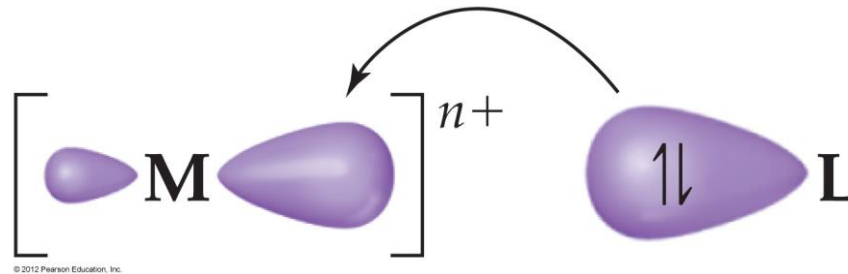


# Central Tenants of Crystal Field Theory

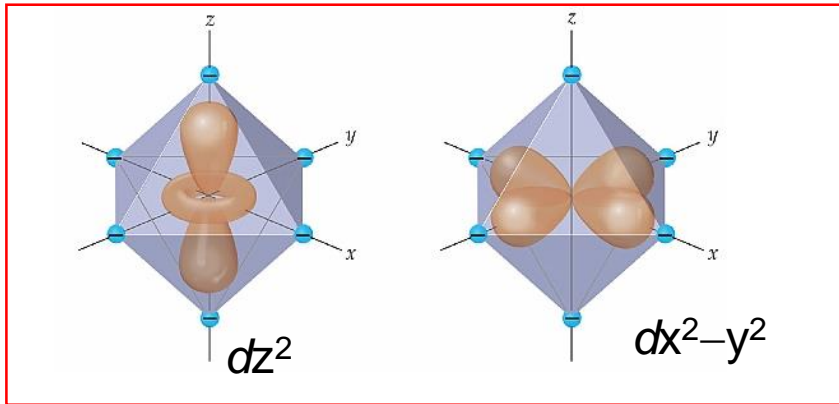
- The metals (**Lewis acids**) have d orbitals that are partially filled with electrons.
- **Ligands**, that are **Lewis bases** with lone pairs, come in and form a covalent bond.



- **Electrostatic repulsion** between the **ligand lone pairs** with the d-orbital subshell leads to **higher energies**
- Each **metal orbital** will either be **stabilized** or **destabilized** depending on the **amount of orbital overlap** with the **ligand**.

