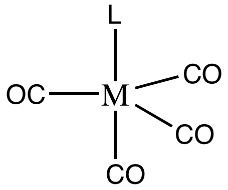
Molecular Orbital Diagrams for TM Complexes with π-interacting Ligands

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 1 $ML(CO)_4$ 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 2**
  - 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

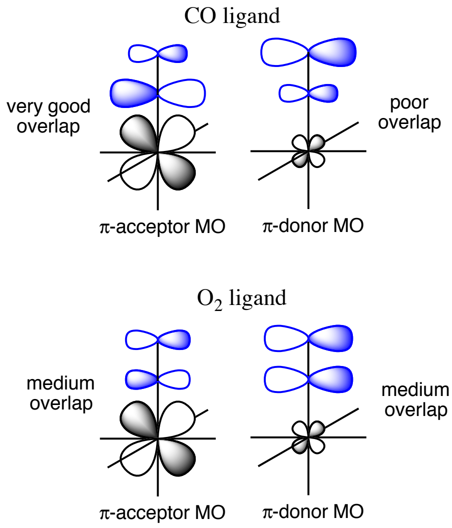


Figure 2 orbital size matters

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

Other π-interacting ligands

- X_2 ligands with multiple bonds can interact end-on or side-on, **Figure 3**, end on is generally favoured
- other ligands with multiple bonds can interact side-on via their π-FOs, including alkenes and alkynes, **Figure 3**
- it is important to distinguish between the ligand FOs and the classification of the ligand-metal interaction, **Figure 4**
  - σ π and δ refer to rotation about the local bond
  - in the ligand this is the E-E bond, in the complex this is the M-L bond
- how to formally describe the bonding (and hence oxidation state of the metal) becomes problematic, **Figure 5**
  - if there is a large amount of back-donation the M-L bond is very strong and the internal ligand bonding is reduced
  - should side on coordinated complexes be considered as cyclic or as π-density donating to a M center?
- MO theory provides part of a description of bonding, however, other considerations must be taken into account, in particular σ- repulsion within π-bonding ligands can be large and destabilise coordination.

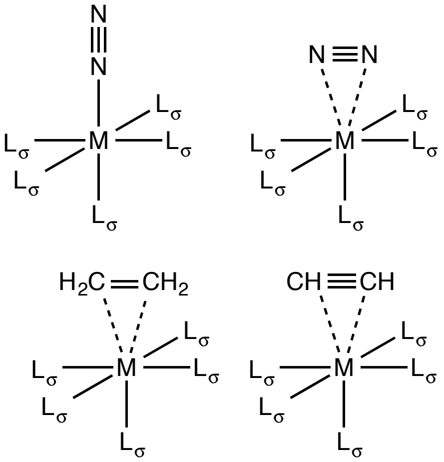


Figure 3 other types of π-interaction with a TM

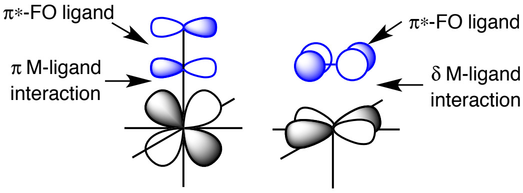


Figure 4 distinguish clearly the internal ligand vs the M-L interactions

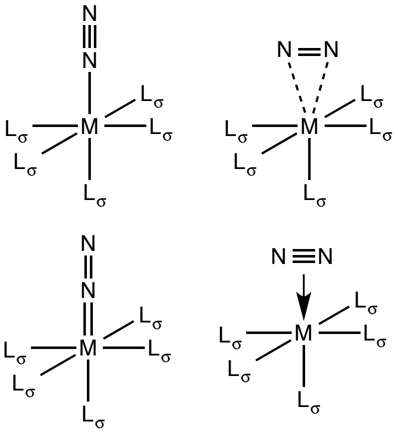


Figure 5 formal classification of the bonding becomes difficult

In-Class Activity

- draw and annotate bonding and antibonding FOs for the π and π* orbitals of trans-$M(L_\sigma)_4(CO)_2$, the first one shown in **Figure 6**

