Molecular Orbital Diagrams for TM Complexes with π-donor and π-acceptor ligands

Beyond sigma ligands: π-donor and π -acceptor ligands

1st year course "Coordination Chemistry"

- ligands can be classified into a number of **ligand types**:
  - σ-donor ligands, (NH_3, py, en, CH_3^-, H^-) (done!), **Figure 1**
  - π-donor ligands which donate an electron from a p-orbital (halides, O, OR, OH^-, OH_2, RCO^{2-}, S SR, N, NR, NR_2^-, P), **Figure 2**
  - π-acceptor ligands which can accept electrons into an empty π*-orbital, (CO, CN, NO, NO_2^-, NCS^-, N_2, O_2, PR_3, BR_2)
  - there are also ligands that are both π-donor and π-acceptor ligands, (alkenes and alkynes) the bonding in these systems is sometimes called Dewar-Chatt-Duncanson bonding, **Figure 3**

2nd year course "TM and Organometallic Chemistry"

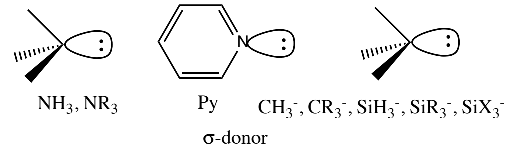


Figure 1 σ-donor ligands

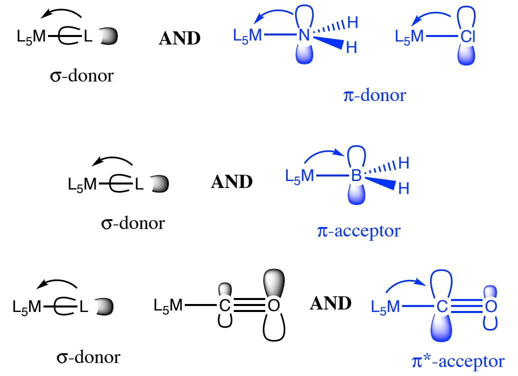


Figure 2 π-donor and π-acceptor ligands

3rd year course "Advanced Organometallics"

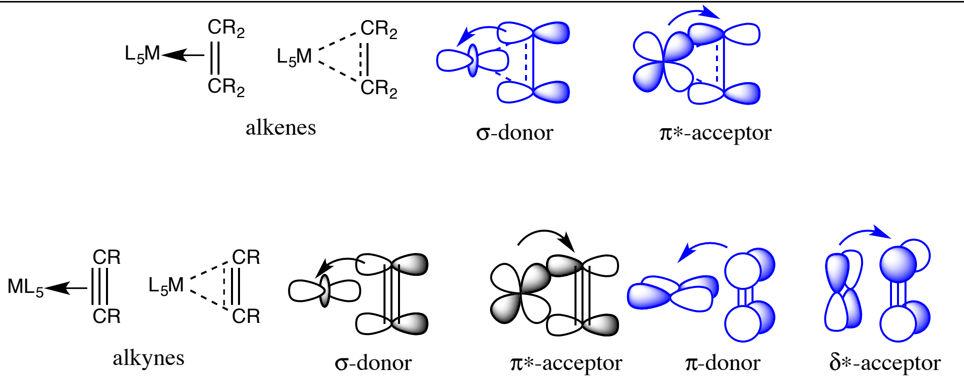


Figure 3 Dewar-Chatt-Duncanson bonding

In-Class Activity

- On each of the MOs shown in Figure 3 identify the "symmetry" of the M-L interaction and the symmetry of the internal ligand .

The sigma-framework

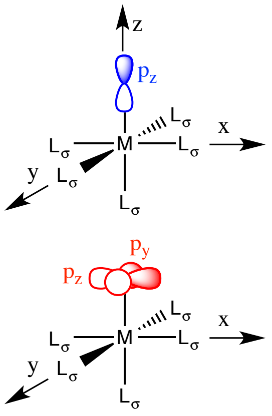


Figure 4 "new" p_π FOs

- all ligands have σ-bonding interactions, as a first approximation we assume there is no significant alteration in the shape and energy of the σ-bonding MOs, and thus we can use the octahedral σ-ligand MO diagram as a base, **Figure 4**
- however the symmetry of the TM complex is reduced from octahedral and thus the **symmetry labels do change**
- we will work through a example now, tracing the effects of changing a single σ-donor ligand from L_σ into a π-donor ligand L_π (Cl)
    - the underlying σ-framework remains the same while the point group is reduced to C_{4v}, **Figure 5**

