g} orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs in going from Ti^{2+} to V^{2+} . Consequently, the observed ionic radius of the V^{2+} ion is significantly smaller than that of the Ti^{2+} ion.

Skipping the Cr^{2+} ion for the moment, we next consider the d^5 Mn^{2+} ion. Because the nuclear charge increases by +2 from V^{2+} to Mn^{2+} , we might expect Mn^{2+} to be smaller than V^{2+} . The two electrons that are also added from V^{2+} to Mn^{2+} occupy the e_g orbitals, however, which point directly at the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually *increases* significantly as we go from V^{2+} to Mn^{2+} , despite the higher nuclear charge of the latter.

Exactly the same effects are seen in the second half of the first-row transition metals. In the Fe^{2+} , Co^{2+} , and Ni^{2+} ions, the extra electrons are added successively to the t_{2g} orbitals, resulting in poor shielding of the ligands from the nuclear charge and abnormally small ionic radii. Skipping over Cu^{2+} , we again see that adding the last two electrons causes a significant increase in the ionic radius of Zn^{2+} , despite its higher nuclear charge.

The Jahn–Teller Effect

Because simple octahedral complexes are not known for the Cr^{2+} and Cu^{2+} ions, only estimated values for their radii are shown in Figure 22.5.6. We see in Figure 22.5.7 that both the Cr^{2+} and Cu^{2+} ions have electron configurations with an odd number of electrons in the e_g orbitals. Because the single electron (in the case of Cr^{2+}) or the third electron (in the case of Cu^{2+}) can occupy either one of two degenerate e_g orbitals, they have what is called a *degenerate ground state*. The **Jahn–Teller theorem** states that

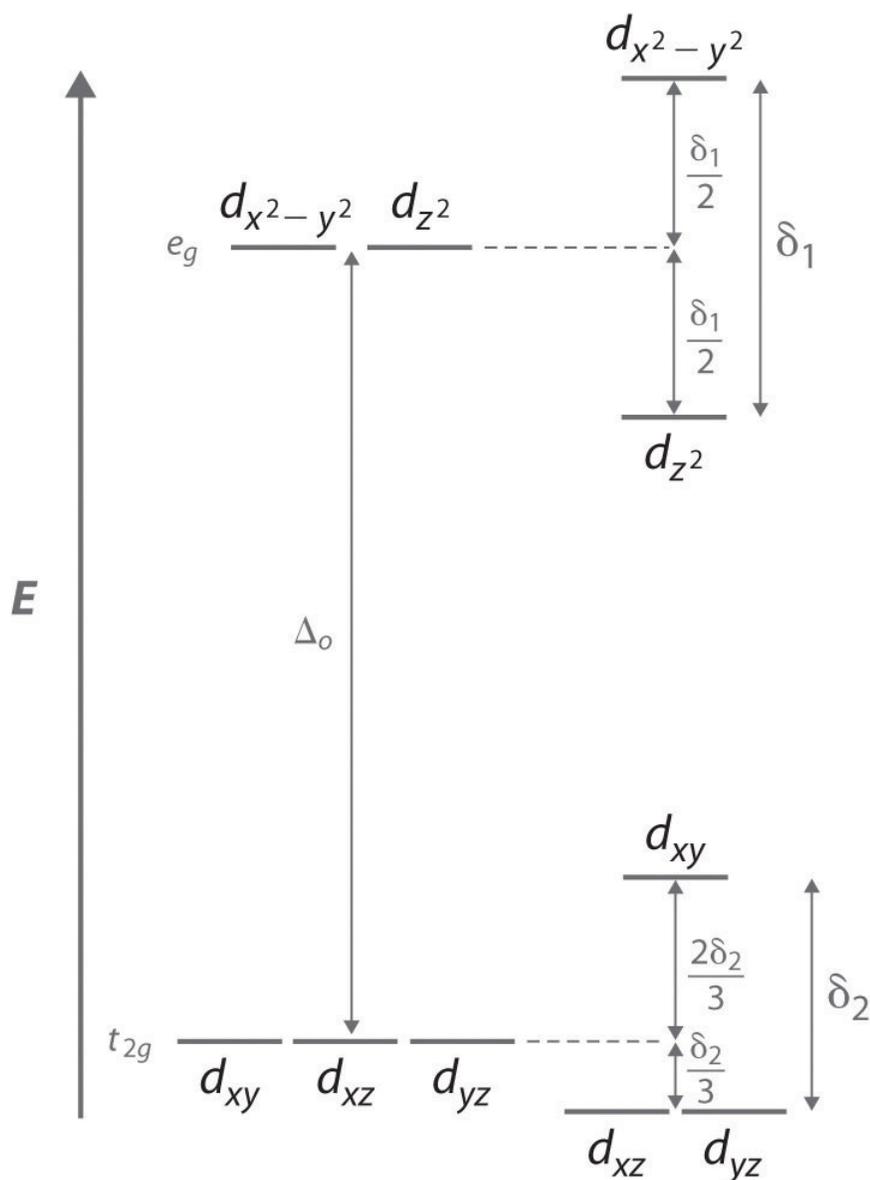
such non-linear systems are not stable; they will undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the *Jahn–Teller effect*. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the e_g orbitals, such as the Cr^{2+} and Cu^{2+} ions.

