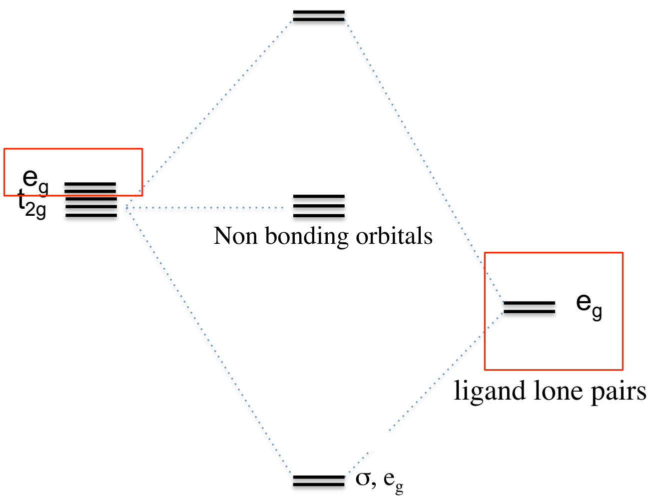
Week 11

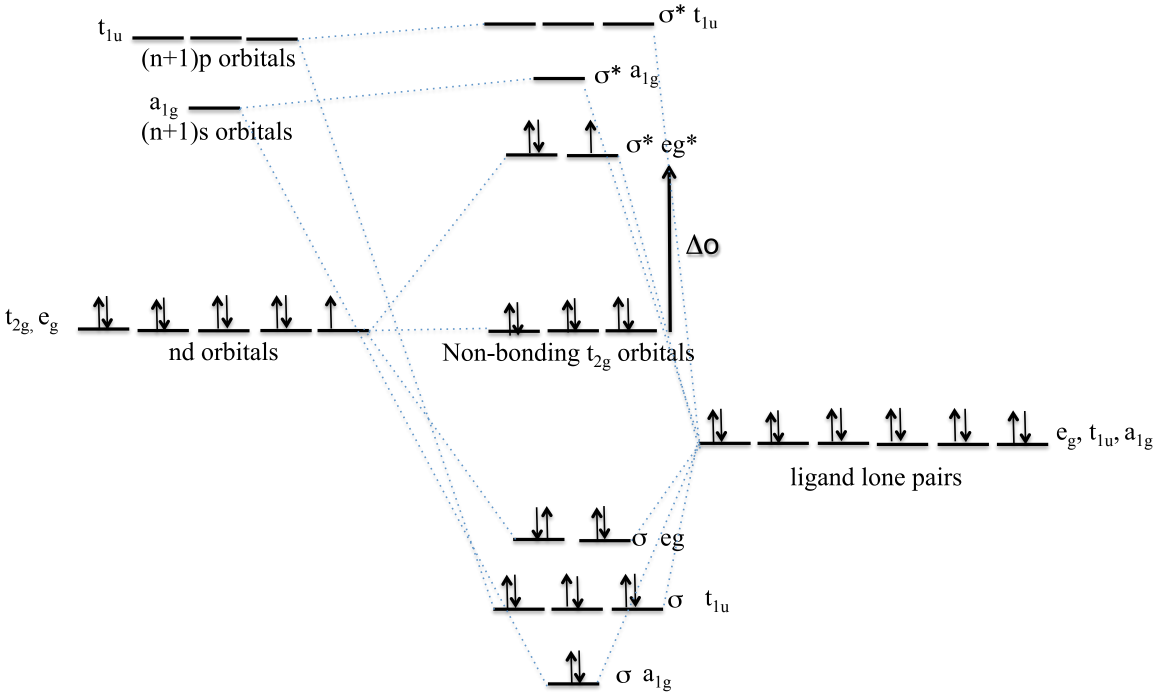


The t_{2g} orbitals are metal dxy, dxz, and dyz, and the e_g σ^* orbitals are based on metal dx^2-y^2 and dz^2. We see that the results of ligand field theory are the same as that of the crystal field theory. The energy difference between e_g and t_{2g} orbitals are the **ligand field splitting energy**, which is the same as the **crystal field splitting energy**.

Exercise: (1) Draw the ligand field diagram for Cu(II) (d^9) assuming an octahedral complex and σ-bonding only. For the metal, consider the relevant s, p, and d orbitals.

Answer: Spin state = ½(Number of unpaired e-)

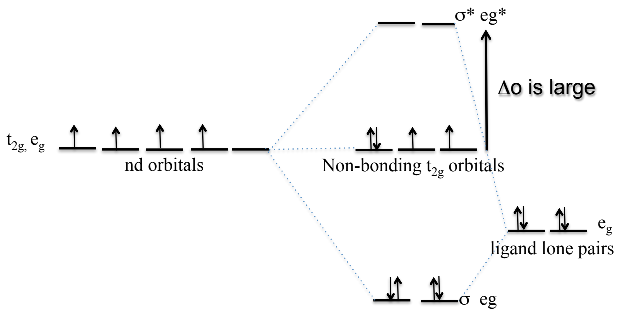
MO diagram Cu^{2+} in a σ-bonding complex



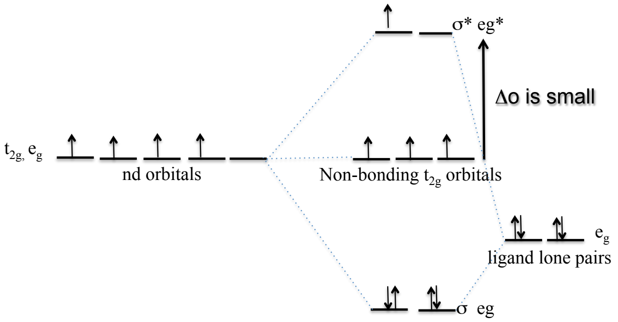
(2) Draw the ligand field diagrams for d^4, d^6, d^8 octahedral complexes, assuming σ-bonding only. For the metal, consider only the metal d orbitals. Calculate the spin state for each complex.

Spin state = ½*(number of unpaired e-)

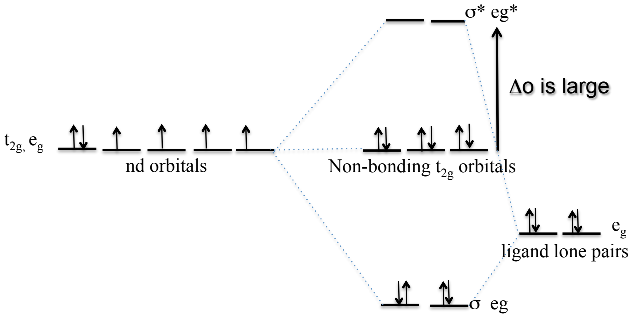
Answer:



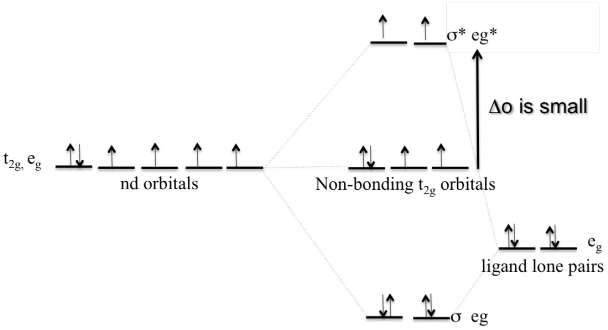
$S = ½(2) = 1$
d^4 low-spin



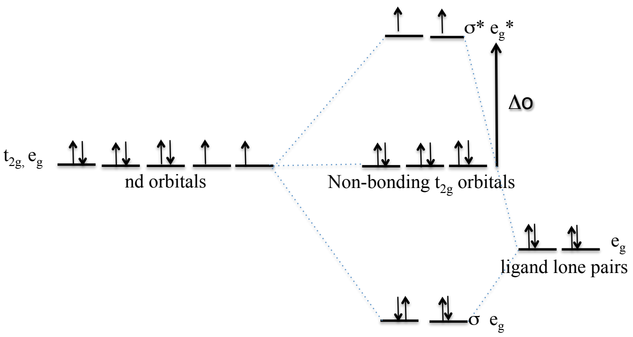
$S = ½(4) = 2$
d^4 high-spin



$S = ½(0) = 0$
d^6 low-spin



$S = ½(4) = 2$
d^6 high-spin



$S = ½(2) = 1$
d^8

➢ σ-Bonding in Tetrahedral and Square Planar Complexes

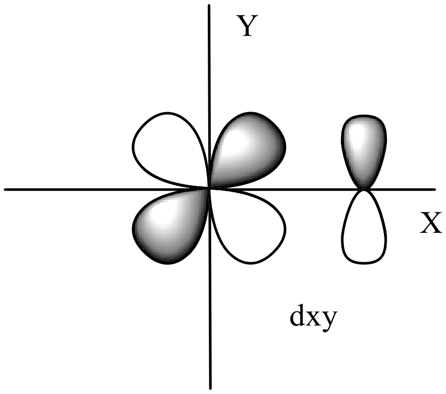
Like for octahedral complexes, the results from Ligand Field Theory treatment of tetrahedral and square planar complexes are the same as the results from Crystal Field Theory. So we will not go into details. Interested readers can consult Chapter 10 of the reference book.