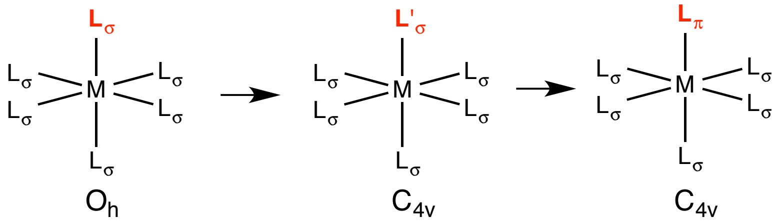


Figure 5 progression from basic O_h MO diagram

- last lecture we went through the process of determining the change in symmetry labels for the σ-framework MOs under C_{4v}, **Figure 6** just reproduces **Figure 22/23** from last lecture

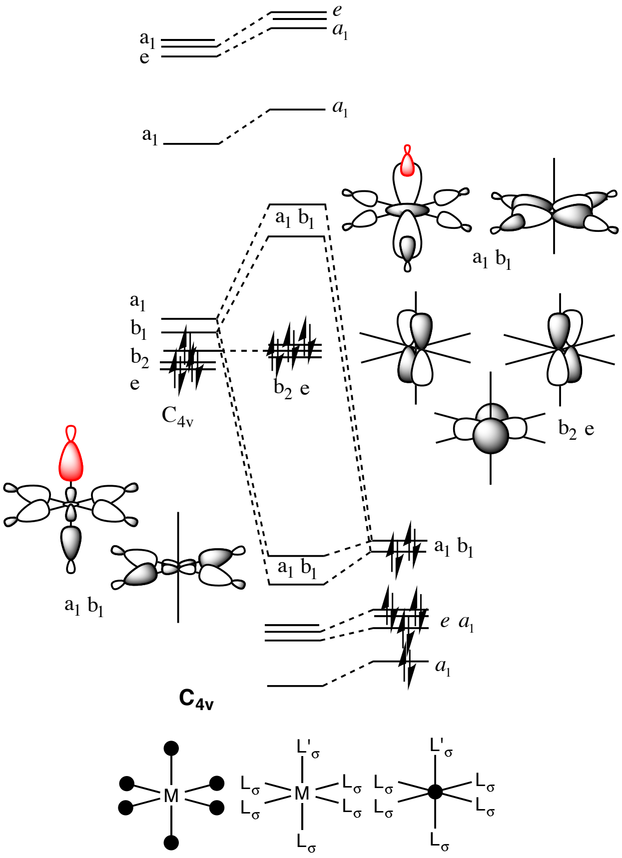


Figure 6 C_{4v} sigma framework energy level diagram

Including a π-donor Ligand

- use Cl as an example of a π-donor ligand
    - the p_z AO on Cl contributes to the σ-donor framework, represented in blue in **Figure 4/Figure 7**
    - the p_x and p_y FOs, will form new interactions with the dAOs, represented in red in **Figure 4**
    - these FOs have the same symmetry as the x and y axes and hence have an e symmetry label under the C_{4v} point group.
    - the π-donor pAOs (p_x and p_y) are non-bonding and hence are slightly higher in energy than the σ-framework FO

