

## 22.5: Bonding in Coordination Compounds

The bonding in complex ions can be described by valence bond theory (first introduced in [Chapter 6](#)).



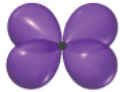

However, many of the properties of these ions are better described by a different model known as crystal field theory. We examine each model separately in this section.

### Valence Bond Theory

The bonding in complex ions, particularly the geometries of the ions, can be described by one of our previous bonding models, valence bond theory. Recall from [Section 6.2](#) that in valence bond theory, a coordinate covalent bond is the overlap between a completely filled atomic orbital and an empty atomic orbital. In complex ions, the filled orbital is on the ligand, and the empty orbital is on the metal ion. The metal ion orbitals are hybridized according to the geometry of the complex ion. The common hybridization schemes are shown in [Figure 22.11](#). An octahedral complex ion requires six empty orbitals in an octahedral arrangement on the metal ion. A full set of  $d^2sp^3$  hybrid orbitals results in the exact orbitals needed for this geometry. A set of  $sp^3$  hybrid orbitals results in a tetrahedral arrangement of orbitals; a set of  $dsp^2$  hybrid orbitals results in a square planar arrangement; and a set of  $sp$  hybrid orbitals results in a linear arrangement of orbitals. In each case, the coordinate covalent bond is formed by the overlap between the orbitals on the ligands and the hybridized orbitals on the metal ion.

**Figure 22.11 Common Hybridization Schemes in Complex Ions**

The valence bond model hybridization schemes are deduced from the geometry of the complex ion.

Geometry	Hybridization	Orbitals
Linear	$sp$	
Tetrahedral	$sp^3$	
Square planar	$dsp^2$	
Octahedral	$d^2sp^3$	

### Crystal Field Theory

Crystal field theory (CFT) is a bonding model for transition metal complexes that helps us understand their colors and magnetic properties. To illustrate the basic principles of CFT, we first examine the central metal atom's  $d$  orbitals in an octahedral complex.

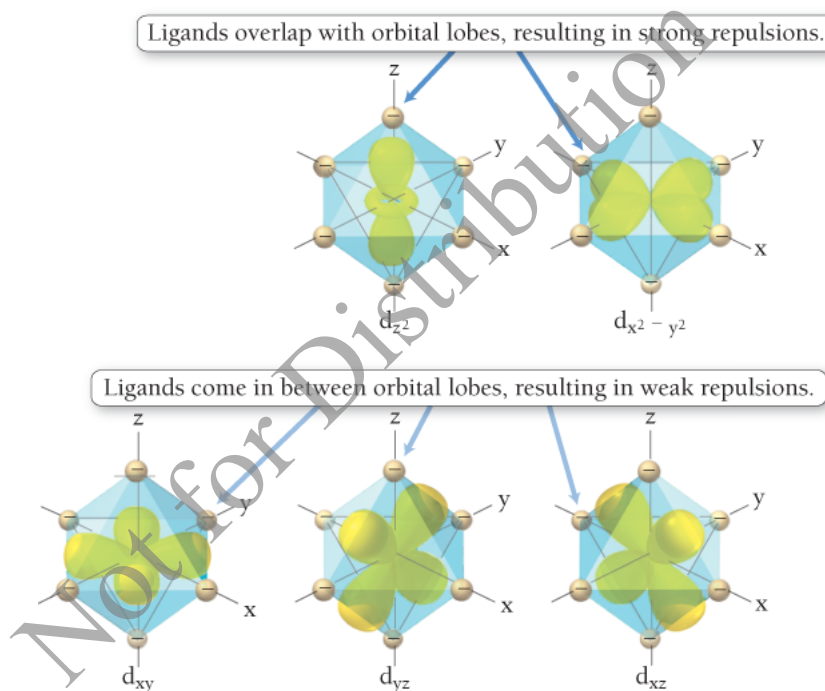
## Octahedral Complexes and $d$ Orbital Splitting

The basic premise of CFT is that complex ions form because of attractions between the electrons on the ligands and the positive charge on the metal ion. However, the electrons on the ligands also repel the electrons in the *unhybridized* metal  $d$  orbitals. CFT focuses on these repulsions.