# CFT (Octahedron)

E ↑

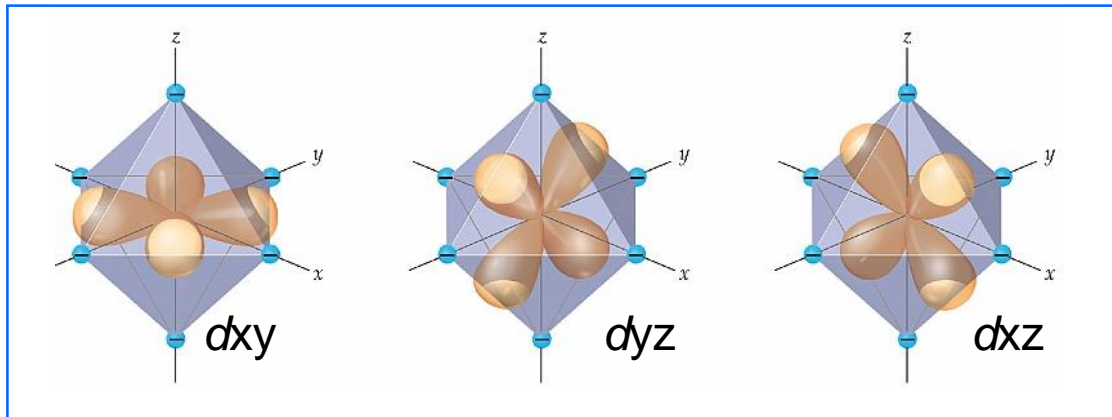


$e_g$

$(d_{z^2}, d_{x^2-y^2})$

Orbitals point directly at ligands

stronger repulsion  
higher energy



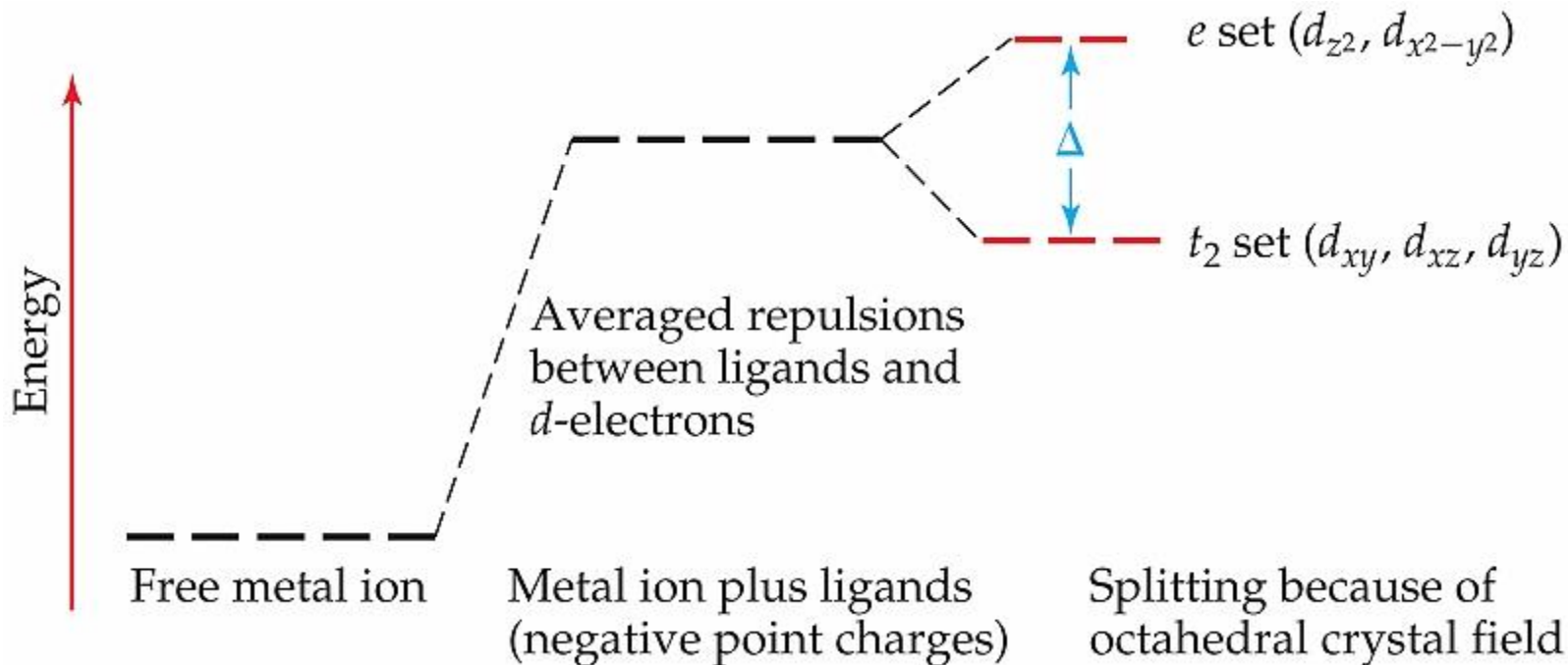
$t_{2g}$

$(d_{xy}, d_{yz}, d_{xz})$

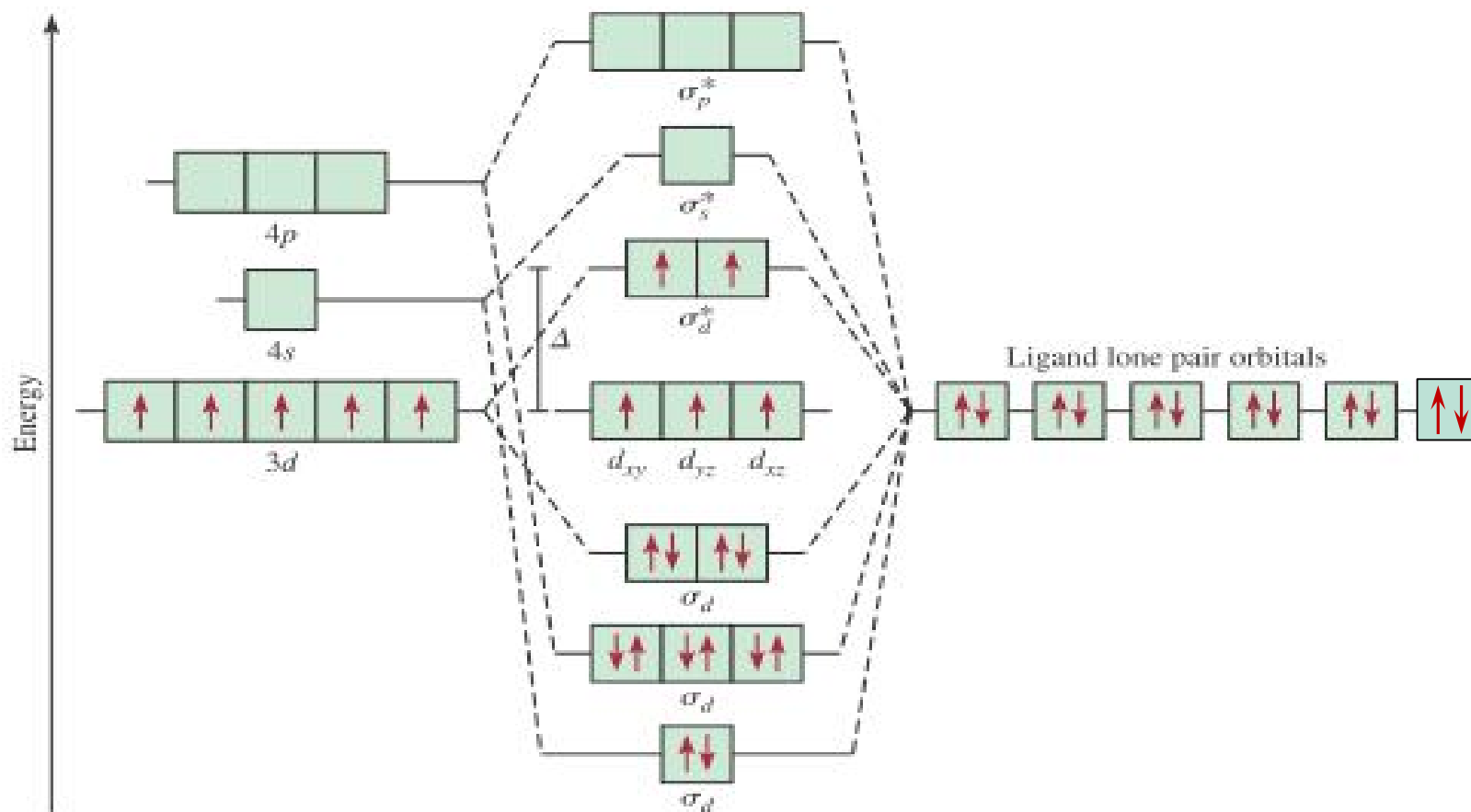
Orbitals point between ligands

weaker repulsion  
lower energy

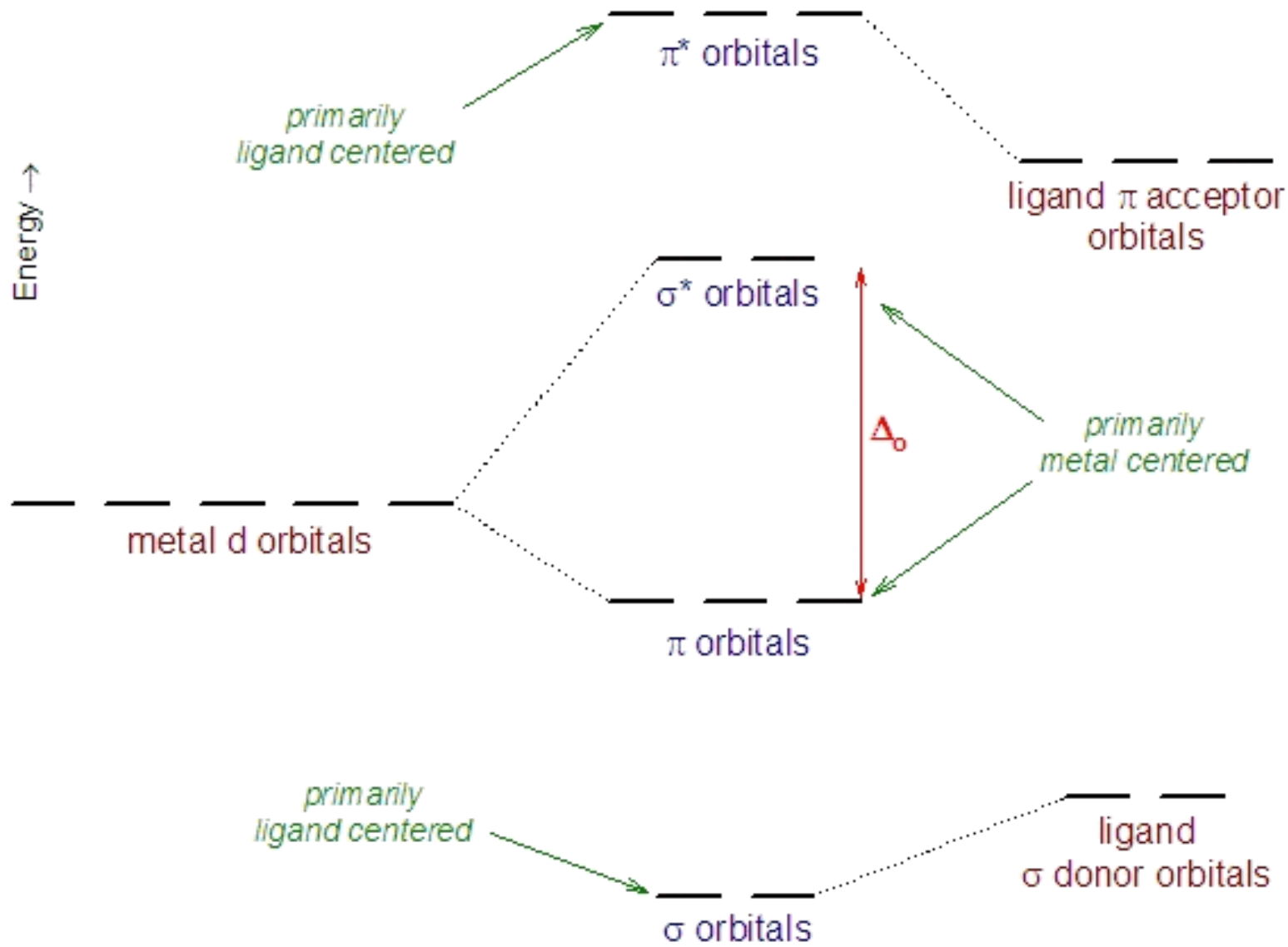
# Energy Levels of $d$ -Orbitals in an Octahedron