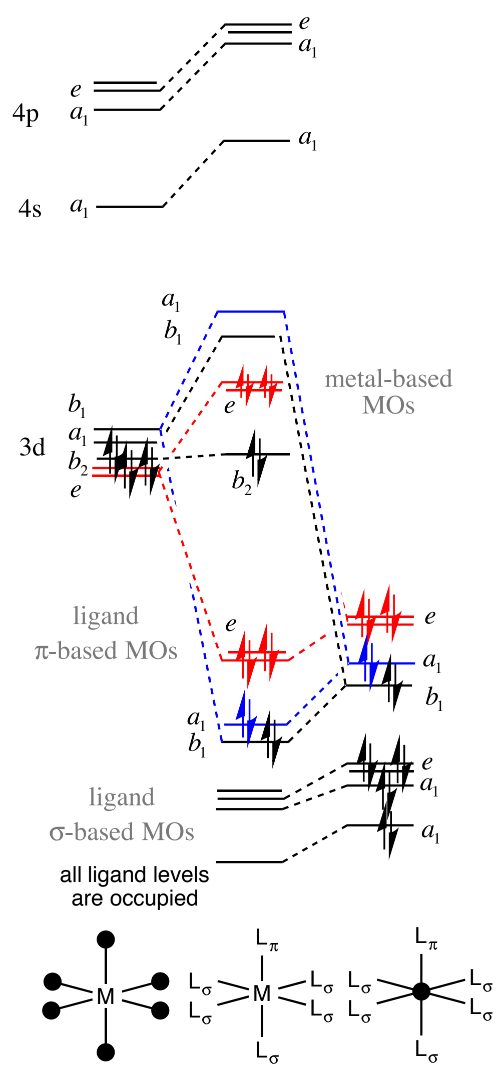


Figure 7 π-donor ligand energy level diagram

- the new π-donor FOs (e) form new bonding and antibonding combinations with the e dAOs, **Figure 7**
    - the energy match between the dAOs and the ligand π-donor FOs can be slightly better than for the σ-orbitals
    - but the overlap is π-type (d-p interaction) and is not as good as σ-type overlap
    - thus overall there is not a large splitting
- to simplify **Figure 7** I have:
    - left off some of the interaction lines for the highest and lowest energy MOs, left off some of the electrons and slightly split the degenerate FOs to emphasise the different symmetry labels (these are still degenerate!)
- because these diagrams are very complex, only important MOs are drawn as shown in **Figure 8**

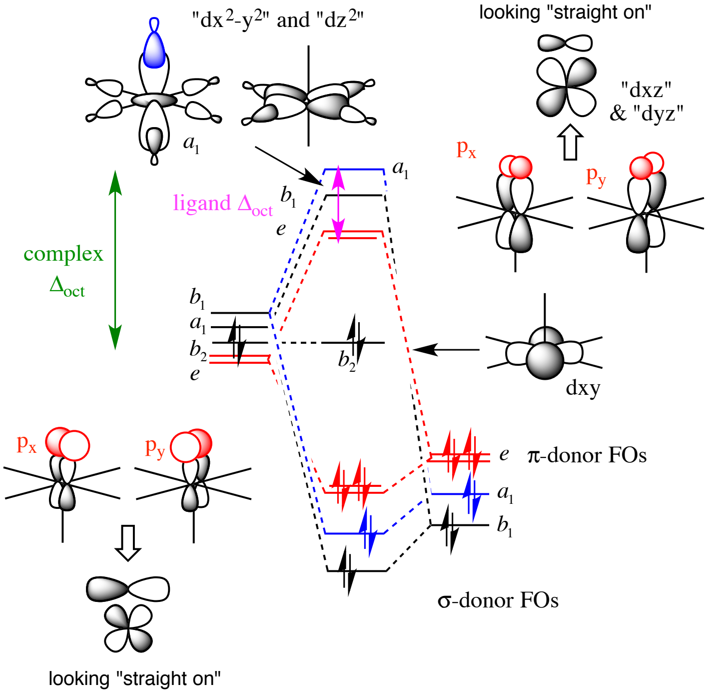


Figure 8 Important MOs for the π-donor ligand TM-complex

- the octahedral splitting parameter
  - in octahedral complexes the Δ_{oct} is splitting of the dAO based MOs
  - in reduced symmetry and mixed complex ligands Δ_{oct} is less well defined, however for ease of reference we often refer to the lower symmetry MOs as being associated with the "t_{2g}" and "e_g" sets they are derived from.
  - thus under C_{4v} the b_2 and e are associated with "t_{2g}" and the a_1 and b_1 are associated with "e_g"
  - in this complex we can differentiate between the Δ_{oct} of the σ-ligands (green in **Figure 8**), and Δ_{oct} of the π-donor ligand (pink in **Figure 8**)
  - the octahedral splitting for a π-donor ligand is generally smaller than that for pure σ-donor ligands (from empirical evidence!)
  - π-donor ligands have the additional set of FOs which interact with the metal, these have the effect of raising the energy of the (previously) non-bonding dAOs, and thus closing the energy gap with the antibonding (σ-based) dAOs.
  - the exact positioning of the energy levels will depend on the π-donor ligand and a number of other influences such as the precise nature of the σ-donor ligands, the metal and its oxidation state and the overall charge on the complex
  - we still call this Δ_{oct} by convention, even though the molecule is not octahedral. You will also see when we move onto treat 6 π-donor ligands (next Lecture) why calling it Δ_{oct} still makes sense.