Figure 22.12 shows how the ligand positions superimpose on the  $d$  orbitals in an octahedral complex. Notice that the ligands in an octahedral complex are located in the same space as the lobes of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. The repulsions *between* electron pairs in the ligands and any potential electrons in the  $d$  orbitals result in an increase in the energies of these orbitals. In contrast, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals lie *between* the axes and have nodes directly on the axes, which results in less repulsion and lower energies for these three orbitals. In other words, the  $d$  orbitals—which are degenerate in the bare metal ion—are split into higher- and lower-energy levels because of the spatial arrangement of the ligands (Figure 22.13). The difference in energy between these split  $d$  orbitals is known as the crystal field splitting energy ( $\Delta$ ). The magnitude of the splitting depends on the particular complex. In **strong-field complexes**, the splitting is large, and in **weak-field complexes**, the splitting is small.

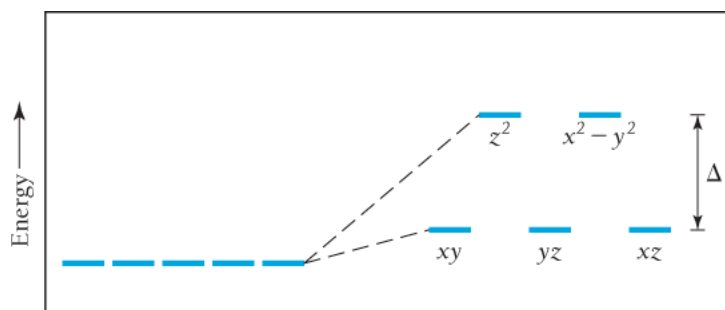
**Figure 22.12 Relative Positions of  $d$  Orbitals and Ligands in an Octahedral Complex**

The ligands in an octahedral complex (represented here as spheres of negative charge) interact most strongly with the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals.



**Figure 22.13  $d$  Orbital Splitting in an Octahedral Field**

The otherwise degenerate  $d$  orbitals are split into two energy levels by the ligands in an octahedral complex ion.



$d$  orbitals on  
free atom

$d$  orbitals in  
octahedral field

## The Color of Complex Ions and Crystal Field Strength

In Section 22.1, we saw that transition metals in host crystals often show brilliant colors because of the crystal field splitting of their  $d$  orbitals. Solutions of complex ions display brilliant colors because of similar splittings. For example, an  $[\text{Fe}(\text{CN})_6]^{3-}$  solution is deep red, and an  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  solution is blue (Figure 22.14). Recall from Chapter 2 that the color of an object is related to the absorption of light energy by its electrons. If a substance absorbs all of the visible wavelengths, it appears black. If it transmits (or reflects) all the wavelengths (absorbs no light), it appears colorless. A substance appears to be a particular color if it absorbs some visible light but also transmits (or reflects) the wavelengths associated with that color. A substance also appears to be a given color if it transmits (or reflects) most wavelengths but absorbs the *complementary color* on a color wheel (Figure 22.15). For example, a substance that absorbs green light (the complement of red) appears red. A solution of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is purple because it absorbs strongly between 490 and 580 nm, the yellow-green region of the visible spectrum (Figure 22.16a).

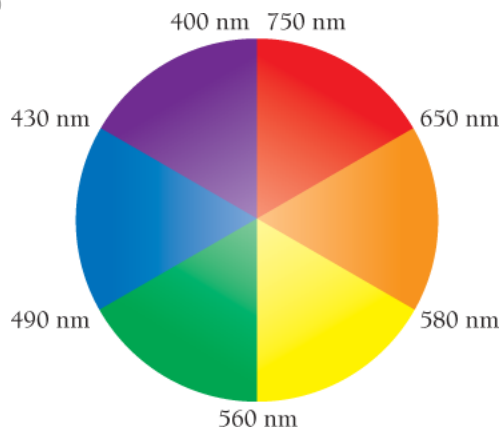
**Figure 22.14 Colors of Complex Ions**

(a) The complex ion  $[\text{Fe}(\text{CN})_6]^{3-}$  forms a deep red solution, and (b)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is blue.