To see how a geometrical distortion can decrease the energy of such a system, consider an octahedral Cu^{2+} complex, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, which has been elongated along the z axis. As indicated in Figure 22.5.7, this kind of distortion splits both the e_g and t_{2g} sets of orbitals. Because the axial ligands interact most strongly with the d_{z^2} orbital, the splitting of the e_g set (δ_1) is significantly larger than the splitting of the t_{2g} set (δ_2), but both δ_1 and δ_2 are much, much smaller than the Δ_o . This splitting does not change the center of gravity of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the e_g set contains one (as in the d^4 ions, Cr^{2+} and Mn^{3+}) or three (as in the d^9 ion, Cu^{2+}) electrons, the distortion decreases the energy of the system. For Cu^{2+} , for example, the change in energy after distortion is $2(-\delta_1/2) + 1(\delta_1/2) = -\delta_1/2$. For Cu^{2+} complexes, the observed distortion is *always* an elongation along the z axis by as much as 50 pm; in fact, many Cu^{2+} complexes are so distorted that they are effectively square planar. In contrast, the distortion observed for most Cr^{2+} complexes is a *compression* along the z axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.

Note the Pattern

Jahn–Teller distortions are most important for d^9 and high-spin d^4 complexes; the distorted system is more stable than the undistorted one.

Figure 22.5.7 *The Jahn–Teller Effect*



Increasing the axial metal–ligand distances in an octahedral d^9 complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of e_g orbitals to split in energy by an amount δ_1 ; δ_1 and δ_2 are much smaller than Δ_o . As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.

Thermodynamic Effects

As we previously noted, CFSEs can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.

Hydration Energies

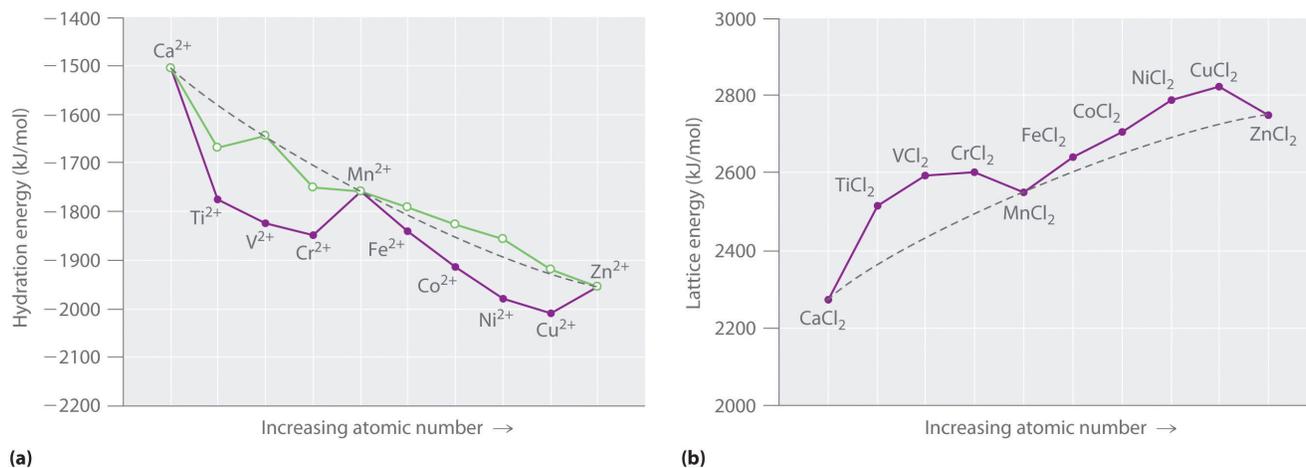
The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:



Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. As shown in part (a) in Figure 22.5.8 a plot of the hydration energies of the fourth-period metal dications

versus atomic number gives a curve with two valleys. Note the relationship between the plot in part (a) in Figure 22.5.8' and the plot of ionic radii in Figure 22.5.6 the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of d electrons (Ca^{2+} , Mn^{2+} , and Zn^{2+}) lie on the dashed lines. In part (a) in Figure 22.5.8 the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Thus CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

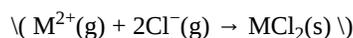
Figure 22.5.8 Thermochemical Effects of d -Orbital Splittings



(a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for Ti^{2+} and Cr^{2+} , are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the Ti^{2+} ion in water are not stable, and Cr^{2+} does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed lines), again illustrating the importance of CFSEs.

Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted versus atomic number in part (b) in Figure 22.5.8. Recall that the lattice energy is defined as the negative of the enthalpy change for the following reaction. Like hydration energies, lattice energies are determined indirectly by using a thermochemical cycle:



The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) in Figure 23.19, with only Ca^{2+} , Mn^{2+} , and Zn^{2+} lying on the smooth curve. It is not surprising that the explanation for the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except MnCl_2 and ZnCl_2 , are more stable than expected due to CFSE.

Summary

Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using 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 (Δ_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 Δ_o is less than P , which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_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 Δ_o , whereas weak-field ligands interact more weakly and give a smaller Δ_o . The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT. Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t . The **crystal field stabilization energy (CFSE)** is the additional stabilization of a complex due to placing electrons in the lower-energy set of d orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic number. The **Jahn–Teller theorem** states that a non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion to remove the degeneracy and lower the overall energy of the system.

KEY TAKEAWAY

- 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.

CONCEPTUAL PROBLEMS

1. Describe crystal field theory in terms of its
 1. assumptions regarding metal–ligand interactions.
 2. weaknesses and strengths compared with valence bond theory.
2. In CFT, what causes degenerate sets of d orbitals to split into different energy levels? What is this splitting called? On what does the magnitude of the splitting depend?
3. Will the value of Δ_o increase or decrease if Γ^- ligands are replaced by NO_2^- ligands? Why?
4. For an octahedral complex of a metal ion with a d^6 configuration, what factors favor a high-spin configuration versus a low-spin configuration?
5. How can CFT explain the color of a transition-metal complex?

STRUCTURE AND REACTIVITY

1. Do strong-field ligands favor a tetrahedral or a square planar structure? Why?
2. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
 1. $[\text{TiCl}_6]^{3-}$
 2. $[\text{CoCl}_4]^{2-}$
3. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
 1. $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 2. $[\text{Ni}(\text{CN})_4]^{2-}$
4. The ionic radii of V^{2+} , Fe^{2+} , and Zn^{2+} are all roughly the same (approximately 76 pm). Given their positions in the periodic table, explain why their ionic radii are so similar.

Answer

- 1.
- 2.
3.
 1. d^9 , square planar, neither high nor low spin, single unpaired electron
 2. d^8 , square planar, low spin, no unpaired electrons

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