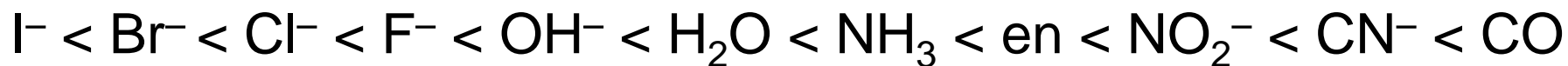
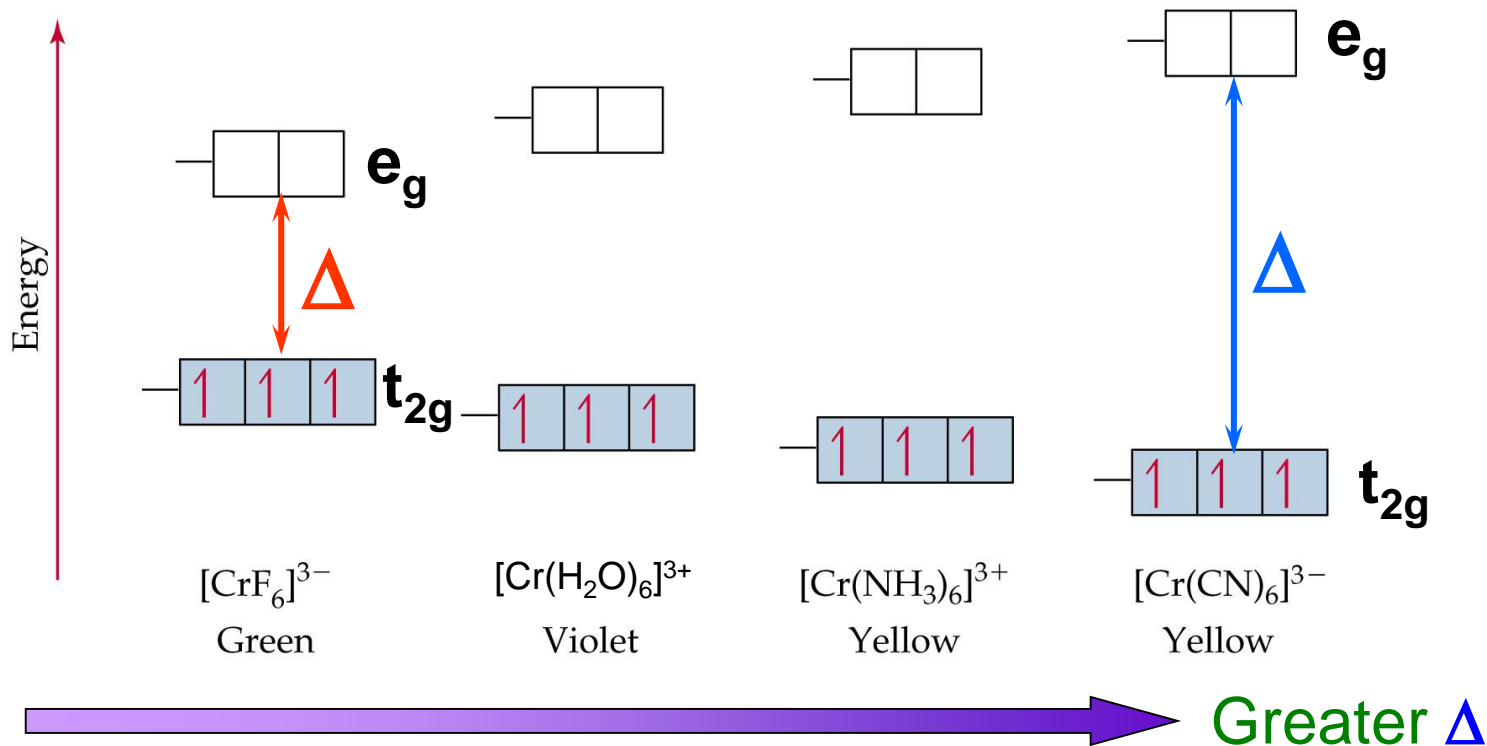
- *crystal field splitting energy* =  $\Delta$
- The size of  $\Delta$  is determined by;
  - *metal* (oxidation state; row of metal,  $\Delta$  for  $5d > 4d \gg 3d$ )
  - *ligand* (*spectrochemical series*)



**Figure 15.22** Molecular-orbital energy-level diagram for the octahedral complex  $\text{FeF}_6^{3-}$ . The  $\sigma_d^*$  molecular orbitals are essentially pure  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals of the central metal ion. In this complex, the crystal field splitting ( $\Delta$ ) between the three non bonding orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) and the two  $\sigma_d^*$  orbitals is small ( $\text{F}^-$  is a weak-field ligand) so Hund's rule applies, and these five orbitals each contain one electron with all the spins parallel.