➢ π-Bonding in Octahedral Complexes

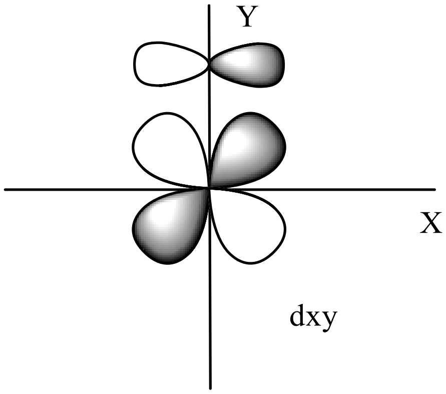
If we only consider σ-bonding, the results from ligand field theory are the same as crystal field theory. What is then the advantage or necessity of Ligand Field Theory? The answer is, Ligand Field Theory can take in account of π-bonding, which exists in many complexes, and which is very important for the understanding of the properties of these complexes.

Again we can use visual inspection to understand the π-bonding. We already know that π-bonding is the side-by-side overlap of orbitals. We already see the π-bonding between two p orbitals (page 2-3, part II). Let's consider metal d orbitals.

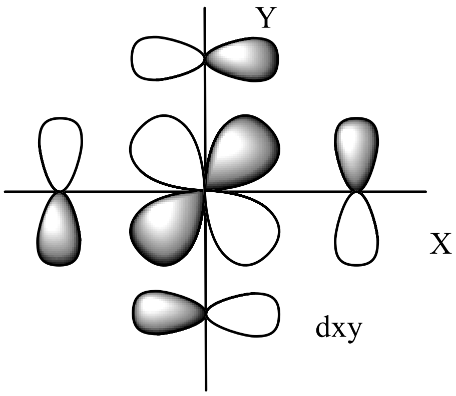
First, the metal dxy orbital. It can overlap with a p_y orbital in a side-by-side fashion in the x axis. Therefore, it can form π-bonding with this p_y orbital.



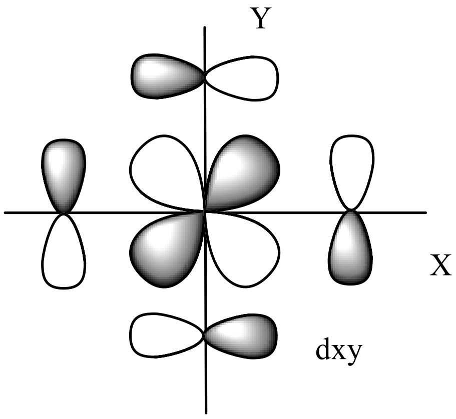
Likewise, it can form π-bonding with a ligand p_x orbital along the y axis.



In fact, it can form π-bonding with the combinations of 4 ligand p orbitals as the following:

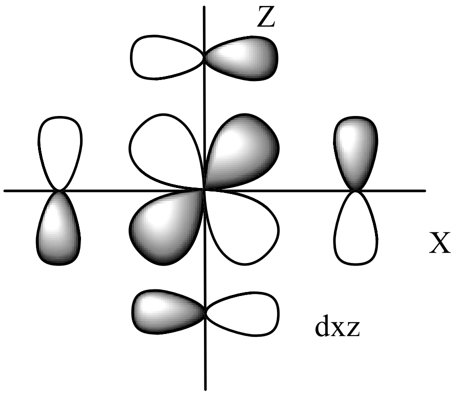


(π)

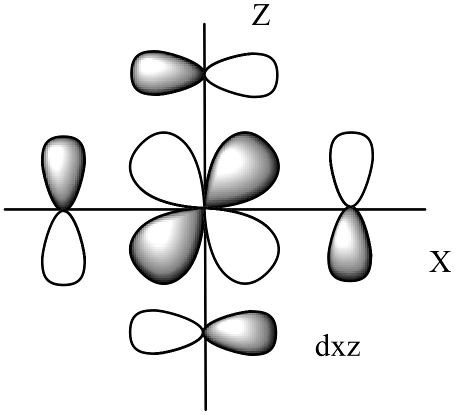


(π*)

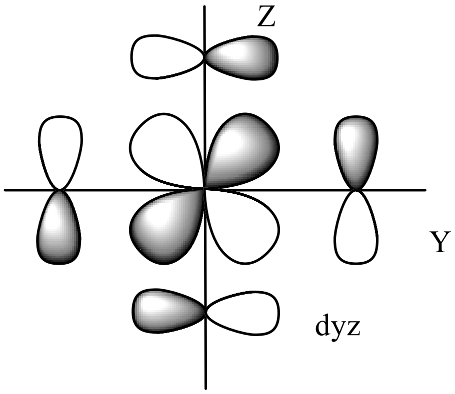
Likewise, the metal dxz and dyz orbitals can form π-bonding with ligand p orbitals.



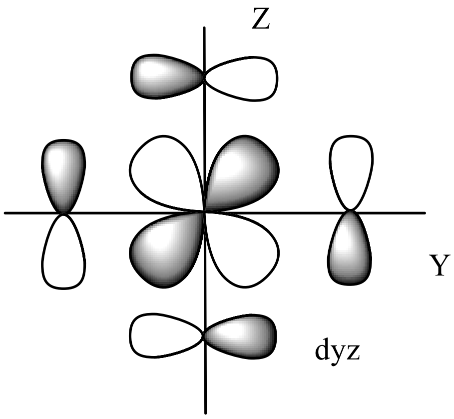
(π)



(π*)



(π)



(π*)

So we can see that the metal t_{2g} orbitals can potentially form π-bonding, if the ligands have orbitals that can form side-by-side overlap with these metal orbitals. We see that ligand p orbitals perpendicular to the axes fulfill this requirement.

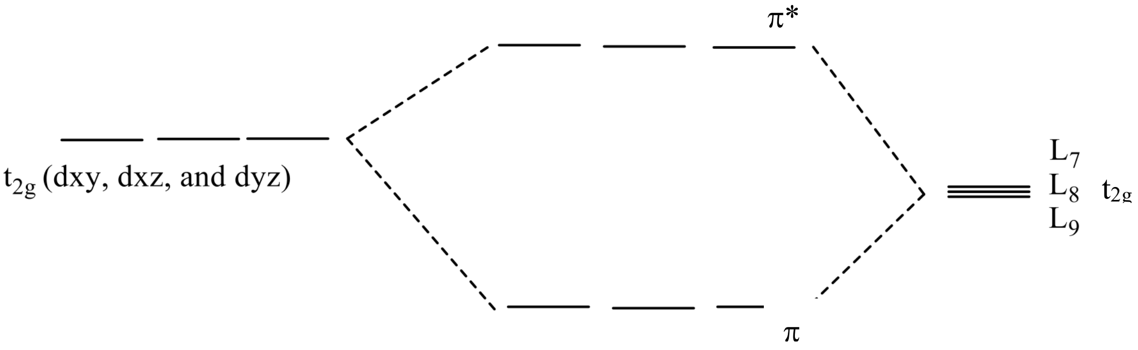
➢ π-Bonding with π-donors ligands

Now we should consider ligands that can be π-donors. These should in addition to having the lone-pairs forming the 6 sigma bonding molecular orbitals have filled p-orbitals that can interact the t_{2g} orbitals of the metal.