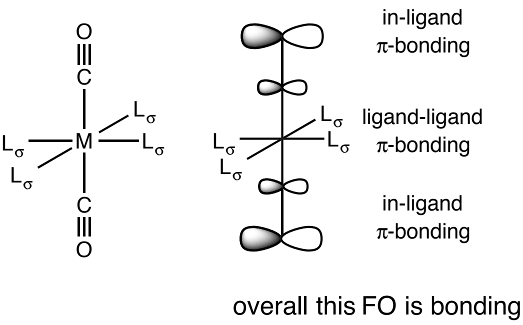


Figure 6 trans-$M(L_\sigma)_4(CO)_2$ and one of the ligand π-FO combinations

TM-MO Diagrams for two π-donor or two π-acceptor ligands

- complexes can have more than one π-donor ligand ($M(L_\sigma)_4Cl_2$) and more than one π-acceptor ligand ($M(L_\sigma)_4(CO)_2$), they can also have one of each type ($M(L_\sigma)_4(CO)Cl$), or include ligands that bind side-on ($M(L_\sigma)_4(HCCH)_2$)
- TM complexes can have a very large range of bonding types and modes and understanding the complex bonding in real molecules must be built up from an understanding of the simpler bonding interactions
- the general process is always the same
  - to start with the underlying octahedral derived σ-framework
  - work out the reduced symmetry labels
  - "add" in the additional orbital interactions
  - these diagrams are complex, do a rough diagram first!
- for example the energy diagram for two π-acceptor ligands can be built up
  - first the symmetry is determined as D_{4h}, the axial system defined and the symmetry elements located and the orbital symmetries are determined for the σ-framework metal and ligand orbitals, **Figure 7**

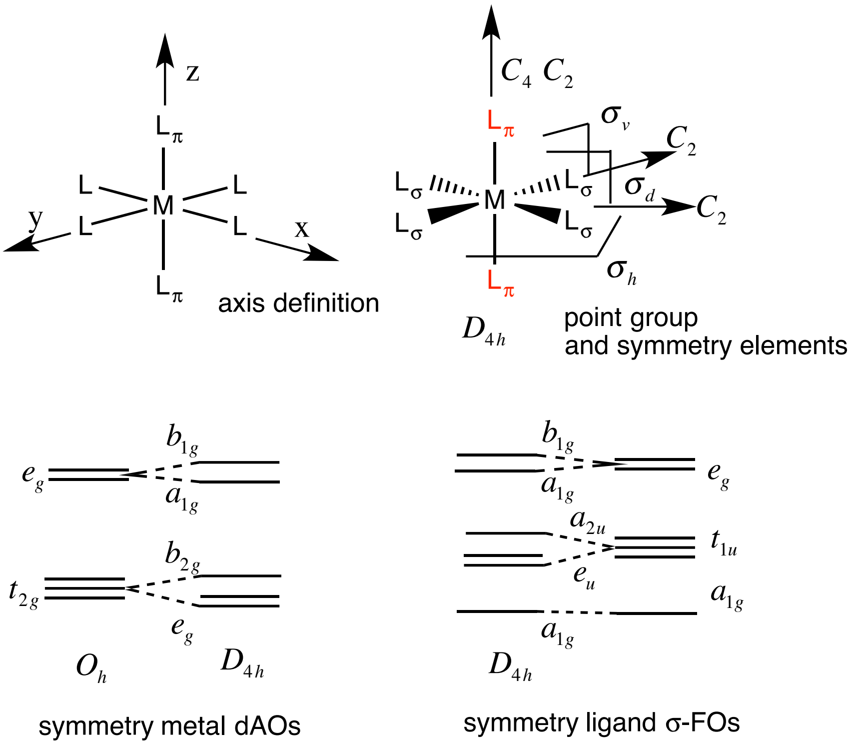


Figure 7 complex and orbital symmetry

  - the next step is to work on the "additional" components, the p_π orbitals, which form a range of FO combinations (see the earlier in-class problem!)
  - the symmetry of these MOs is easily guessed by analogy to axial or dAO symmetry or alternatively by knowing that they must be degenerate and examining their transformation under inversion.
  - because these sets of p_π orbitals are well separated there is almost no splitting and they are essentially degenerate.