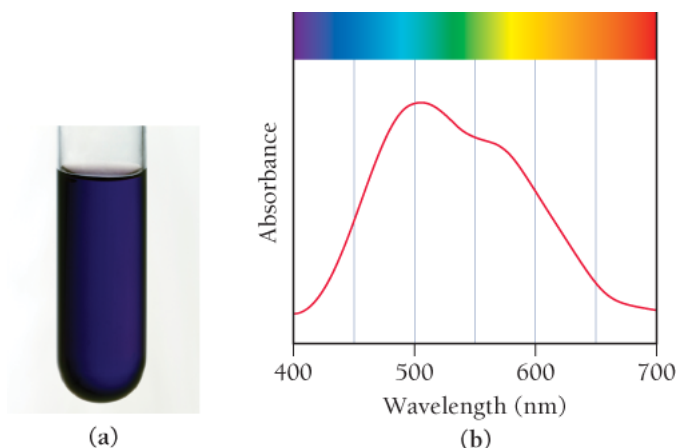
**Figure 22.15 The Color Wheel**

Colors across from one another on the color wheel are complementary. A substance that absorbs a color on the wheel appears to be its complementary color.



**Figure 22.16 The Color and Absorption Spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$**

(a) A solution containing  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is purple. (b) The absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  extends across the green-yellow region of the spectrum.



The easiest way to measure the energy difference between the  $d$  orbitals in a complex ion is to use spectroscopy to determine the wavelength of light absorbed when an electron makes a transition from the lower-energy  $d$  orbitals to the higher-energy ones. With that information we can calculate the crystal field splitting energy,  $\Delta$ :

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = \Delta$$

Consider the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorption spectrum shown in Figure 22.16b. The maximum absorbance is at 498 nm. Using this wavelength, we calculate  $\Delta$ :

$$\begin{aligned}\Delta &= hc/\lambda = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s}) / (498 \text{ nm} \times 1 \times 10^{-9} \text{ m/nm}) \\ \Delta &= 3.99 \times 10^{-19} \text{ J}\end{aligned}$$

This energy corresponds to a single  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion. We can convert to kilojoules per mole:

$$\Delta = (3.99 \times 10^{-19} \text{ J/ion}) (6.02 \times 10^{23} \text{ ion/mol}) (1 \text{ kJ}/1000 \text{ J}) = 240 \text{ kJ/mol}$$

### Example 22.8 Crystal Field Splitting Energy

The complex ion  $[\text{Cu}(\text{NH}_3)_6]^{2+}$  is blue in aqueous solution. Estimate the crystal field splitting energy (in kJ/mol) for this ion.

**SOLUTION** Begin by consulting the color wheel (Figure 22.15) to determine approximately what wavelength is being absorbed.

Because the solution is blue, you can deduce that orange light is absorbed since orange is the complementary color to blue.

Estimate the absorbed wavelength.

The color orange ranges from 580 to 650 nm, so you can estimate the average wavelength as 615 nm.

Calculate the energy corresponding to this wavelength, using  $E = hc/\lambda$ . This energy corresponds to  $\Delta$ .

$$\begin{aligned}E &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{(615 \text{ nm}) (1 \times 10^{-9} \text{ m/nm})} \\ E &= 3.23 \times 10^{-19} \text{ J} = \Delta\end{aligned}$$

Convert J/ion into kJ/mol.

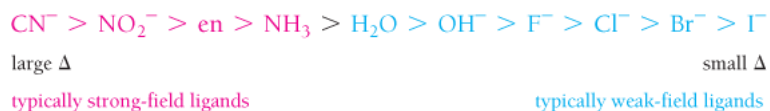
$$(3.23 \times 10^{-19} \text{ J/ion}) (6.02 \times 10^{23} \text{ ion/mol})$$

$$\Delta = \frac{hc}{\lambda} \quad \left( \frac{1000 \text{ J}}{\text{kJ}} \right)$$

$$\Delta = 195 \text{ kJ/mol}$$

**FOR PRACTICE 22.8** The complex ion  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$  is yellow. Estimate the crystal field splitting energy (in kJ/mol) for this ion.