# Spectrochemical Series



Small  $\Delta$

Weak Field

Weak M-L interactions

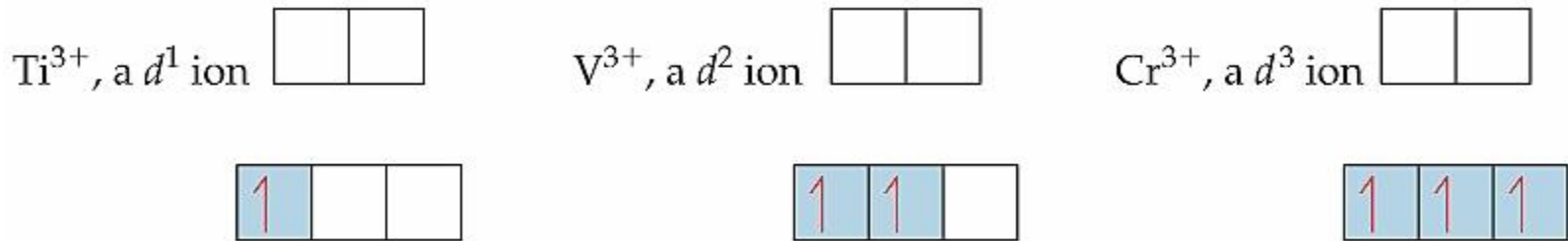
Large  $\Delta$

Strong Field

Strong M-L interactions

# How Do the Electrons Go In?

- Hund's rule: one electron each in lowest energy orbitals first



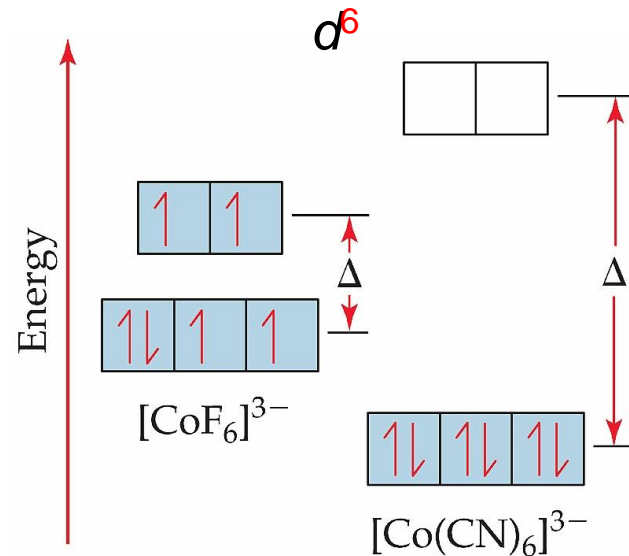
- what happens from  $d^4$  to  $d^7$ ?

Crystal Field  
Splitting

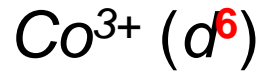


vs.