π-donors is a ligand that has filled p orbitals that can be used for bonding in a side-on fashion to the metal. For example, ligands like Cl^-, F^-, I^-, and even H_2O, have free lone pair electrons in p orbitals that are available for π-bonding. These available p orbitals can be called ligand π orbitals.

The energy of the filled ligand π orbitals is lower than the metal d orbitals, because the ligand has a higher electronegativity than metal.

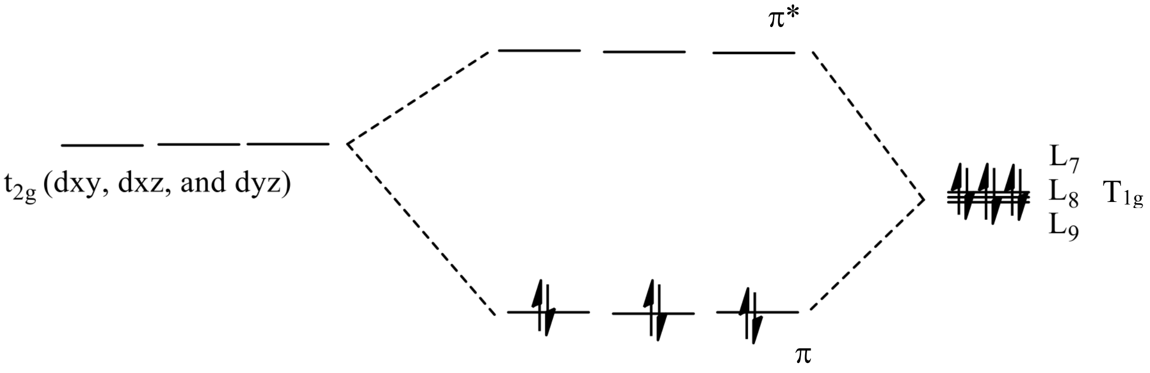
The interaction of metal t_{2g} orbitals with the combinations of ligand π orbitals, which also have t_{2g} symmetry, can be drawn as:



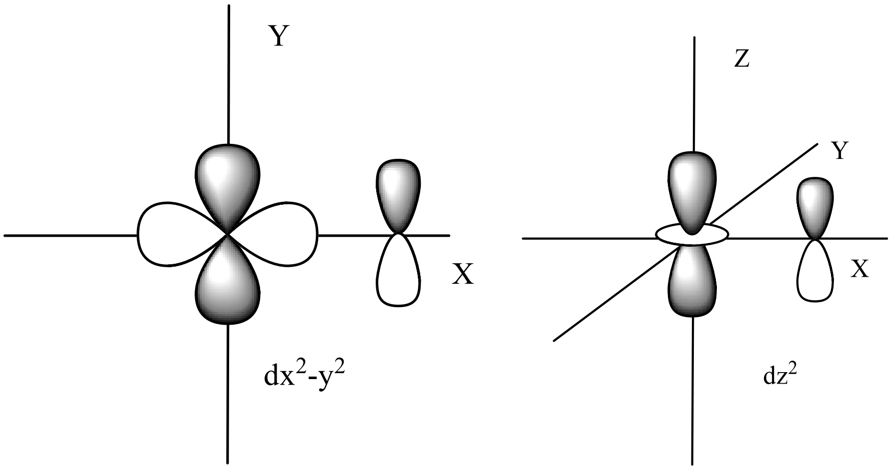
The t_{2g} metal orbitals are no longer non-bonding with π-donors.

L_7, L_8, and L_9 are combinations of ligand π orbitals, just as L_1-L_6 are combinations of ligand σ orbitals.

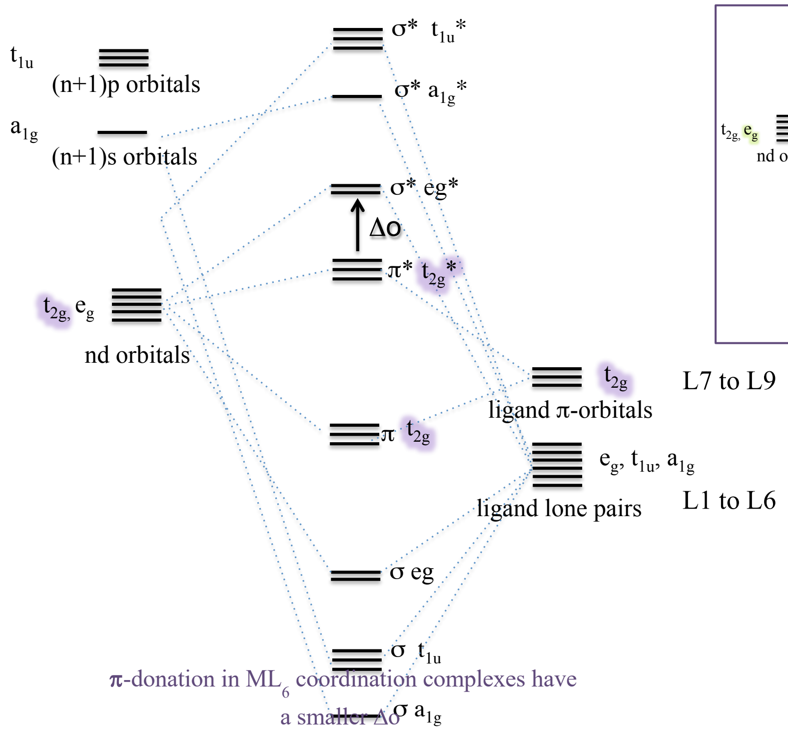
Because the ligand π orbitals are filled with electrons, these electrons then filled the π bonding orbitals, which are mainly based on ligand orbitals. The π* orbitals are antibonding, and are mainly based on metal d orbitals. This kind of bonding is referred as **ligand-to-metal π bonding**.

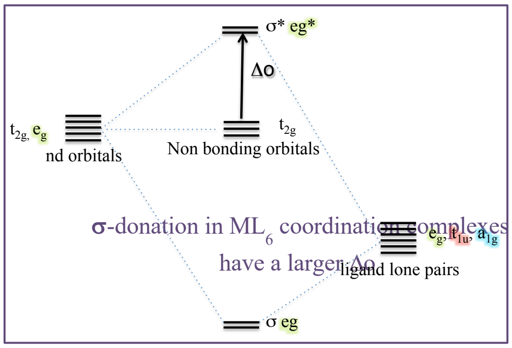


The metal e_g orbitals (dx^2-y^2, dz^2), however, cannot participate in π-bonding, because there is no net overlap with ligand p orbitals.

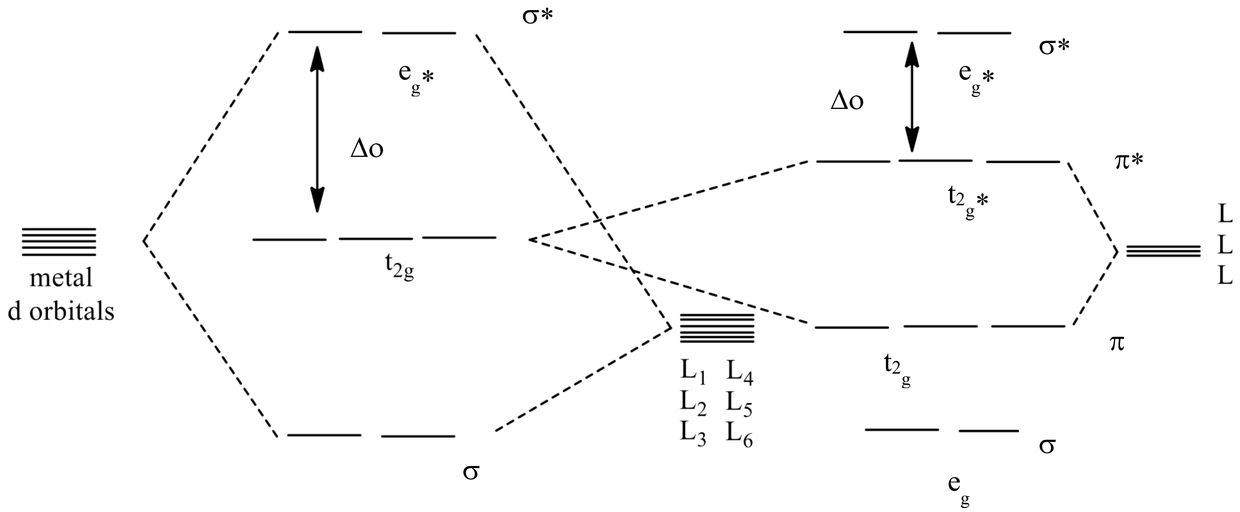


If we add the σ-bonding and the π bonding with filled ligand π orbitals together, we have the ligand field diagram for an octahedral complex with a π-donor ligand as follows:



