Molecular Orbital Diagrams for Octahedral and Related Complexes

Why is the Understanding the Bonding in TM complexes Important?

- octahedral complexes are the an extensive and important class for TM complexes
- TM complexes can be catalysts and play an important role in many industrial chemical processes. To improve a catalyst we need to understand the electronic structure and not be limited by influencing just the steric factors
- the magnetic properties and visible colour of many TM complexes are a result of varying occupation and transitions between the dAO dominated MOs

Form the MO diagram of an octahedral TM complex

- first let us remind ourselves of the steps for forming a MO diagram

Forming a MO diagram

1. determine the molecular shape and identify the point group of the molecule
2. define the axial system and find all of the symmetry operations on the molecule
3. identify the fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment orbitals
5. combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs
6. determine the number of electrons in each fragment and hence the central region
7. identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
8. use the MO diagram check-list!
9. analyse the MO diagram

Steps 1-2: Point-Group

- *determine the molecular shape*: octahedral
- *determine the point group of the molecule*: octahedral, **Figure 1**

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	h=48
A_{1g}	1	1	1	1	1	1	1	1	1	1	$(x^2+y^2+z^2)$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
Eg	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
Eu	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(T_x, T_y, T_x)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

Figure 1 O_h character table

- *define the axial system*: **Figure 2**
- and be aware of all the symmetry operations of the point group

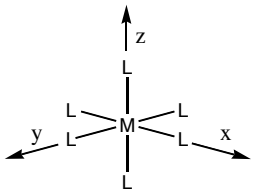

Figure 2 coordinate system

Steps 3-4: The Fragment Orbitals

- *determine the fragments*: we will use L_6 for the ligands and a central M atom **Figure 3**

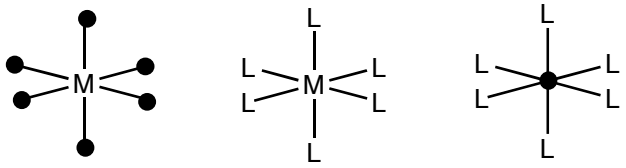

Figure 3 Fragments for the MO diagram

- *determine the energy levels and symmetry labels of the fragments* we covered these last lecture:
  - the **metal orbitals** for the 3d TMs are shown in **Figure 4**, symmetries are easily read off the character table

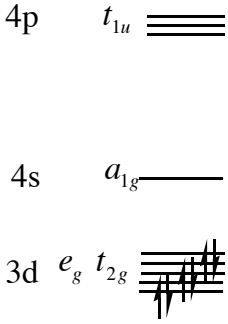

Figure 4 Metal FO energies and symmetry for the O_h point group

IMPORTANT

  - for the **ligand orbitals** we use the symmetry adapted "sigma" orbitals shown in **Figure 5**. Symmetries and energy ordering are determined by examining the orbital phase pattern.

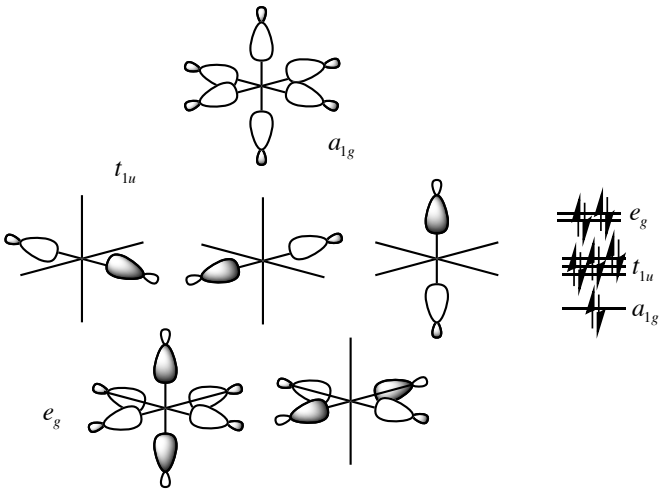

Figure 5 Ligand FO energies and symmetry adapted FOs for the O_h point group

Step 5: Set up the MO Diagram and Combine the FOs

- *setup the MO diagram* by presenting the FO information, **Figure 6**
  - draw the fragments
  - add the TM FOs higher in energy (electropositive M)
  - add the ligand FOs lower in energy (electronegative E)