The magnitude of the crystal field splitting in a complex ion—and, therefore whether it is a strong-field or a weak-field complex—depends in large part on the ligands attached to the central metal ion. Spectroscopic studies of various ligands attached to the same metal allow us to arrange different ligands in order of their ability to split the  $d$  orbitals. This list is known as the *spectrochemical series* and is arranged from ligands that result in the largest  $\Delta$  to those that result in the smallest:



Ligands that produce large values of  $\Delta$  are *strong-field ligands*, and those that give small values of  $\Delta$  are *weak-field ligands*.

The metal ion also has an effect on the magnitude of  $\Delta$ . If we examine different metal ions with the same ligand, we find that  $\Delta$  increases as the charge on the metal ion increases. A greater charge on the metal draws the ligands closer, causing greater repulsion with the  $d$  orbitals and therefore a larger  $\Delta$ . An example of this behavior occurs in the complex ions between  $\text{NH}_3$  (a ligand in the middle of the spectrochemical series) and the +2 or +3 oxidation states of cobalt. Hexaamminecobalt(II) ion,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ , has a weak crystal field (small  $\Delta$  and hexaamminecobalt(III) ion,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , has a strong field (large  $\Delta$ ).

### Conceptual Connection 22.2 Weak- and Strong-Field Ligands

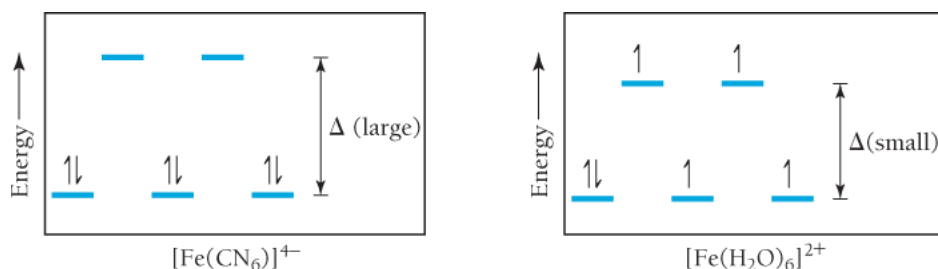
## Magnetic Properties and Crystal Field Strength

The strength of the crystal field can affect the magnetic properties of a transition metal complex. Recall that, according to Hund's rule, electrons occupy degenerate orbitals singly as long as an empty orbital is available. When the energies of the  $d$  orbitals are split by ligands, the lower-energy orbitals fill first. Once they are half-filled, the next electron can either: (1) pair with an electron in one of the lower-energy half-filled orbitals by overcoming the electron–electron repulsion associated with having two electrons in the same orbital; or (2) go into an empty orbital of higher energy by overcoming the energy difference between the orbitals—in this case, the crystal field splitting energy,  $\Delta$ . The magnitude of  $\Delta$  compared to the electron–electron repulsions determines which of these two actually occurs.

Recall from Section 3.7 that a paramagnetic species contains unpaired electrons and a diamagnetic one does not.

We can compare two iron(II) complexes to see the difference in behavior under strong- and weak-field conditions.  $[\text{Fe}(\text{CN})_6]^{4-}$  is known to be diamagnetic and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is known to be paramagnetic. Both of these complexes contain  $\text{Fe}^{2+}$ , which has an electron configuration of  $[\text{Ar}] 3d^6$ . In the case of  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\text{CN}^-$  is a strong-field ligand that generates a large  $\Delta$ , so it takes more energy to occupy the higher-energy level than it does to pair the electrons in the lower-energy level. The result is that all six electrons are paired and the compound is diamagnetic, as shown in the figure on the left below.

In  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{H}_2\text{O}$  is a weak-field ligand that generates a small  $\Delta$ , so the electron pairing energy is greater than  $\Delta$ . Consequently, the first five electrons occupy the five  $d$  orbitals singly and only the sixth pairs up, resulting in a paramagnetic compound with four unpaired electrons, as shown in the figure on the right below.