- I first drew in the black lines which mark the σ-framework, **Figure 8**
- we can use our knowledge of the simple CO ligand FO energy positioning to locate the orbitals on the energy diagram, next I added in the π and π^* FOs
  - we have twice the degenerate sets because there are two CO ligands
  - in CO the π-FOs are deeper in energy and remain near the σ-FOs (blue)
  - in CO the π^*-FOs lie close to and above the metal dAOs (pink)
- then combine FOs of the same symmetry, combining orbitals which are close in energy first.
- sketch out the MOs around the d-manifold of orbitals (those important for the complex bonding and reactivity)

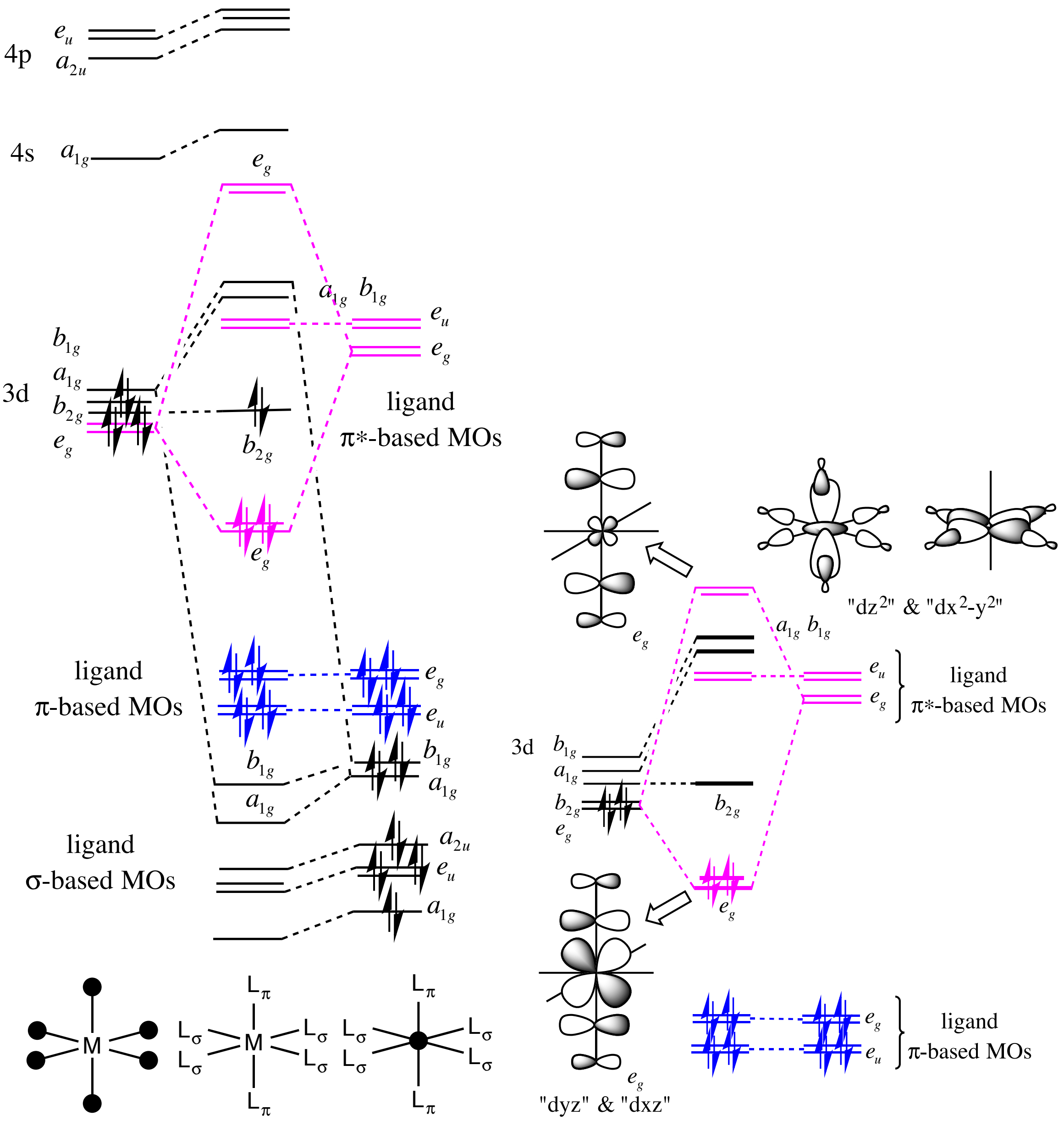
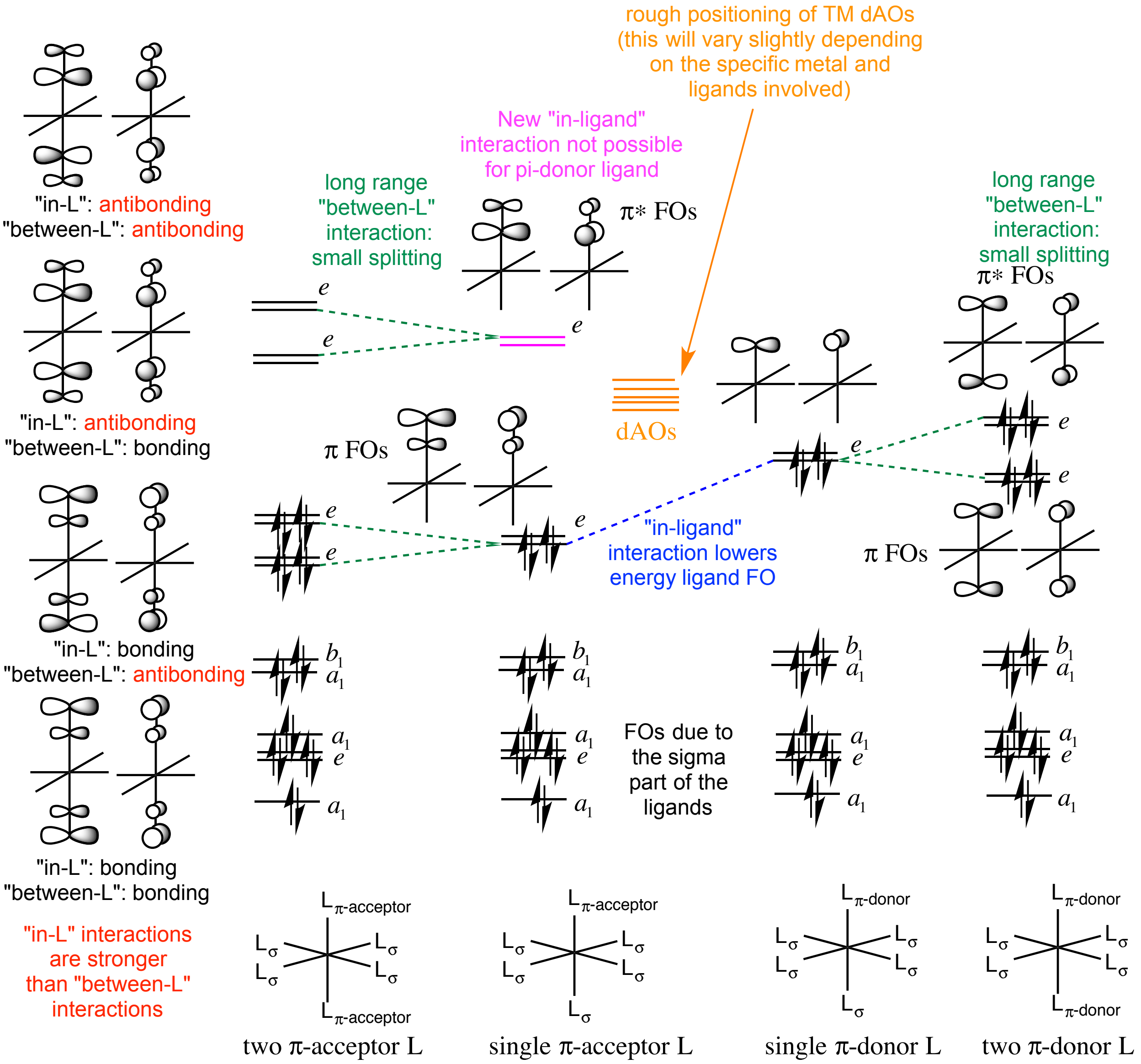


Figure 8 double π-acceptor ligand energy level diagram and key MOs

Summary Diagram

- generated after a student request in 2014!