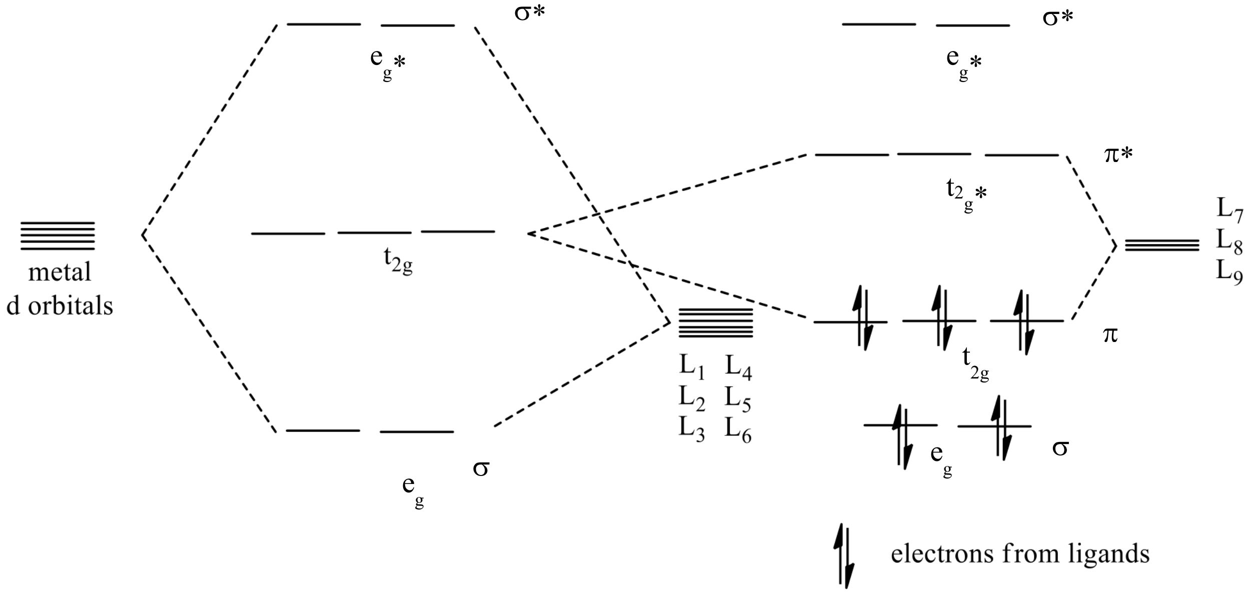


As ligand orbitals L1 to L9 are filled, all the σ and π bonding orbitals are filled with electrons from ligand orbitals as these orbitals have a higher ligand character. The electrons from the metal d orbitals will then occupy the σ* and π* orbitals, which can be considered as the metal e_g (dx^2-y^2, dz^2) and t_{2g} (dxy, dxz, and dyz) orbitals.



Let's now look at the consequence of π-bonding with filled ligand π orbitals on the energy of the metal based t_{2g} and e_g orbitals.

The energy of the metal e_g orbitals stay the same because there is no interaction with the ligand π orbitals. The energy of the metal t_{2g} orbitals is raised due to the π-bonding with ligand π orbitals. As a consequence, the energy difference of the e_g and t_{2g} orbitals is smaller due to π-bonding. The ligand field splitting energy (Δo) is smaller.



We can say that π-donor ligands decrease the ligand field splitting energy.
The decrease of the ligand field splitting energy has an important consequence on the spin state of the metal complexes. We show earlier that the spin states of octahedral complexes of d^4, d^5, d^6, and d^7 depend on the magnitude of Δo and the pairing energy (P). If Δo < P, then the complex has a **weak field**, and the complex is **high spin**. If Δo > P, then the complex has a **strong field**, and the complex is **low spin**.

By decreasing the ligand field splitting energy, π-donor ligands favor high spin configurations for metal complexes.

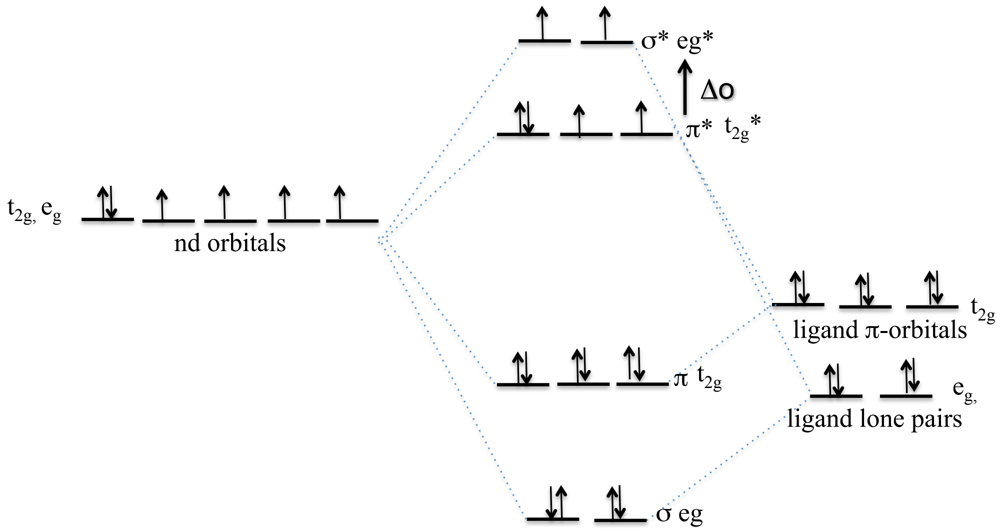
In reality, metal complexes of H_2O, F-, Cl-, Br-, I- are mostly high spin. **For water, the $[M(H_2O)_6]^{n+}$ complexes are always high spin, except for Co^{3+}.**

Exercise: Consider both σ and π bonding, draw the ligand field splitting diagrams of the following complexes assuming they are octahedral. For the metal, only consider the d orbitals but not the unfilled s and p orbitals. Fill all the electrons from the metal d orbitals and the ligand σ and π orbitals.

(1) $[Fe(H_2O)_6]^{2+}$
(2) $[MnCl_6]^{3-}$

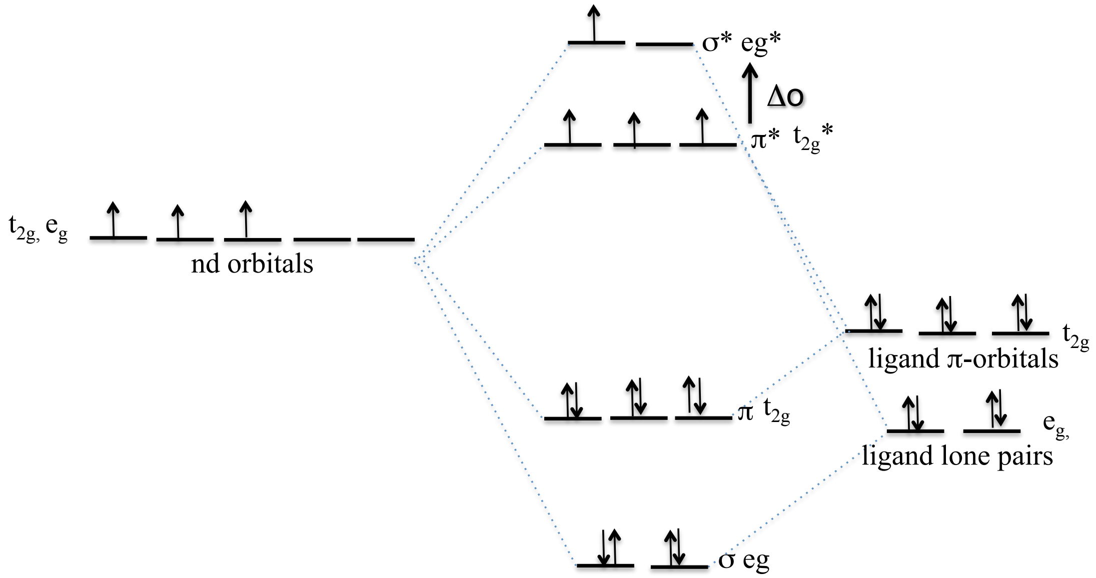
Answer: Both are π-donor that result from a filled p-orbitals. For $[Fe(H_2O)_6]^{2+}$ it is d^6. It must be high spin.