The spectrochemical series

- last year **crystal field theory** was presented
  - negative point charges are placed equidistant on the x,y and z axes, **Figure 9**
  - these charges repel the dAO electrons, the dAOs that lie along the axes (dx^2-y^2 and dz^2) are destabilised more than those that point between the axes (dxy, dyz and dxz)
  - this causes splitting of the dAOs into two manifolds, the t_{2g} and the e_g and the extent of splitting is given by the octahedral splitting parameter, Δ_{oct}
  - the size of Δ_{oct} depends on the strength of the interaction between the ligand and metal

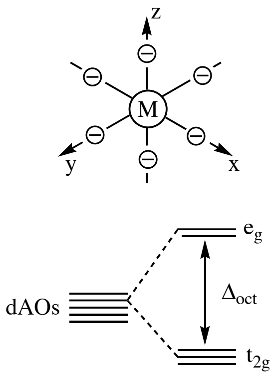


Figure 9 crystal field theory

- the colour of a TM compound often depends on the octahedral splitting
  - for example the colour of rubies and emeralds is due to this effect, **Figure 10**
  - the colour of rubies is due to a few Cr^{3+} ions taking the place of Al^{3+} ion in Al_2O_3
  - the colour of emeralds is due to a few Cr^{3+} ions occupying the octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$)
  - in both minerals the Cr^{3+} ions are in an octahedral environment surrounded by O^{2-}

Figure 10 red ruby and green emerald

- the **spectrochemical series** has been obtained by studying complexes and ranking them based on the empirically (spectroscopically) determined size of Δ_{oct}

$$I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < O^{2-} < H_2O < NH_3 < en < NO_2^- < CH_3^- < C_6H_5^- < PPh_3 < CN^- < CO$$

Figure 11 some ligands in the spectrochemical series

- a problem with the crystal field theory is that anions, and dianions should produce the largest splitting (due to e-e Coulomb repulsion), however neutral ligands like CO produce the largest Δ_{oct}!
- how ligands like CO produce such a large octahedral splitting cannot be explained using crystal field theory, we require **molecular orbital theory**

Including a π*-acceptor Ligand

- CO is an example of a π-acceptor ligand
- you will be studying complexes with CO ligands extensively in your “TM and Organometallic” chemistry course
  - for example: $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$.
  - $Mn_2(CO)_{10}$ is an interesting compound because it contains both a M-M bond and π-acceptor ligands, **Figure 12**

2nd year course "TM and Organometallic Chemistry"

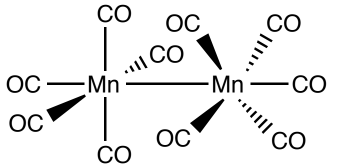


Figure 12 Structure of $Mn_2(CO)_{10}$

- you have already studied the MO diagram of CO in 1st year and previously within this course, **Figure 13**
- CO contains the 5σ σ-bonding FO as well as the 1π π-donor FOs, in addition there are the higher lying empty 2π* π-acceptor FOs