Spin Pairing

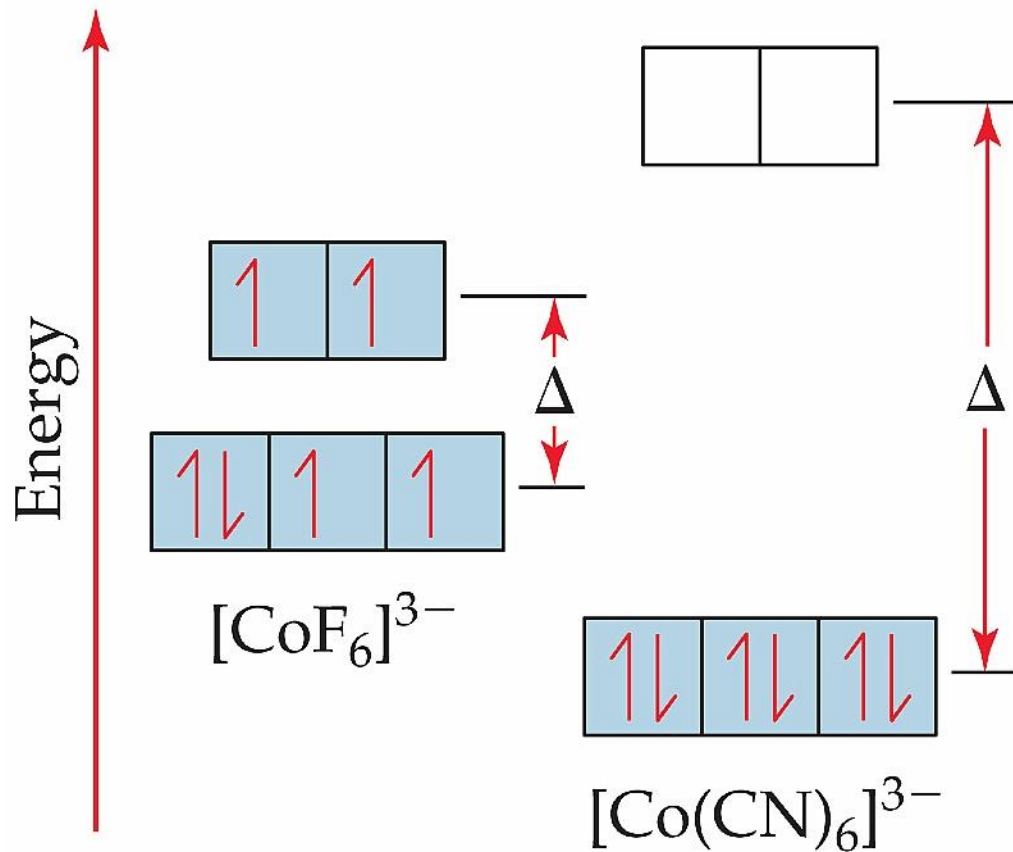


# High Spin vs. Low Spin



High Spin

$$\Delta < P$$



Low Spin

$$\Delta > P$$

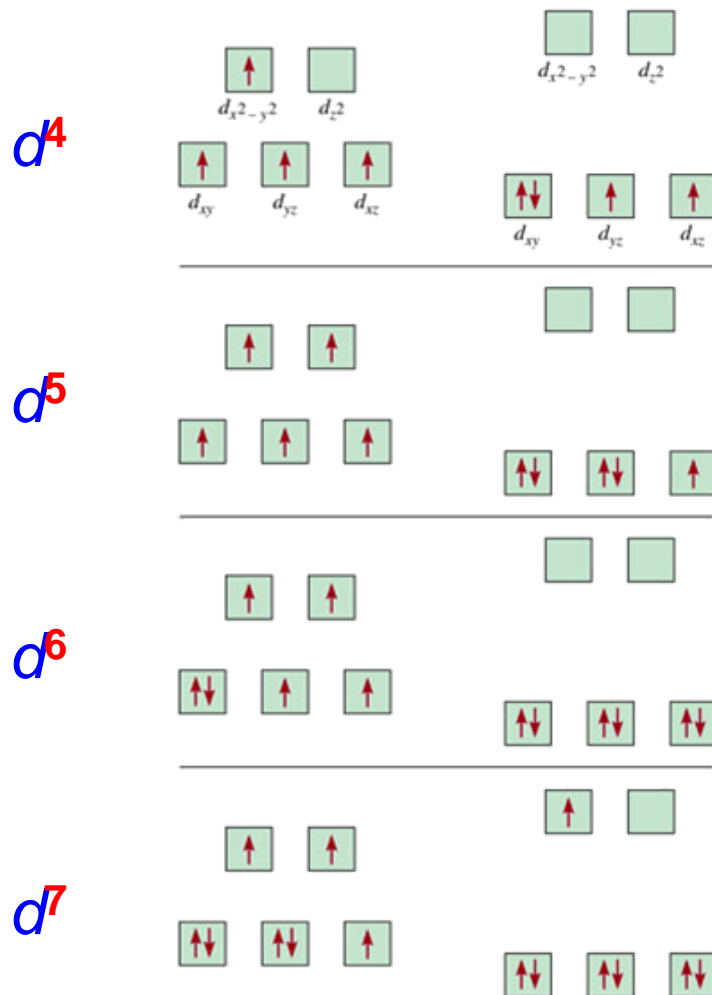


# High Spin vs. Low Spin Configurations

# High Spin vs. Low Spin Configurations

high spin

3d metal  
weak field  
ligand



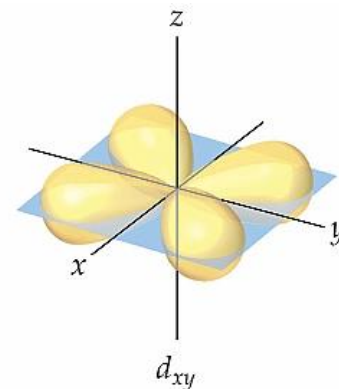
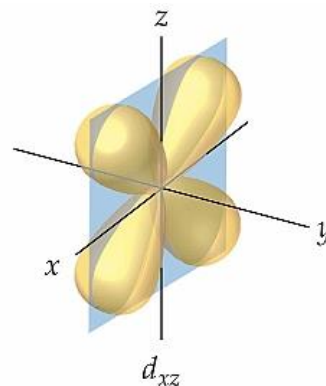
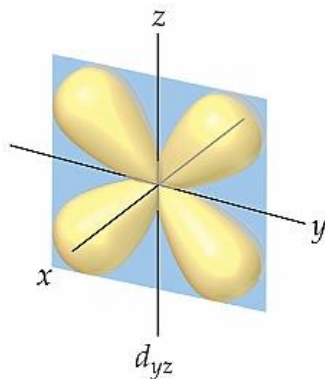
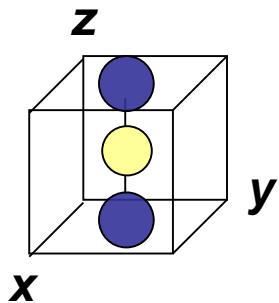
low spin

3d metal  
strong field  
ligand

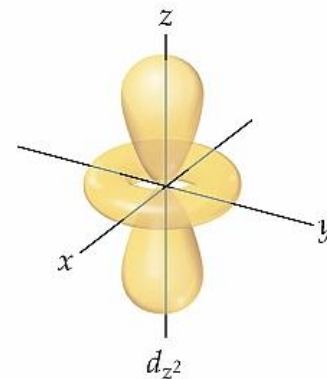
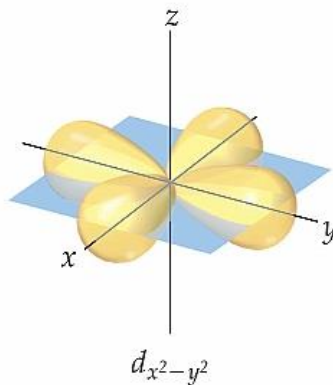
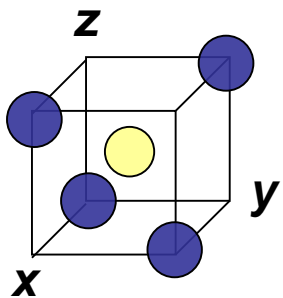
4d & 5d  
always

# What About **Other** Geometries?

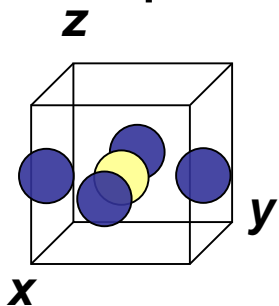
linear (CN = 2)



tetrahedral (CN = 4)

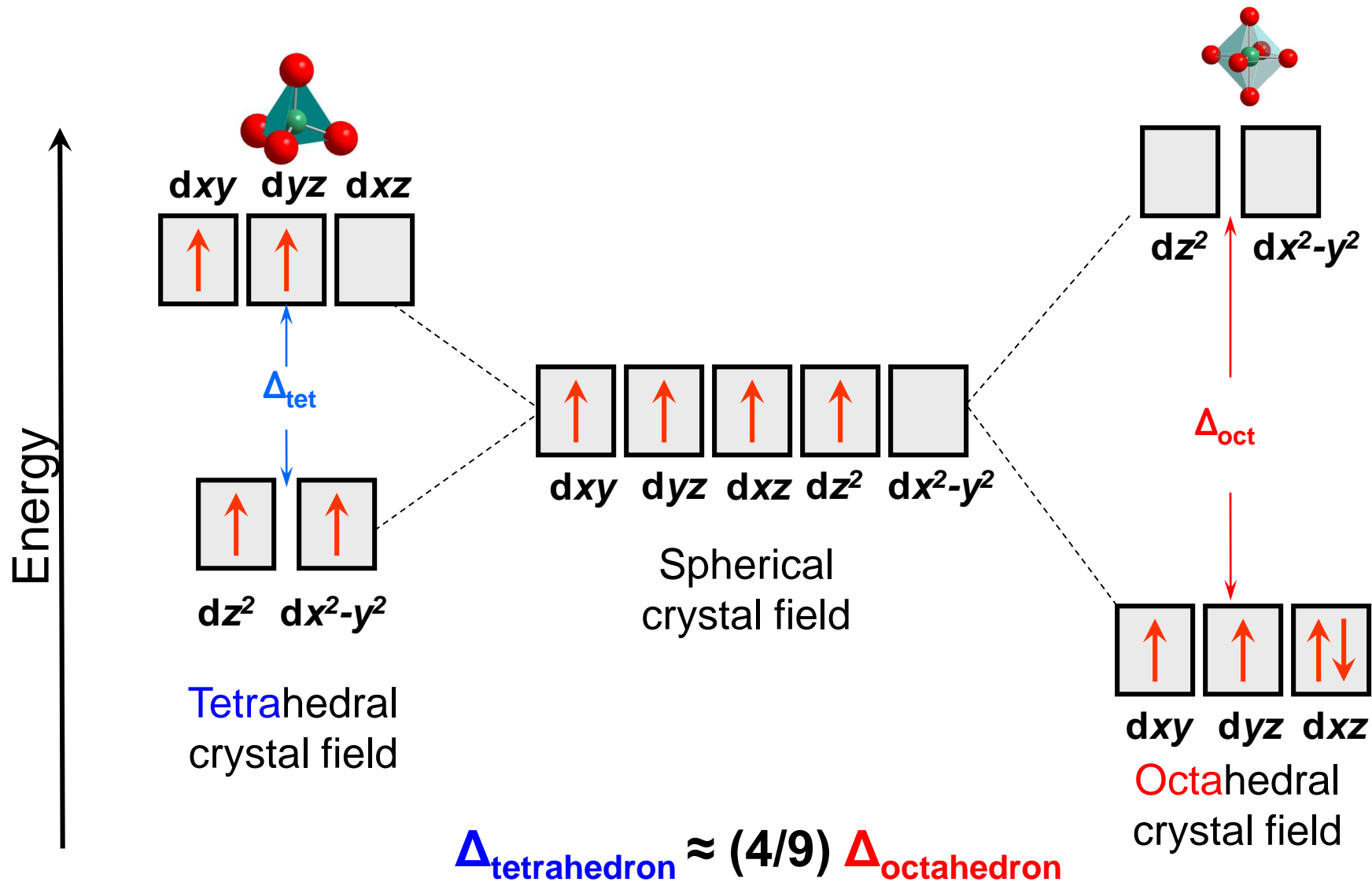


square planar (CN = 4)