Simplified MO diagram $[Fe(H_2O)_6]^{2+}$



Answer: $[MnCl_6]^{3-}$ is high spin d^4 and again must be high spin.

Simplified MO diagram $[MnCl_6]^{3-}$



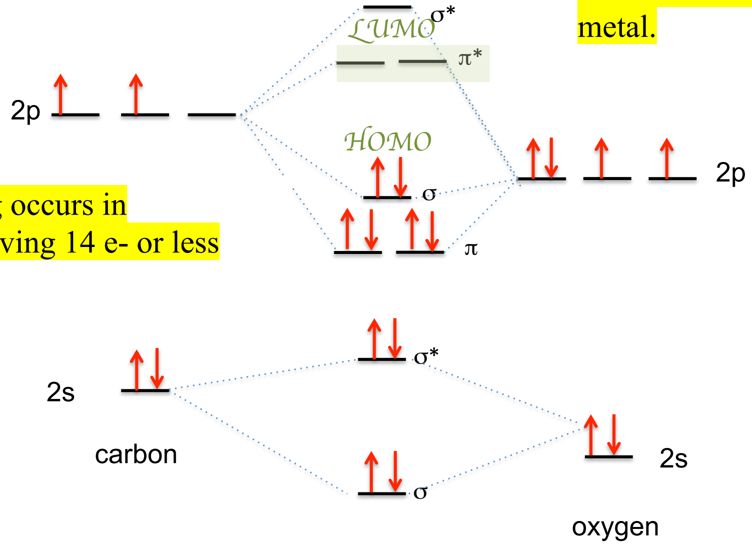
➢ π-Bonding with π-acceptor ligands

Metal ligand π-bonding also exist when the ligands have empty π orbitals. These ligands are called **π-acceptor ligands**. The most typical examples are CO and CN^-.

Exercise: Can you draw the MO diagram for CO?

Answer: The molecular orbital diagram of CO looks like the following:

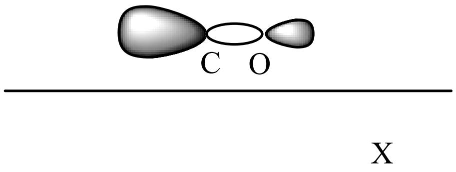
LUMO is empty and can accept donated electron density from the metal.



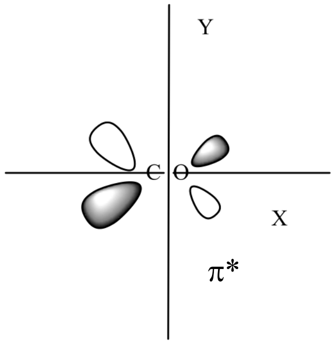
s and p mixing occurs in compounds having 14 e- or less

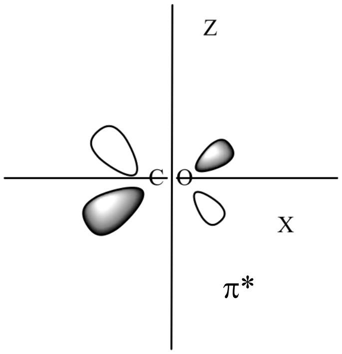
Bond Order is = 3.0.
B. O. = ((# bonding e-) –(# nonbonding e-))/ 2

The highest occupied molecular orbital (HOMO) for CO is a σ-orbital. This orbital is formed by σ-bonding of the carbon and O p orbitals. We can see that there is a lone pair on the carbon. This lone pair can form σ-bonding with a metal. Because the lobe is bigger at the carbon center, almost all metal carbonyl complexes bind through M-C bonds. Let's assume the M-CO bond lines in the x-axis. There are two electrons in this HOMO. It is a σ-donor.



There are two lowest unoccupied molecular orbitals (LUMO) for CO. They have the same energy and symmetry. They are π orbitals, formed by π-bonding of C and O p_y and p_z orbitals.