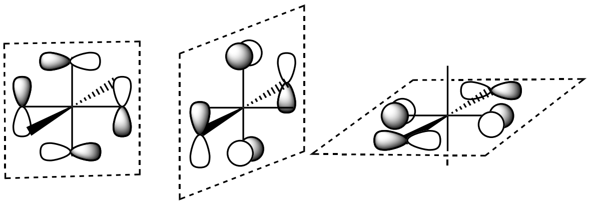


NOTE: symmetry labels are for C_{4v} and will change as the symmetry of molecule changes due to the changing ligands

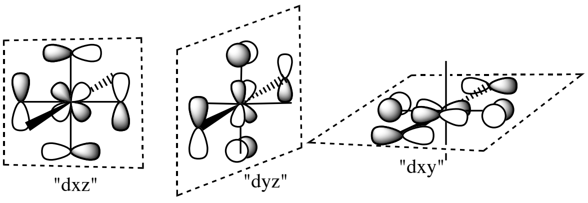
Figure 9 Δ_{oct} for single and double π-acceptor ligand complexes

Octahedral Complexes with six π-donor or six π-acceptor ligands

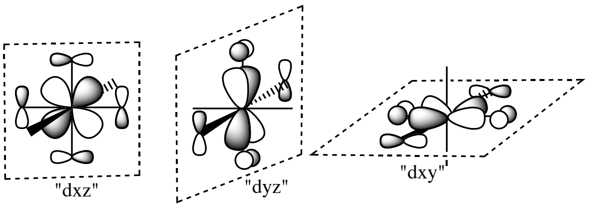
- complexes with six π-donor or six π-acceptor ligands are common, these molecules **retain octahedral symmetry** (O_h)
- complexes that form with π-donor ligands include halide salts $[MX_6]^{n-}$, for example: $[MnCl_6]^{3-}$, $[CoCl_6]^{3-}$, $[RhCl_6]^{3-}$ $[NiF_6]^{4-}$, $[CoF_6]^{3-}$ and $[FeF_6]^{3-}$. Complexes that form with π-acceptor ligands include CO complexes $M(CO)_6$ and CN- complexes $[M(CN)_6]^{n-}$, for example: $[Fe(CN)_6]^{3-}$.
- the σ-framework remains the same
- for π-donor ligands, there are now 12 p_π-AOs contributing to the ligand FOs (a p_x and p_y orbital on each of the six ligands).
  - the symmetry for these can be complicated to work out but resolves into a set of $t_{1g}+t_{1u}+t_{2g}+t_{2u}$ FOs (one of each "t" symmetry in O_h)
  - that is 4 groups of triply degenerate orbitals (making 12 FOs in total)
  - the key π-donor t_{2g} ligand FOs and the resulting bonding and antibonding MOs are shown in **Figure 10** and one of each t_{2g} set are shown for the π-acceptor, **Figure 11**
  - **I don't expect you to be able to reproduce these complex ligand MOs!**, but you should now their symmetry labels for the O_h energy diagram.



t_{2g} ligand FOs

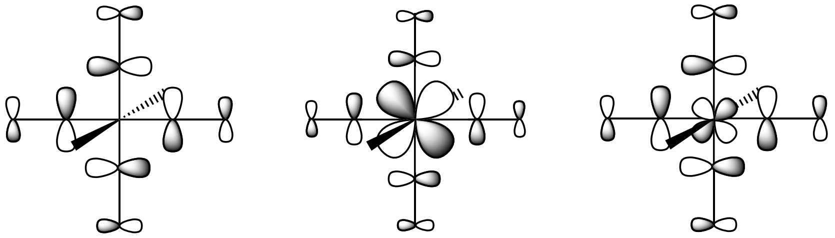


t_{2g} bonding MOs
ligand dominated



t_{2g} antibonding MOs
dAO dominated

Figure 10 Key MOs for ML_6 where L is π-donor ligand



t_{2g} ligand FO

t_{2g} bonding MO
dAO dominated

t_{2g} antibonding MO
ligand dominated

Figure 11 Key MOs for ML_6 where L is π-acceptor ligand

- we know where the ligand π-donor FOs are positioned, around the same place as for the single or two π-donor ligand FO, **Figure 12a**
  - the t_{1g}+t_{1u}+ t_{2u} do not have the correct symmetry to interact with the metal and remain non-bonding, I have represented these 9 FO as a solid "block" on the energy diagram (ie a band of FOs!)
  - the t_{2g} FOs are kept separate as these do have the correct symmetry to interact with the metal t_{2g} dAOs.