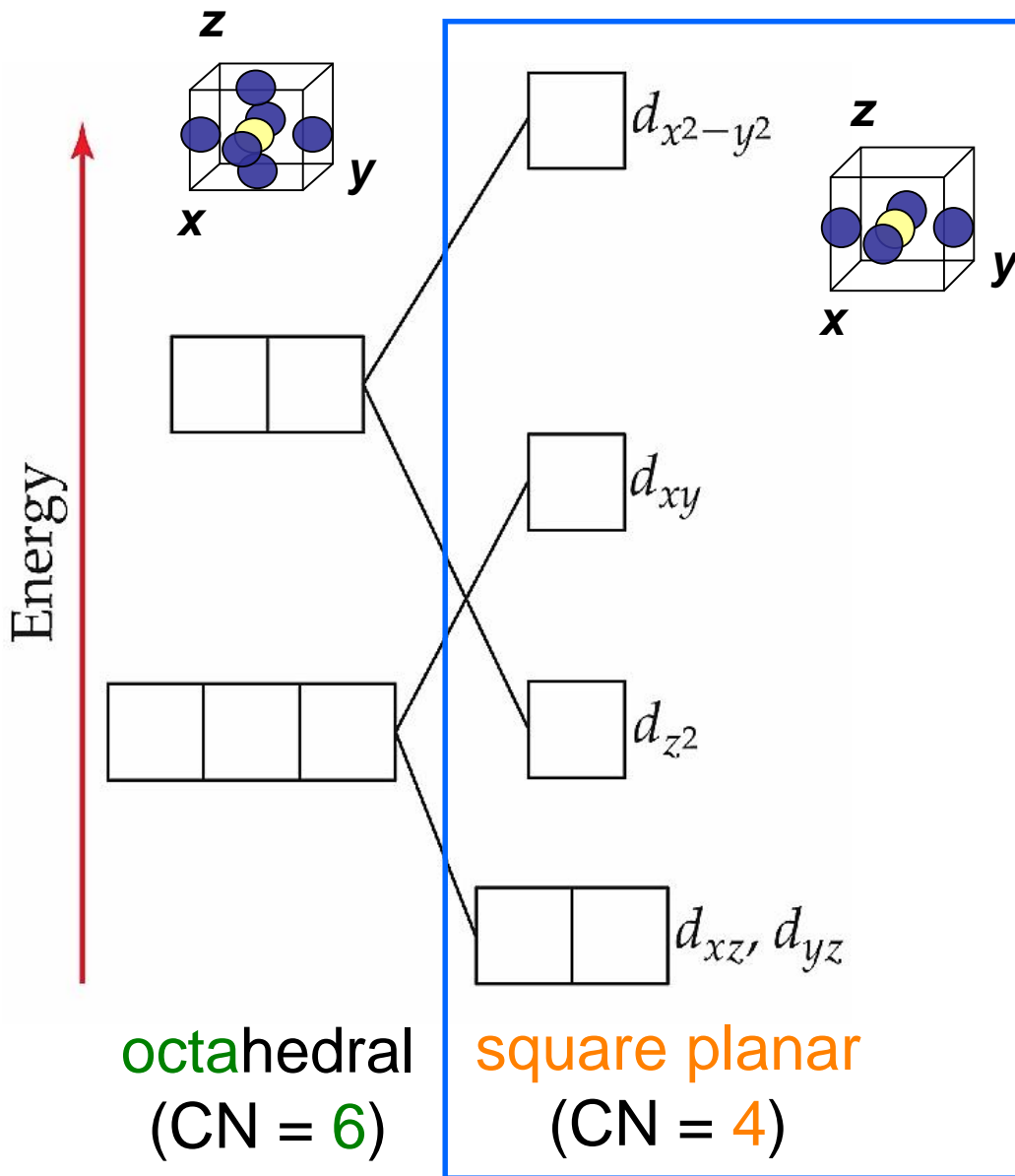
*how do the electrons on the d orbitals interact with the ligands in these cases?*

# Tetrahedral vs. Octahedral



Consequently, *tetrahedral* complexes are always **high spin**.

# Square Planar d-level Splitting



All  $z$ -levels lower in energy due to less  $e^-$  repulsion

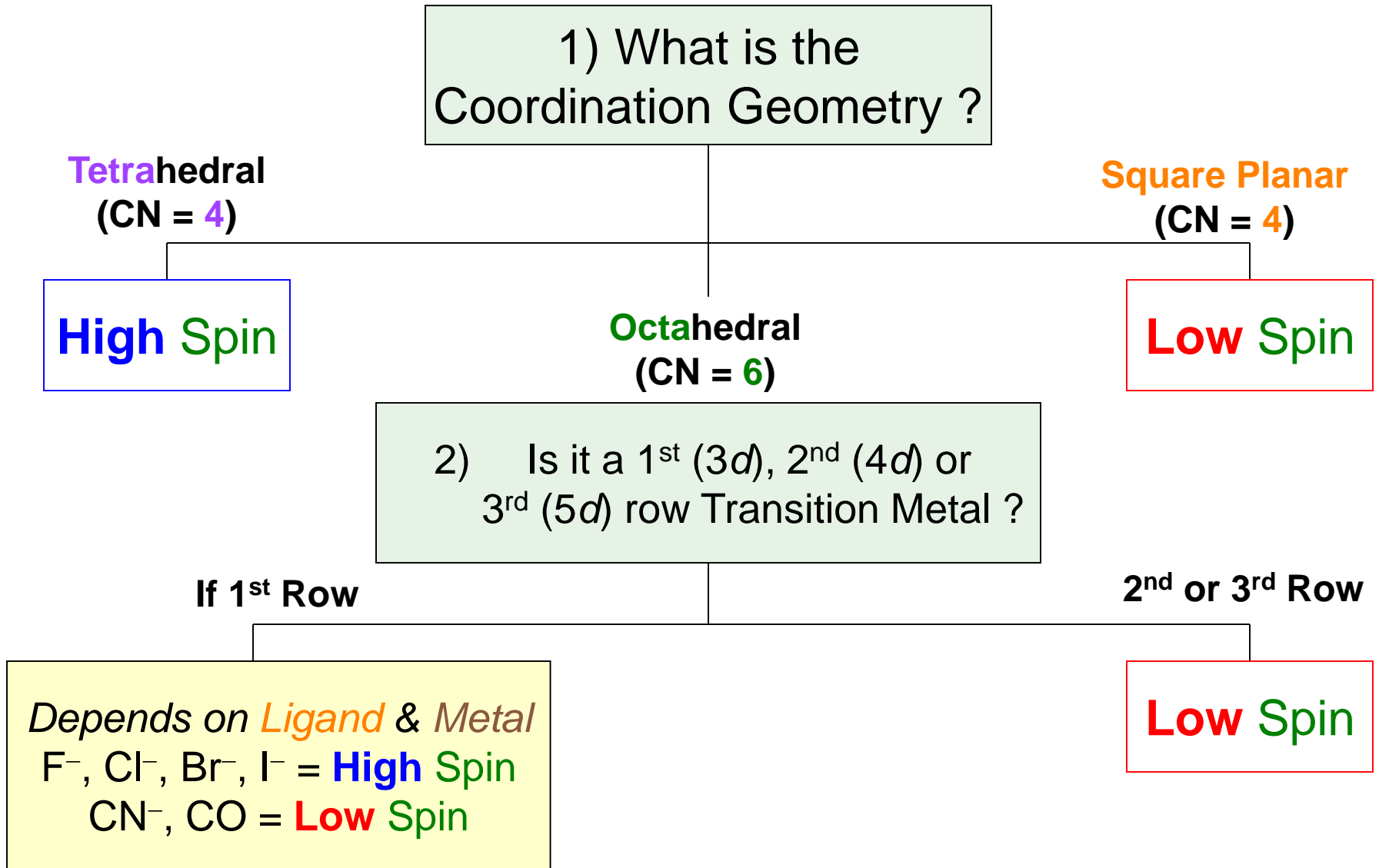
$d_{z^2}$  more stable so lower in energy than  $d_{xy}$  orbital