1st year chemical structure course

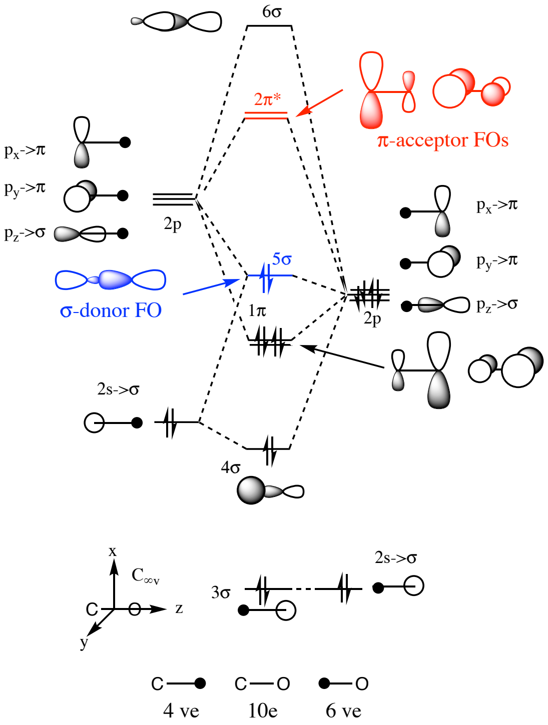
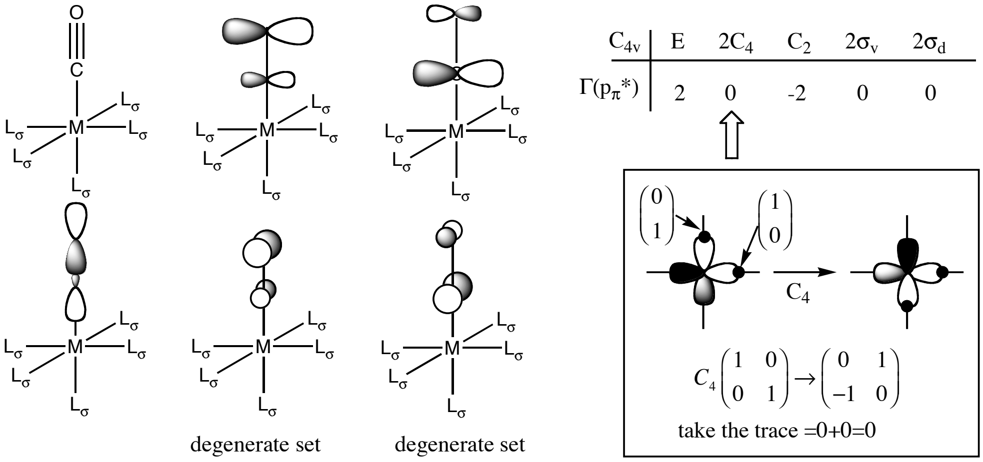


Figure 13 MO diagram of CO



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\Gamma(p_\pi{*})$	2	0	-2	0	0

$$C_4\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\rightarrow\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}$$

Figure 14 (a) $M(L_\sigma)_5CO$ and the FO involved in TM bonding and (b) the irreducible representation of the $2\pi*$ orbitals

- the relevant CO FOs for the TM diagram are summarised in **Figure 14(a)**
    - the 5σ-FO of CO is encapsulated within the σ-manifold of the complex
    - the symmetry labels for the CO ligand 2π∗ FO transform as e under C_{4v}, **Figure 14(b)**
- the energy level diagram for this complex (**Figure 15**) is based on that of the octahedral complex but with reduced symmetry
    - to simplify the diagram I have spread the degenerate orbitals slightly, left some of the interaction lines off and left off some of the electrons!!
- the filled π-donor FOs (1π) lie below the 5σ in CO, however often the π-FOs are shown above the σ-FOs (blue energy levels in **Figure 15**). Why? This is because the 5σ are participating in σ-manifold which can lower the energy. However, we should treat the π- and σ-donor FOs as being very close in energy.
- we now add the π∗-ligand orbitals (e) of CO which lie *slightly above and very close* to the TM dAOs, they are at just the right energy to interact strongly with the TM dAOs (red energy levels in **Figure 15**)