2nd year course "TM and Organometallic Chemistry"

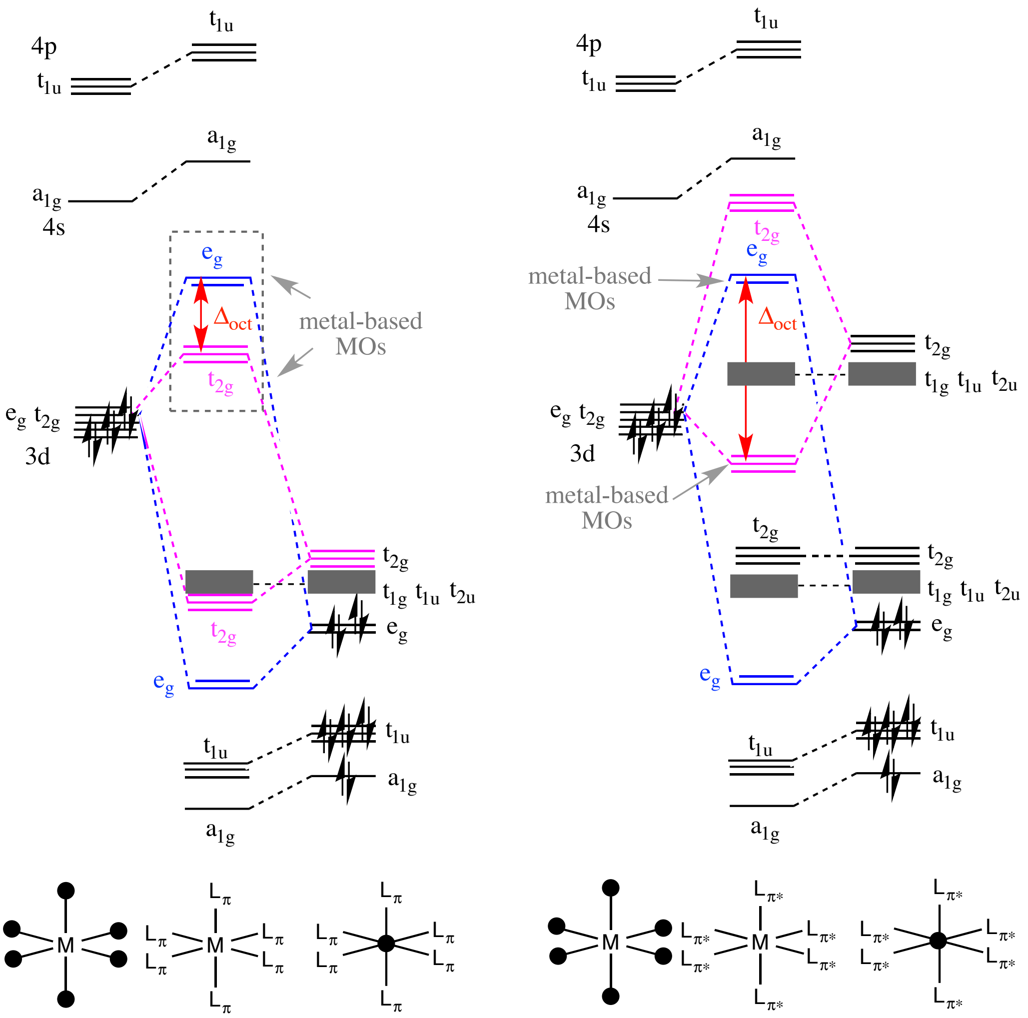


Figure 12 energy diagram ML_6 where (a) L is π-donor and (b) L is π-acceptor ligand

- an analogous procedure is followed for the π*-acceptor FOs (**Figure 12b**), there are an additional 12 π*-FOs contributing to the ligand FOs. The symmetry for these also resolves into a set of t_{1g}+t_{1u}+t_{2g}+t_{2u} FOs
- we know where the ligand π-acceptor FOs are positioned, around the same place as for the single π-acceptor ligand FO
  - again the t_{1g}+t_{1u}+ t_{2u} do not have the correct symmetry to interact with the metal and remain non-bonding and I have represented these 9 FO as a solid "block" on the energy diagram.
  - the t_{2g} FOs are kept separate as these do have the correct symmetry to interact with the metal t_{2g} dAOs.