In general, complexes with strong-field ligands have fewer unpaired electrons relative to the free metal ion and are therefore called **low-spin complexes**. Complexes with weak-field ligands, by contrast, have the same number of unpaired electrons as the free metal ion and are **high-spin complexes**.

When we examine the orbital diagrams of the  $d^1$  through  $d^{10}$  metal ions in octahedral complexes, we find that only  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  metal ions have low- and high-spin possibilities. Since there are three lower-energy  $d$  orbitals, the  $d^1$ ,  $d^2$ , and  $d^3$  metal ions always have unpaired electrons, independent of  $\Delta$ . In the  $d^8$ ,  $d^9$ , and  $d^{10}$  metal ions, the three lower-energy orbitals are completely filled, so the remaining electrons fill the two higher orbitals (as expected according to Hund's rule), also independent of  $\Delta$ .

### Example 22.9 High- and Low-Spin Octahedral Complexes

#### Determining the Number of Unpaired Electrons in Octahedral Complexes

How many unpaired electrons are there in the complex ion  $[\text{CoF}_6]^{3-}$ ?

**PROCEDURE** Begin by determining the charge and number of  $d$  electrons on the metal.

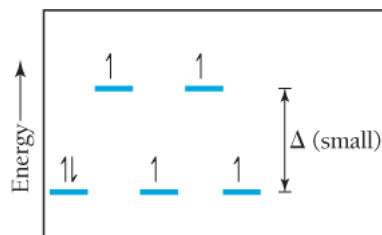
**SOLUTION** The metal is  $\text{Co}^{3+}$  and has a  $d^6$  electronic configuration.

**PROCEDURE** Look at the spectrochemical series to determine whether the ligand is a strong-field or a weak-field ligand.

**SOLUTION**  $\text{F}^-$  is a weak-field ligand, so  $\Delta$  is relatively small.

**PROCEDURE** Decide if the complex is high- or low-spin and draw the electron configuration.

**SOLUTION** Weak-field ligands yield high-spin configurations.



**PROCEDURE** Count the unpaired electrons.

**SOLUTION** This configuration has four unpaired electrons.

**FOR PRACTICE 22.9** How many unpaired electrons are there in the complex ion  $[\text{FeCl}_6]^{3-}$ ?

**Example 22.10 High- and Low-Spin Octahedral Complexes****Determining the Number of Unpaired Electrons in Octahedral Complexes**

How many unpaired electrons are there in the complex ion  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ ?

**PROCEDURE** Begin by determining the charge and number of  $d$  electrons on the metal.

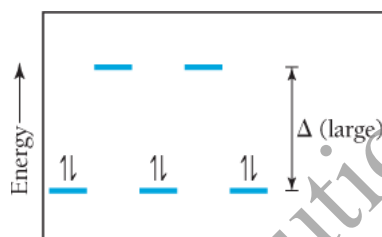
**SOLUTION** The metal is  $\text{Co}^{3+}$  and has a  $d^6$  electronic configuration.

**PROCEDURE** Look at the spectrochemical series to determine whether the ligand is a strong-field or a weak-field ligand.

**SOLUTION**  $\text{NH}_3$  and  $\text{NO}_2^-$  are both strong-field ligands, so  $\Delta$  is relatively large.

**PROCEDURE** Decide if the complex is high- or low-spin and draw the electron configuration.

**SOLUTION** Strong-field ligands yield low-spin configurations.



**PROCEDURE** Count the unpaired electrons.

**SOLUTION** This configuration has no unpaired electrons.

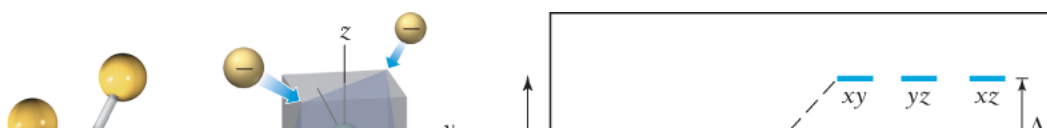
**FOR PRACTICE 22.10** How many unpaired electrons are there in the complex ion  $[\text{Co}(\text{CN})_6]^{4-}$ ?