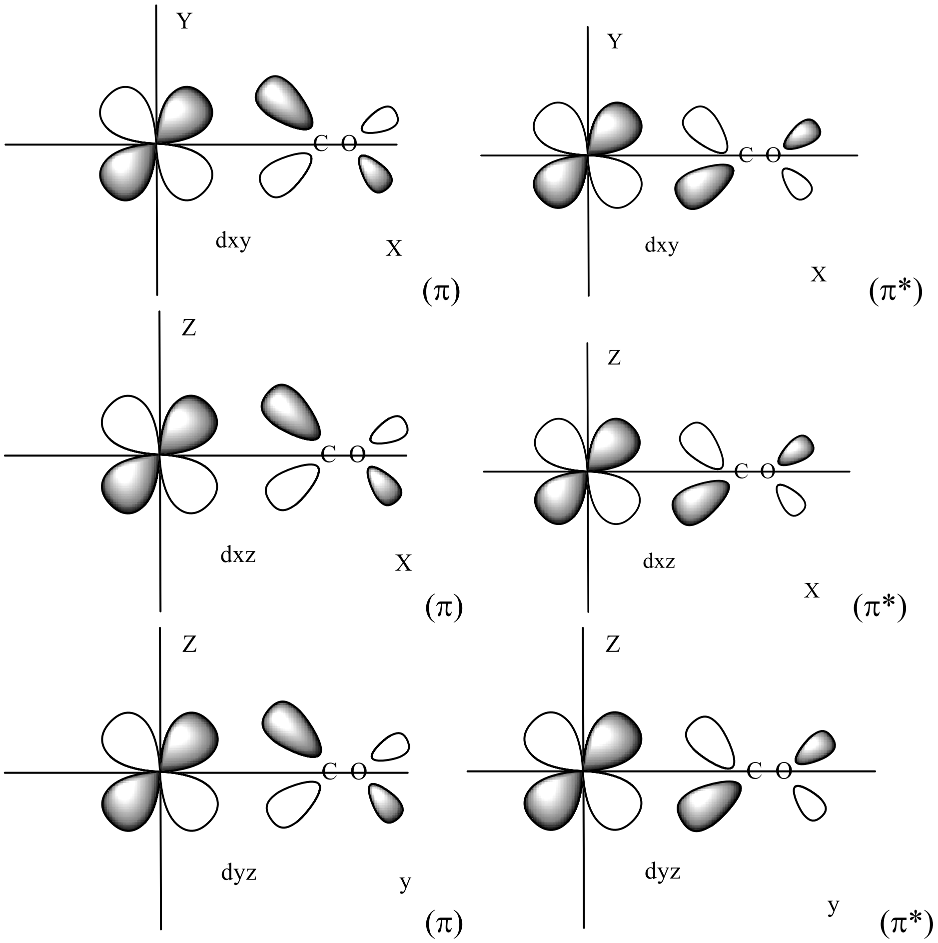




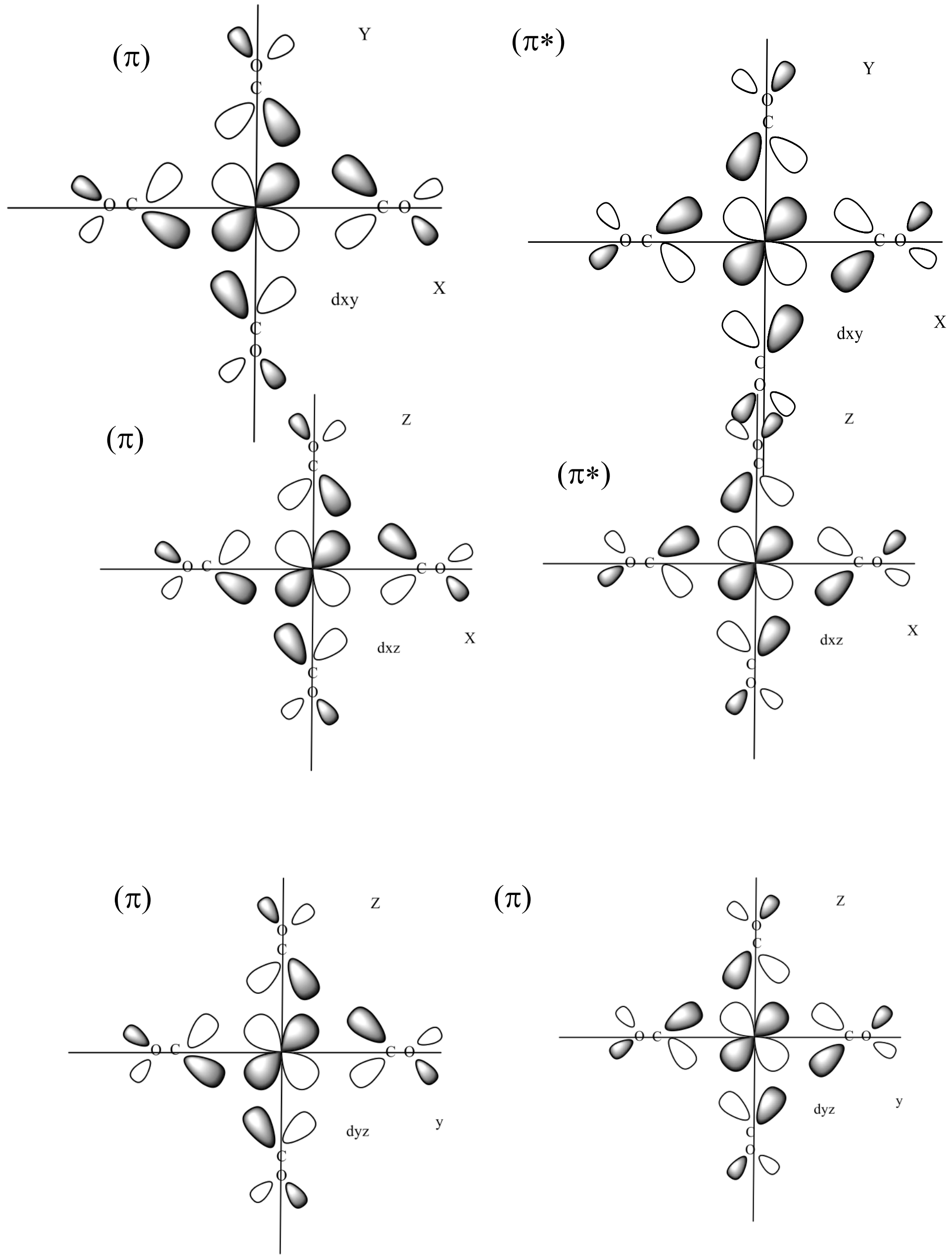
They are located along the y and z axes. These orbitals are empty. They are π acceptors. They are often called π* orbitals of the ligands (* means anti-bonding).

The situation is the same for CN^-. It has a HOMO that is a σ-donor, and two LUMOs that are π-acceptors.

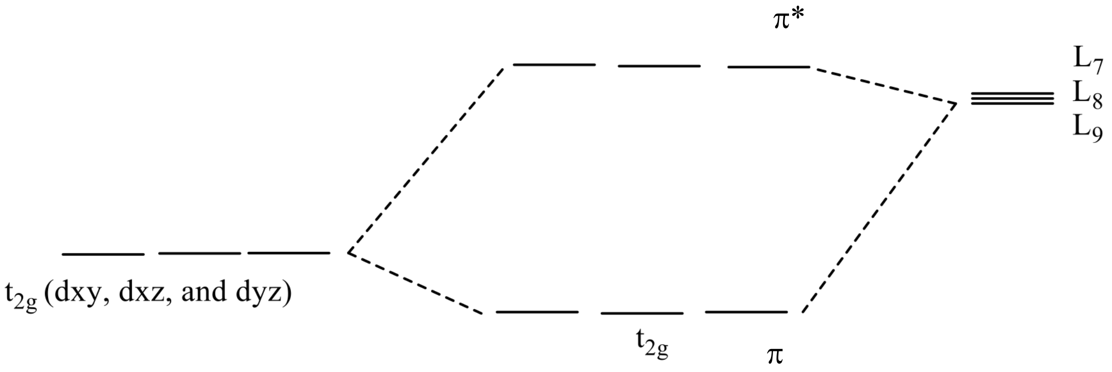
When ligands like CO or CN^- coordinate to metal, in addition to the σ-bonding between the filled σ orbital with the metal e_g orbital, there is the π bonding between the metal t_{2g} orbital with the empty ligand π acceptor orbitals.



For a metal hexacarbonyl complex $[M(CO)_6]^{n+}$, the π-bonding looks like:



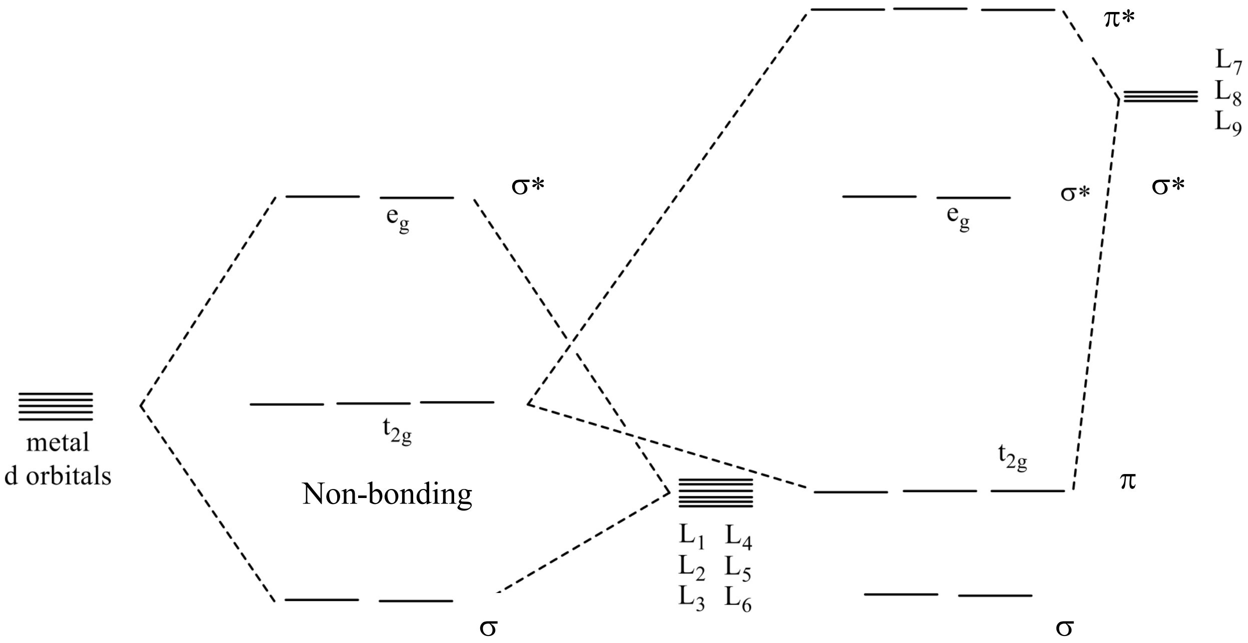
We know that the ligand π* orbitals are empty. **The empty ligand orbitals have higher energies than metal d orbitals.** So for an octahedral complex with 6 π-acceptor ligands, we have:



Where L_7, L_8, and L_9 are three combinations of ligand π* orbitals, as shown in pages 20-22, part II.