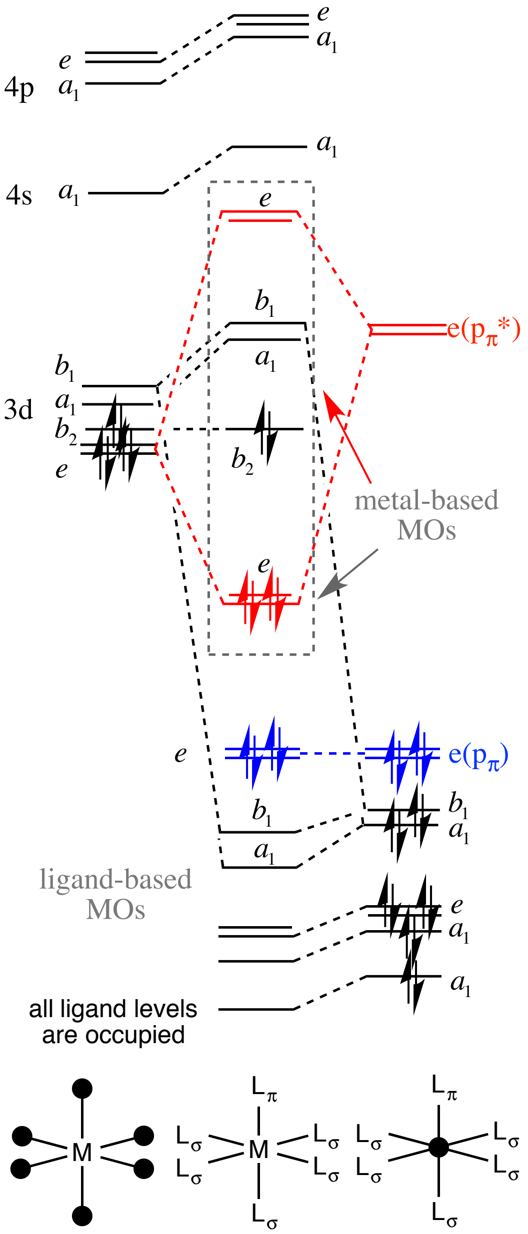


Figure 15 π∗-acceptor ligand energy level diagram

- the metal dAOs prefer to interact with the closer 2π* FOs, (red), the 1π orbitals of CO lie deeper in energy and now remain non-bonding (blue).
- there is no significant mixing between the non-bonding ligand e(p_π) MOs and the metal based e MOs as both orbitals are occupied
- the ligand π* FOs and dAOs form a bonding/antibonding pair, **Figure 16**
  - there is a strong interaction and the MO splitting energy is relatively large
  - because the ligand energy levels for the π* FOs are above the dAOs, the dAO based MOs are the lower energy *bonding MOs* (with respect to the ligands)

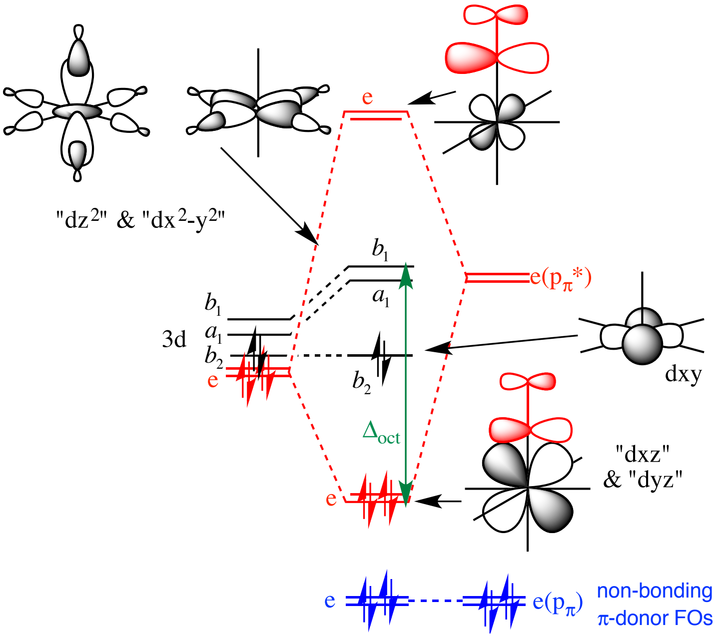


Figure 16 Important MOs for the π-acceptor ligand TM-complex

- the octahedral splitting parameter
  - the octahedral splitting for a π-acceptor ligand is generally very large, much larger than that for pure σ-donor ligands.
  - the energy match between the dAOs and the ligand π*-acceptor FOs is very good leading to strong splitting
  - the MOs that are considered "dAO" based has changed
  - the ligand π*-acceptor FOs lie above the dAOs, this means the dAOs are now the dominant contributor to the bonding e-MOs and not the antibonding e-MOs, **Figure 16**

Octahedral splitting and the spectrochemical series

- we are now ready to explain the ordering observed in the spectrochemical series, as we can now compare Δ_{oct} for σ-donors, π-donors and π-acceptors in detail, **Figure 17**