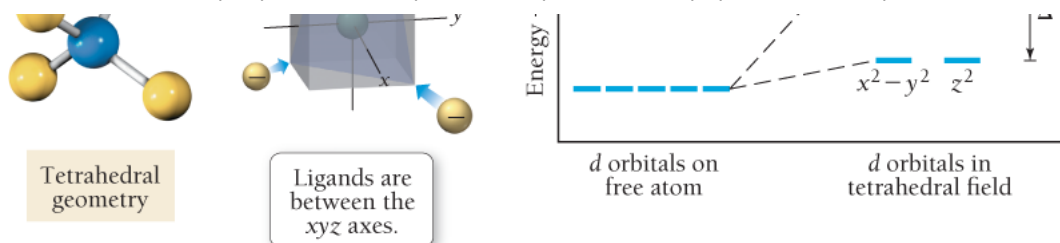
## Tetrahedral and Square Planar Complexes and $d$ Orbital Splitting

So far, we have examined the  $d$  orbital energy changes only for octahedral complexes, but transition metal complexes can have other geometries, such as tetrahedral and square planar. We use crystal field theory to determine the  $d$  orbital splitting pattern for these geometries as well. For a tetrahedral complex, the  $d$  orbital splitting pattern is the opposite of the octahedral splitting pattern: three  $d$  orbitals ( $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ ) are higher in energy, and two  $d$  orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) are lower in energy (Figure 22.17). Almost all tetrahedral complexes are high-spin because of reduced ligand–metal interactions. The  $d$  orbitals in a tetrahedral complex interact with only four ligands, as opposed to six in the octahedral complex, so the value of  $\Delta$  is generally smaller.

**Figure 22.17 Splitting of  $d$  Orbitals by a Tetrahedral Ligand Geometry**

In tetrahedral complexes, the pattern of the splitting of the  $d$  orbitals is the opposite of the octahedral splitting pattern. The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are higher in energy than the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals.



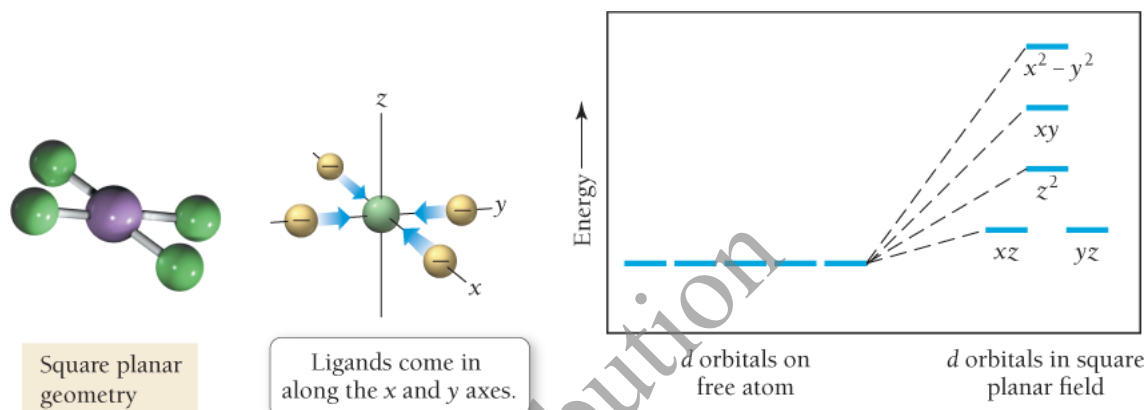


A square planar complex results in the most complex splitting pattern of the three geometries (Figure 22.18□).

As we discussed previously, square planar complexes occur in  $d^8$  metal ions, such as  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ir}^+$ , or  $\text{Au}^{3+}$ , and in nearly all cases they are low-spin.

**Figure 22.18 Splitting of  $d$  Orbitals by a Square Planar Ligand Geometry**

Square planar complexes produce the  $d$  orbital energy pattern shown here.





*Not for Distribution*

*Not for Distribution*