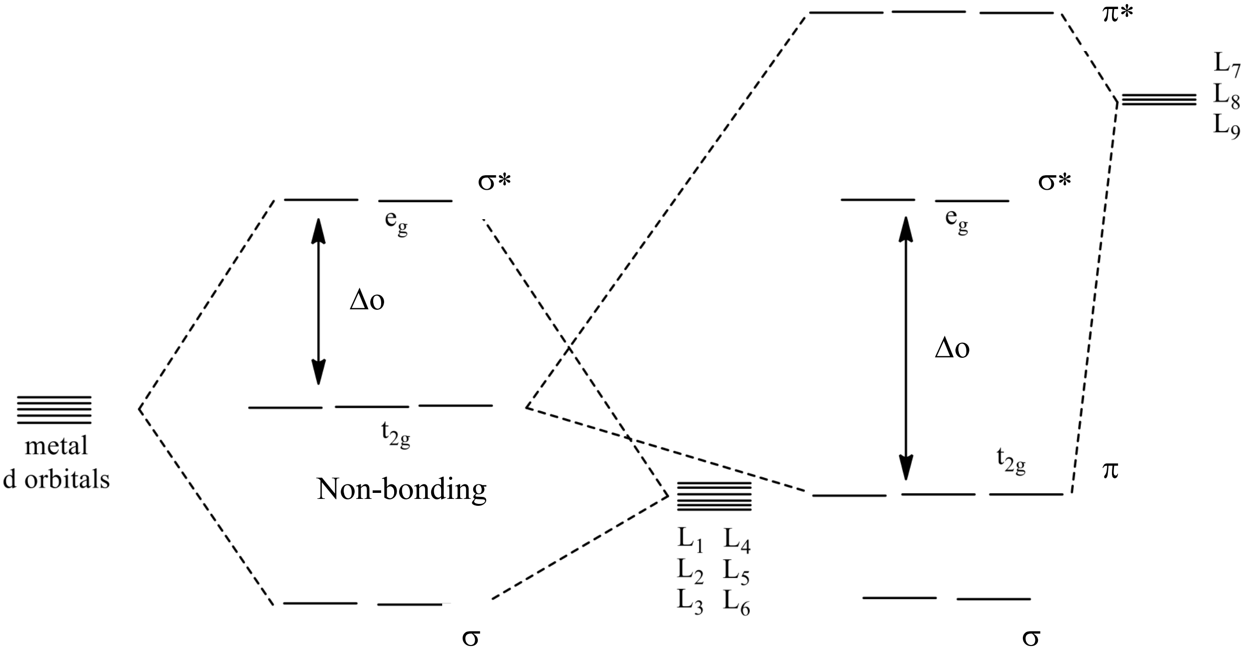
The π molecular orbitals are mostly based on metal t_{2g} d orbitals, and the π* orbitals are mostly based on ligands. This type of bonding is called **metal-to-ligand backbonding**, or simply **π-backbonding**.

If we add the σ-bonding and the π back bonding with empty ligand π orbitals together, we have the ligand field diagram for an octahedral complex as the following:



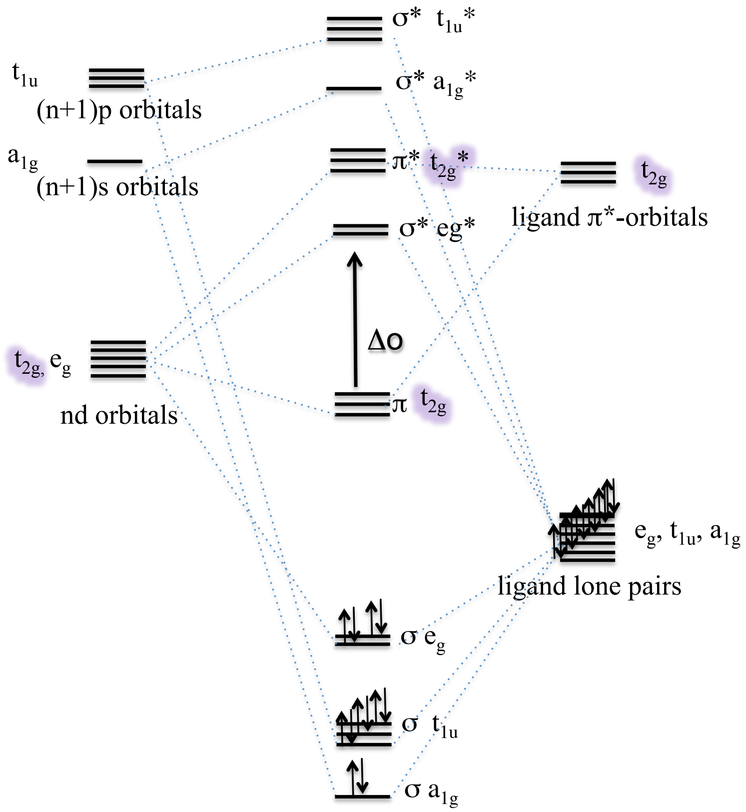
The orbitals labeled t_{2g} and e_g in the above graph are mostly based on metal d orbitals, and for simplicity we can treat them as if they are the metal d orbitals. Because L_7, L_8, and L_9 are empty, there are no new electrons from the ligands that need to be considered.

Let's now look at the consequence of π-bonding with filled ligand π orbitals on the energies of the metal based t_{2g} and e_g orbitals.



The energy of the metal e_g orbitals stay the same because there is no interaction with the ligand π orbitals. The energy of the metal t_{2g} orbitals is lowered due to the π-backbonding with empty ligand π* orbitals. As a consequence, the energy difference of the e_g and t_{2g} orbitals is bigger due to π-backbonding. The ligand field splitting energy (Δo) is bigger. The overall diagram looks like the following:

π-acceptors in ML_6 coordination complexes have a larger Δo



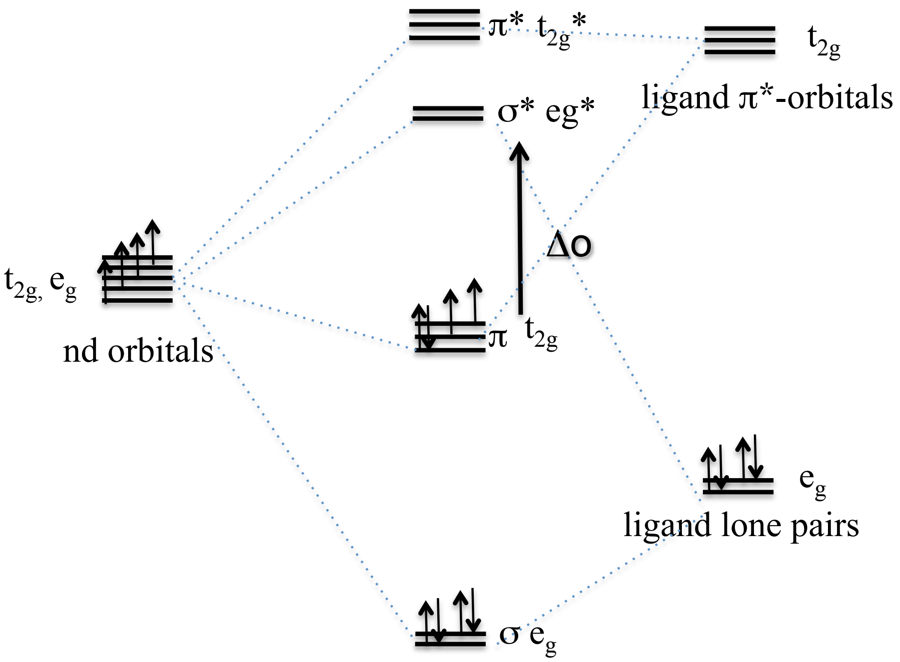
We can say that π-acceptor ligands increase the ligand field splitting energy.
The increase of the ligand field splitting energy also has an important consequence on the spin state of the metal complexes. **By increasing the ligand field splitting energy, π-acceptor ligands favor low spin configurations for metal complexes.**

Therefore, metal CO and CN complexes are often low-spin. Examples of **π-acceptor ligands include Phen, NO^+, N_2, O_2, H_2, PR_3, and alkenes**