$d^8$

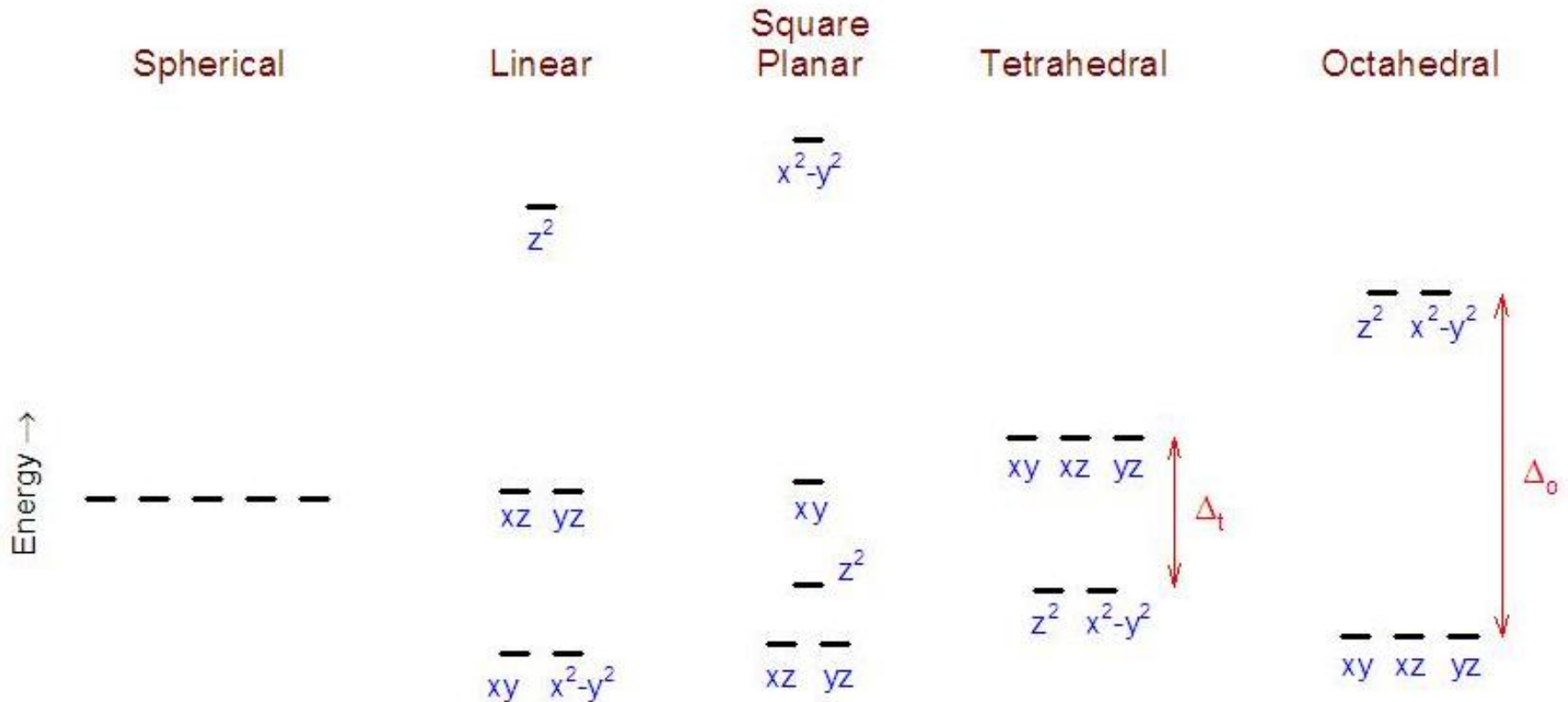
Common for 4d & 5d metals

Low Spin

# High Spin or Low Spin?



# Orbital Splitting vs. Geometry

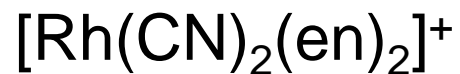


# Electron Configurations of Complexes

coord. #

geom.

*d*-e<sup>-</sup> config.





# Electron Configurations of Complexes

coord. #

geom.

*d*-e<sup>-</sup> config.



$[\text{FeCl}_4]^{2-}$  is tetrahedral. How many unpaired electrons will  $[\text{FeCl}_4]^{2-}$  have?

# Magnetism

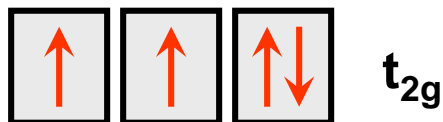
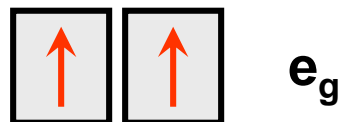
- **paramagnetism**

- compounds with **one or more unpaired electrons** are *attracted* by a magnetic field
- *The more unpaired electrons* the **greater** the *attractive* force

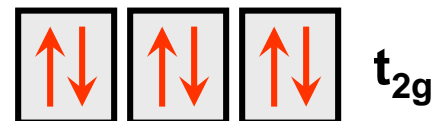
- **diamagnetism**

- compounds with **no unpaired electrons** *repel* a magnetic field
- much **weaker** effect

## Octahedral Crystal Field



$d^6$  **High Spin** (i.e.  $\text{Co}^{3+}$ )



$d^6$  **Low Spin** (i.e.  $\text{Co}^{3+}$ )

# Color of Transition Metal Complexes



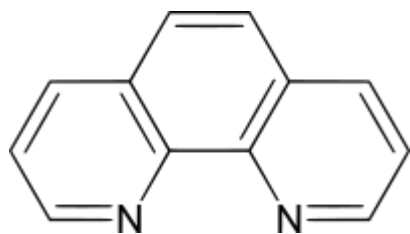
The color of these compounds comes from the absorption of light that causes an excitation of an electron from *one* *d*-orbital to a *different* *d*-orbital on the *same metal cation*.