The octahedral splitting parameter

- for the six σ-donors the t_{2g} dAOs are non-bonding and the e_g are antibonding (with respect to the ligands), this is the origin of the t_{2g}-e_g splitting pattern you have been told to use, now you know where it comes from!
- with six π-donors the **t_{2g} MOs are all antibonding**, the energy gap between the t_{2g} and e_g MOs is reduced and hence Δ_{oct} is small relative to $M(L_\sigma)_6$ complex. Highly symmetry complexes with six π-donor ligands have a small Δ_{oct}
- with six π-acceptors the **t_{2g} MOs are all bonding** and are stabilised increasing the energy gap between the t_{2g} and e_g MOs, Δ_{oct} is increased. Highly symmetry complexes with six π-acceptor ligands have a very large Δ_{oct}
- notice that there now also exists a manifold of ligand MOs within the region spanned by Δ_{oct} (the non-bonding ligand π* MOs) these are almost always ignored in text books!

Other types of interaction to consider

- all 6 σ-donor ligands in an octahedral complex do not necessarily need to be the same
- you should be able to describe the MO diagram for a system in which the two axial σ-donor ligands are of a different type from the equatorial σ-donor ligands, Figure 13

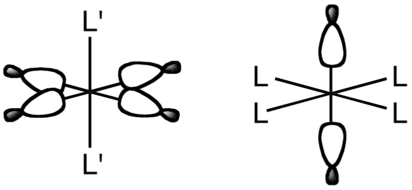


Figure 13 forming an intermediate MO diagram for the fragment orbitals

- π-donor and π-acceptor ligands can add in more than one coordination site around the metal, you should be able to describe the MO diagram for 2 axial π-acceptor or π-donor ligands (ie in a trans configuration)
- in the tutorial for Lecture 7 you considered a square planar complex with 4 σ-bonding ligands, however these could be 4 π-donor or π-acceptor ligands. Examples of square planar complexes include: $PtBr_2(PPh_3)_2$, $PtCl_2(NH_3)_2$, $[Ni(PMe_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ and $[PdBr_4]^{2-}$.
- of course the all 6 π-donor (or π-acceptor) ligands in an octahedral complex do not need to be the same, and there can be a reduction in symmetry. For example: trans and cis $[FeCl_2Br_4]^{4-}$, $[ReOCl_5]^-$
- most complexes contain a mix of σ-donor, π-donor and π-acceptor ligands, in this case the final MO diagram can be extremely complex, and contains components from all the types of diagram examined so far. Examples of mixed complexes include $FeCl_2(OH_2)_4$, $[FeCl_2en_2]^+$ and $Rh(CO)(H)(PPh3)_3$

The Real Thing!

- MOs from a real calculation

Key Points:

- be able to discuss back-bonding and ligand orientation (side-on or end-on) in relation to the different orbital overlap and the energy match between σ-donor π-donor and π-acceptor orbitals
- be able to draw the energy level diagram for a TM complex with sigma-bonding ligands and one or two (trans) π-donor or π-acceptor ligands.
- be able to draw energy level diagrams for octahedral and square planar transition metal complexes with all π-donor and π-acceptor ligands
- be able to draw and describe the important MOs for these diagrams
- be able to discuss key features of these diagrams, especially features relating to the character of the MOs and Δ_{oct}.

Self-Study Problems / Exam Preparation

- Use MO diagrams and specific examples to explain how a very large Δ_{oct} could be obtained
- Explain (employing an energy diagram including key MOs) why NH_3 generates a larger Δ_{oct} than H_2O in the following complexes; $[Cr(NH_3)_6]^{2+}$ $\Delta_{oct} \approx 21{,}600\ cm^{-1}$ and $[Cr(OH_2)_6]^{2+}$ $\Delta_{oct} \approx 17{,}400\ cm^{-1}$
- N_2 can interact either side-on or end-on, however end on coordination is almost exclusively found, rationalise why N_2 prefers to coordinate end-on based on the π^*-FO interactions with a TM
- Construct the MO diagram for M_2L_{10} where L=σ-donor ligand, ensure you consider the formation of a quadruple M-M bond