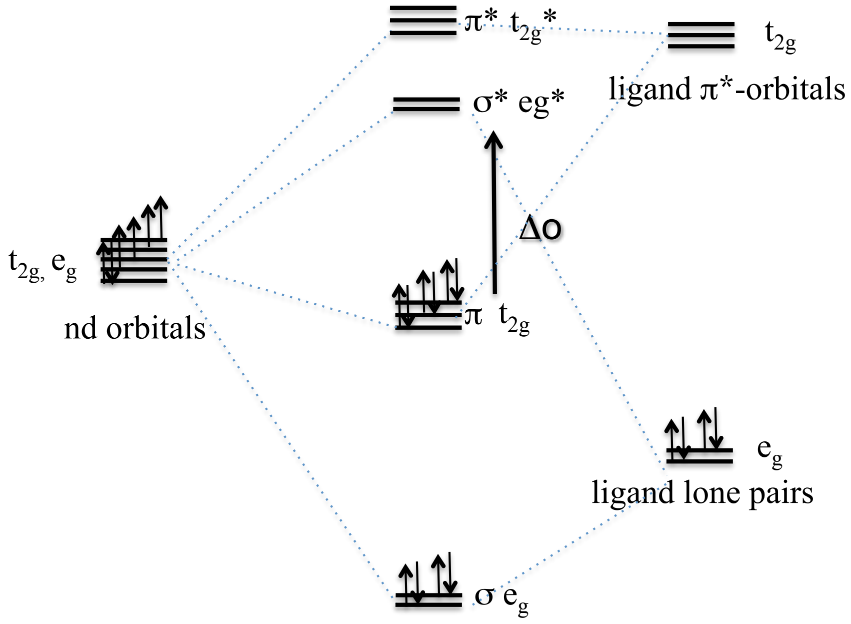
Exercise: Consider both σ and π bonding, draw the ligand field splitting diagrams of the following complexes. For the metal, only consider the d orbitals but not the unfilled s and p orbitals. Fill all the electrons from the metal d orbitals and the ligand σ and π orbitals with symmetry that is the same as the metal d orbitals.

(1) $[Cr(CO)_6]^{2+}$
(2) $[Co(CN)_6]^{3-}$

Answer (1): Cr^{2+} is d^4. So the simplified diagram only including the metal d orbitals is below.



Answer (2): Co^{3+} is d^6. So the simplified diagram only including the metal d orbitals is below.



In summary, ligand field theory can be used to describe π-bonding in metal complexes. Both ligand to metal π-bonding and metal to ligand π-backbonding are possible, depending on the availability of ligand orbitals. π-donor ligands decrease the ligand field splitting energy, and favors high-spin configurations. π-acceptor ligands increase the ligand field splitting energy, and favors low-spin configurations.

5.0 Spectrochemical Series: From a Ligand Field Theory Perspective

The ligand field splitting energy (Δo) can be experimentally determined (by electronic spectroscopy, for example). From the values obtained, some generalizations can be made.

(1) For a give ligand, Δo does not vary much among ions of the first transition series (3d metals) in the same oxidation state. For example, values of Δo for $M(H_2O)_6^{2+}$ are in the range of 7500 – 12000 cm^{-1}.

(2) For a given ligand, Δo increases rapidly with increase in oxidation state of the metal. For example, values of Δo for $M(H_2O)_6^{3+}$ are in the range of 14000 – 25000 cm^{-1}.

(3) For a given ligand, the metal ions can be arranged in order of increasing Δo. This order is more or less independent of the nature of the ligand. The order is:

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} <$
Pt^{4+} Larger Δo leads to low spin complex!

(4) For a given metal, the ligands can be arranged in order of increasing Δo. This order is more or less independent of the nature of the metal ion. The order is:

$I^- < Br^- < \underline{S}CN- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < H_2O < SC\underline{N}^- < py < NH_3 < en < bipy < phen <$
$NO_2^- < PPh_3 < CN^- < CO$ Larger Δo leads to low spin complex!

The order series in (3) and (4) are called **spectrochemical series**.

For the order in metals, you are required to remember that a metal ion in a higher oxidation state has a bigger Δo.

And you should remember the order in ligand. It is very easy to remember if you can rationalize the order. How?

The ligand field theory we just learned can indeed be used to explain this order qualitatively. Ligands can be divided into three classes: π-donor, pure σ-donor, and π-acceptor. We know that π-donor decreases Δo, and π-acceptor increases Δo.

In the ligand spectrochemical series, on one end, we have π-donor like I^-, Br^-, Cl^-, and F^-, OH^-, and OH_2. The anionic ligands are better π-donors than the neutral water. And among the halides, the bigger ions are more likely to donate the electrons in the π orbitals. Therefore, the Δo has the order: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O$.

On the other end of the spectrochemical series, we have π-acceptor ligands, such as CO, CN^-, PPh_3, NO_2^-, and Phen. CO and CN^- are strong π-acceptors than PPh_3, which is a stronger π-acceptor than NO_2^- and Phen. Therefore, the Δo has the order: phen $< NO_2^- < PPh_3 < CN^- <$ CO.
And then we have ligands like NH_3, en, py, which have weak or no π-bonding with metals. They situate in the middle of the spectrochemical series.

The magnitude of Δo has a consequence in the spin state of the metal. A large Δo favors the low-spin configuration, and a small Δo favors the high-spin configuration.

For first-row metal complexes (3d elements), the border line is Phen. With ligands that are stronger π-acceptors than Phen, the complexes are often low-spin. With ligands that are weaker π-acceptors, pure σ-donors, or π-acceptors, the complexes are often high-spin.

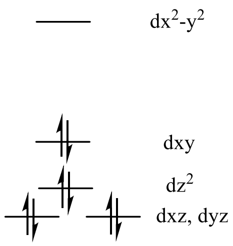
However, with the second and third row transition metals (4d and 5d), almost all octahedral complexes are low-spin. This is because these metals have big radii. As a result, the electrons have more space to occupy near the nuclei, and the pairing energy (P) is then always smaller than Δo < P. Second, the orbitals being more polarizable have a much easier time forming more strong covalent type bonding that leads to larger splitting. Therefore, the complexes prefer a low-spin configuration.

The above discussion is on octahedral complexes. **For tetrahedral complexes, because Δt is much smaller (as explained in Chapter IV, part I, Δt = 4/9 Δo), they are almost always high-spin.**

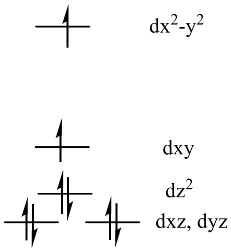
For square-planar complexes, the ligand field splitting energy (Δsp) is the energy difference between dx^2-y^2 and dxy (same as the crystal field theory). The dxy orbital can form π-bonding. Like in octahedral complexes, π-donor decreases Δsp, and π-acceptor increases Δsp. π-acceptor ligands favor low-spin configuration.

For 2nd and 3rd row metals, the pairing energy (P) is small, and electrons tend to fill up all the other orbitals before dx^2-y^2. For this reason, square planar complexes of 2nd and 3rd row transition metal ions are normally low spin.

Attention: It is not always easy to predict the geometry for 4-coordinate complexes. In general, tetrahedral structure is preferred unless there is a special stabilization for square planar case. This is because there is less steric interaction for ligands in tetrahedral complexes than in square planar complexes. **Special stabilization for square planar comes in the case of d8 configuration for certain scenario.** If a square planar d8 complex is low spin, then there is a huge stabilization due to the occupation of all lower-energy orbitals. In this case, square planar is more stable than tetrahedral. As 2nd and 3rd row transition metals have lower pairing energies, their square planar complexes are low spin, and thus, have the extra stabilization energy. Therefore, 2nd and 3rd row 4-coordinate d8 complexes are square planar rather than tetrahedral. For first-row transition metals, their square planar complexes can be either low spin or high spin. π-acceptor ligands favor low-spin, and π-donor ligands favor high spin. So for first row transition metal d^8 4-coordinate complexes, if there are strong π-acceptor ligands such as CO and CN-, the square planar geometry gives low spin, has the extra stabilization energy, and is more stable than tetrahedral geometry. If they don't have strong π-acceptor ligands, then they are high spin. In this case, the square planar geometry is less stable than the tetrahedral geometry.



low spin
very stable



high spin
not stable