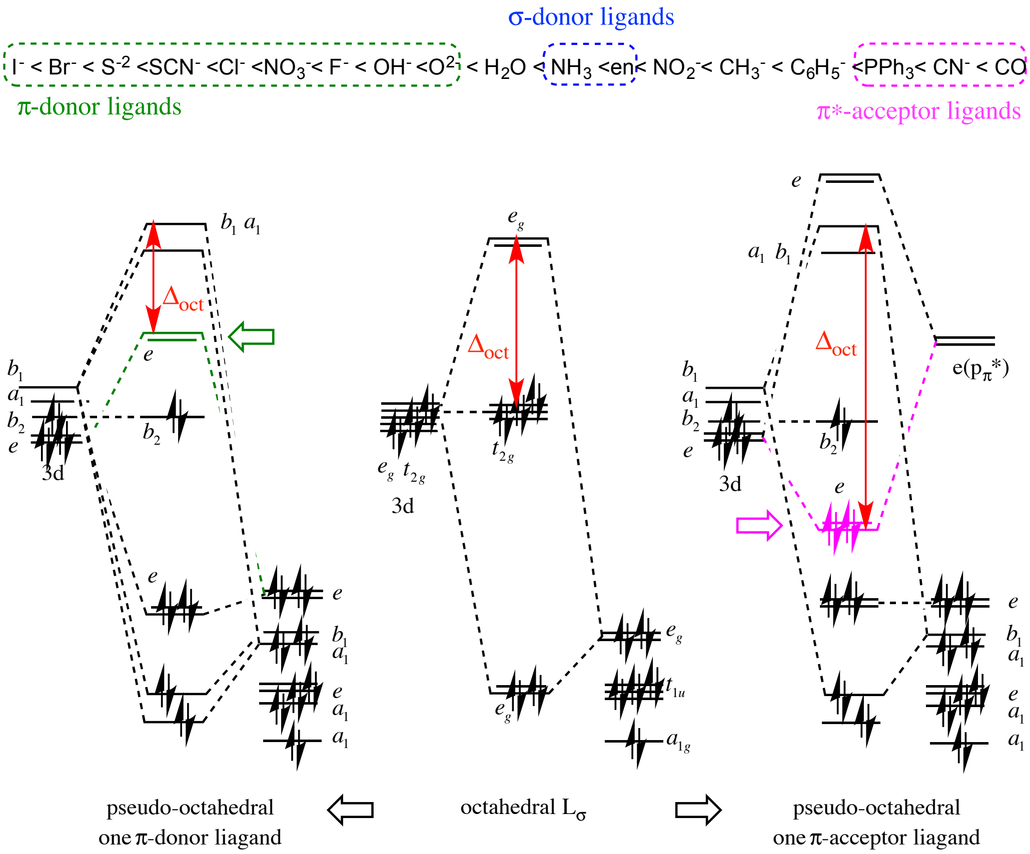


Figure 17 Comparing ligands from the spectrochemical series and the associated change in Δ_{oct}

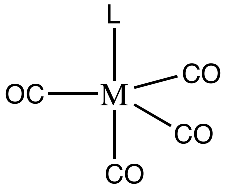
- when there are purely σ-donor ligands (such as NH_3 or NR_3) the familiar e_g above t_{2g} pattern of dAOs is derived, the strength of the interaction is determined by the relative energy (Δε) and overlap (S_{ij}) and H_{ij} of the ligand σ-FOs with the metal dAOs.

IMPORTANT

- when π-donor ligands (such as Cl^-, Br^- I^-) are introduced the additional π-donor FOs, which lie *below* the dAOs in energy, interact. The key MOs are the dAO dominated antibonding e MOs which are destabilised relative to the non-bonding dAOs, thus reducing Δ_{oct}.
- when π-acceptor ligands (such as CO or CN^-) are introduced the additional π*-FOs which lie *above* the dAOs in energy, interact. The key MOs are the dAO dominated bonding e MOs which are stabilised relative to the non-bonding dAOs, thus increasing Δ_{oct}. Δ_{oct} is dramatically increased because the π-acceptor and dAOs are very close in energy and interact strongly.
- notice that the non-bonding dxy (t_{2g} or b_2) orbital remains constant for all three examples, this is because we have introduced only one π-acceptor or π-donor ligand.

CO and other iso-electronic π-acceptor ligands

- CO ligands are very useful for characterising the amount of back donation in *other* ligands
  - the vibrational IR spectrum of CO, and in particular the peak associated with the C-O stretch is very sensitive to the amount of back donation
  - as other ligands "take" some of the finite amount of electron density, back-donation into CO decreases and the CO vibrational peak moves to lower wavenumber



L=CO,CN$^-$,NO$^+$

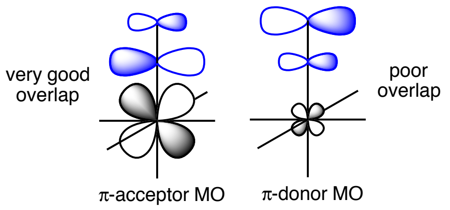
Figure 18 ML$(CO)_4$ complex

complex	σ-donation	π-acceptance
$Fe(CO)_4CN^-$	0.62	0.08
$Fe(CO)_4CO$	0.47	0.29
$Fe(CO)_4NO^+$	0.19	0.42