# Color of Transition Metal Complexes

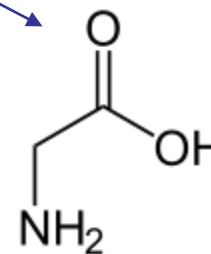
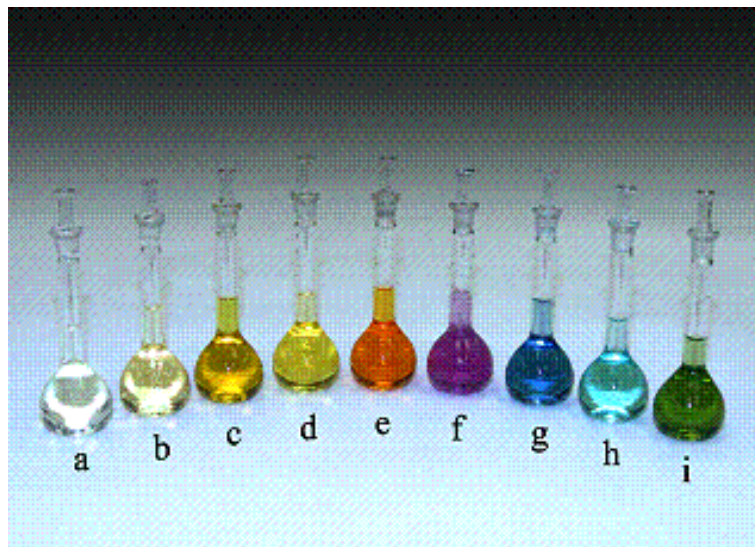
- Spectrochemical series
  - relative strength of metal ion/ligand interactions
  - independent of metal

octahedral cobalt(III) complex ions

a.  $\text{CN}^-$  b.  $\text{NO}_2^-$  c. phen d. en e.  $\text{NH}_3$  f. gly g.  $\text{H}_2\text{O}$  h. ox i.  $\text{CO}_3^{2-}$



1,10-phenanthroline

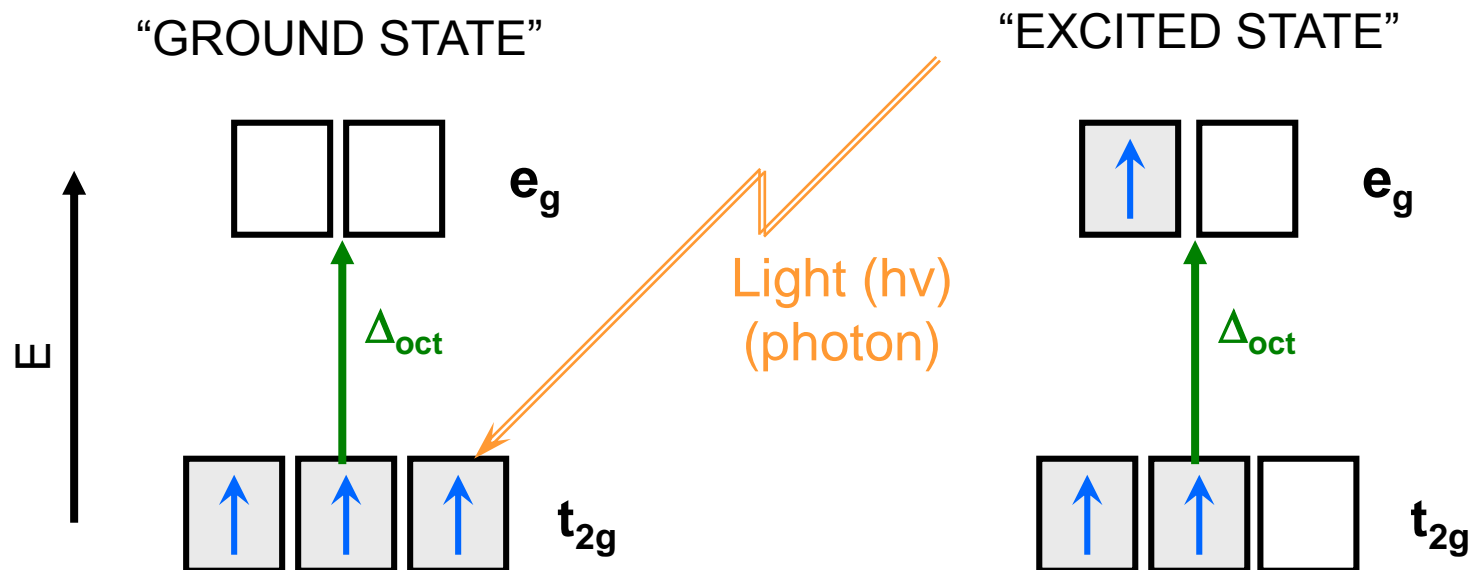


glycine

# Absorption Of Light

- compounds absorb light *if* the light has the *correct energy* to cause an electron to move from a **lower energy state** to a **higher energy state**

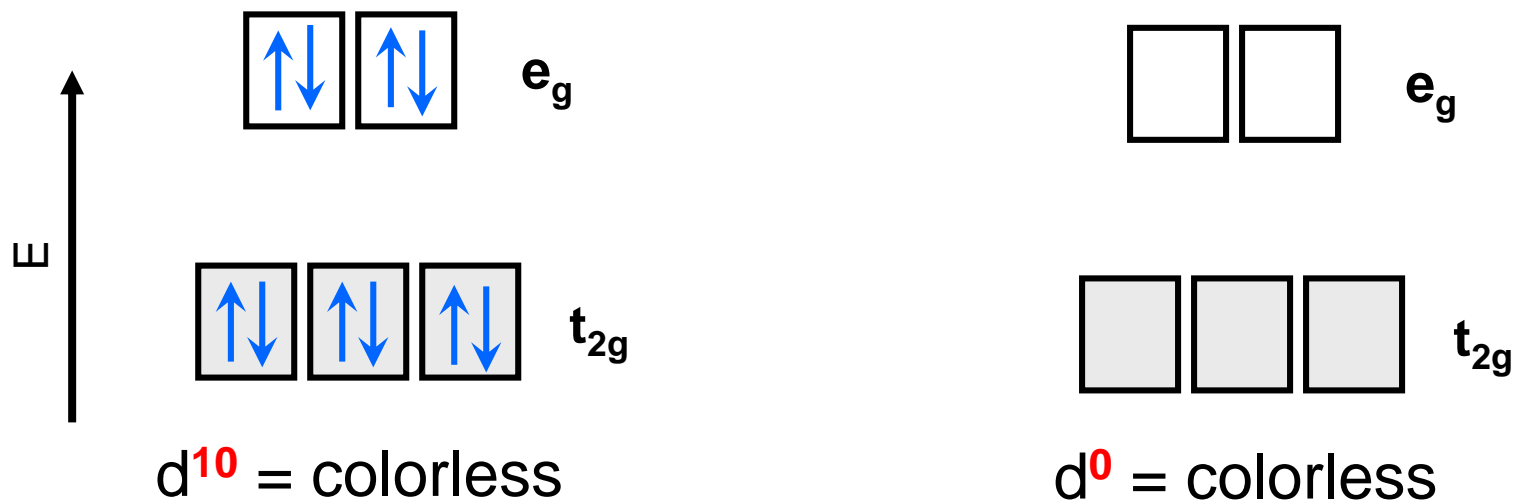
octahedral  $d^3$  (i.e.  $\text{Cr}^{3+}$ )



The size of  $\Delta_{\text{oct}}$  dictates the **wavelength** of **light** needed, and therefore, the **color** of the compound.

# Absorption Dependence on $d$ -electrons

Different numbers of transitions will occur for different  $d$ -electron configurations



$d^1$ - $d^9$  = various **visible** transitions