Table 1 **Data from the CDA analysis for equatorial CN$^-$, CO and NO$^+$ ligands**[1]

- this is a very qualitative explanation, how can we quantify the amount of forward and back donation a ligand contributes?
  - carry out a calculation and perform a population analysis! This tells us how much of the electron density is on the metal and how much is on the ligand, and even which orbitals it ends up in **Table 1.**
  - NO$^+$ is one of the strongest π-acceptors, but σ-donation is poor
  - CN$^-$ is a poor π-acceptor however it is a strong σ-donor
  - we can deduce that if the energy of the π* orbitals line up well with the TM dAOs, this tends to mean that the σ-orbitals have a poor match, and vice vera
  - the carbonyl ligand has an almost optimal orbital alignment and is a strong σ-donor AND good π-acceptor.
- we know that along with a small difference in FO energies (Δε) a good overlap (S_{ij}) is required for a strong interaction
  - CO has a large contribution on the O atom for the bonding π-FO and a very small contribution on the O for the antibonding π*-FO
  - this has the effect of substantially strengthening the dAO-π*-acceptor MO overlap, **Figure 19**
  - other homonuclear diatomic ligands do not have this advantage, for example N_2 and O_2 have equal orbital contributions, which reduce the dAO-π*-acceptor interacton

CO ligand



O_2 ligand

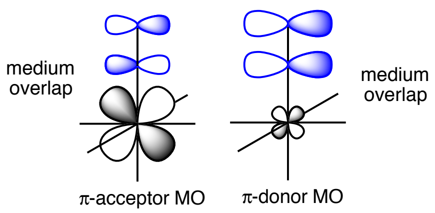


Figure 19 orbital size matters

---

[1] Y. Chen, M Hartmann and G. Frenking, *Z. Anorg. Allg. Chem.*, **2001**, Vol 627, p985

Key Points:

- be able to draw the energy diagram for a transition metal complex with sigma-bonding ligands and pi-donor or pi-acceptor ligands
- be able to draw and describe the important MOs for these diagrams, and be be able to discuss key features of these diagrams
- be able to describe crystal field theory, and discuss the empirical spectrochemical series and be able to explain the contradiction that arises between these two
- to be able to discuss key properties that impact on or effect the octahedral splitting parameter (such as energy alignment, orbital overlap, symmetry)
- to be able to compare and contrast the size of the octahedral splitting parameter and relate this information back to the spectrochemical series and in particular σ-donor, π-donor and π-acceptor ligands.

Self-Study Problems / Exam Preparation

- In what situations is the value of Δ_{oct} difficult to identify?
- Why is it easy for the oxo ligand O^{2-} to convert between a double and triple bond with a metal?
- O_2 can coordinate to the the TM end on or side on, what type of ligand is O_2 in each orientation?
- Draw out the possible M-O_2 dAO-FO interactions for O_2 interacting side-on, label each component of the interaction, **Figure 20** is an example for you.
- Draw the relevant MOs for O_2 coordinated to a TM end on (linear), clearly show what type of ligand O_2 is for this orientation.

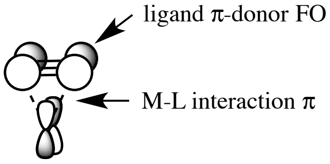


Figure 20 example illustrating labelling the ligand FO and the M-L interaction type

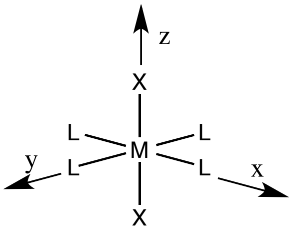


Figure 21 ML_4X_2 where X are a π-donor ligands positioned axially

- Extra for experts! What happens to the MOs when the O_2 bends away from linear?
- Draw the relevant MOs for O_2 coordinated to a TM side on, clearly show what type of ligand O_2 is for this orientation.
- What type of ligand is H_2O? Draw a diagram showing the M-OH_2 orbitals that will interact. Explain why there is a dichotomy associated with H_2O being a stronger field ligand than O^{2-}.
- Extra for experts! Explain using MO theory and diagrams why cis-$[CoCl_2(NH_3)_4]^+$ is violet and trans-$[CoCl_2(NH_3)_4]^+$ is green.
- Form the energy diagram for a complex ML_4X_2 where L= σ-bonding ligand and X are π-donor ligands positioned axially, **Figure 21**. Include diagrams of the key MOs.