- *combine fragment orbitals of the same symmetry, estimate bonding and antibonding character and hence the extent of energy splitting*
  - the **ENERGY level diagram** for ML_6 is shown in **Figure 6,** you need to be able to generate this diagram
  - the associated MOs are pictured separately in **Figure 7**
  - overall , the interaction of these orbitals involves d- σ overlap which is weak, the diagram is "expanded" to show the individual interactions.
  - the lowest energy ligand a_{1g} FO combines with the TM 4s a_{1g} orbital
  - the ligand t_{1u} ligand orbitals combine with the TM 4p t_{1u} orbitals
  - the ligand e_g orbitals combine with the TM dAO e_g orbitals
  - there are no ligand orbitals of t_{2g} symmetry, and so these dAOs remain non-bonding.

IMPORTANT

- the size of the AO contributions matters
  - the **bonding MOs** have a larger **ligand contribution** (since the ligand orbitals are lower in energy)
  - the **anti-bonding MOs** have a large **metal contribution** (since the metal orbitals are higher in energy)

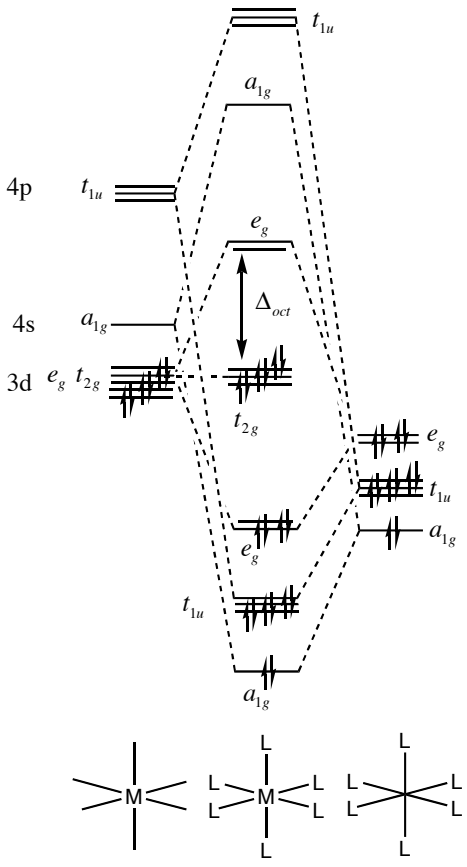

Figure 6 ML_6 energy level diagram

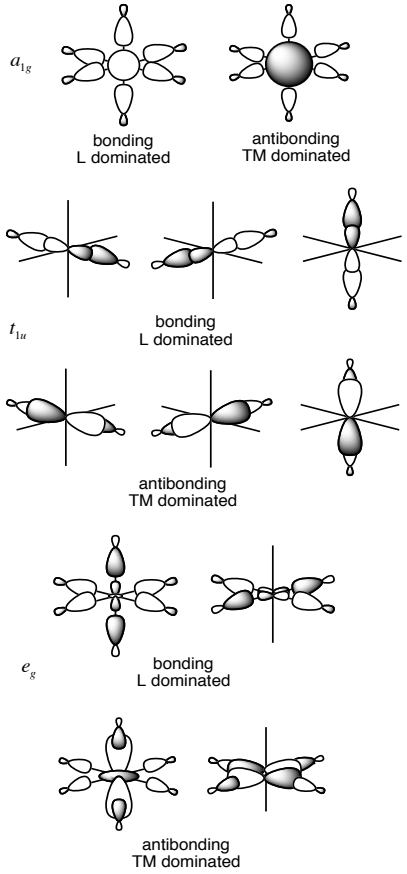

Figure 7 ML_6 MOs

Step 6: Electronic configuration

- *determine the number of electrons in each fragment and hence the central region, add them to the diagram*
  - the ligands are all 2-electron donors and so there are 12e from the ligands
  - in this case I have drawn in 6 dAO electrons, this number will depend on the metal and its oxidation state. (Revise determining the d electron count from your first year Coordination Chemistry course)

Steps 7 and 8 : Mixing and MO Diagram Checklist!

- *identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs*
  - there are no orbitals suitable for mixing in this system
- *use the MO checklist to ensure you have not missed any components*
- the full MO diagram is shown in **Figure 8**
  - this is a very complex diagram and the full diagram is seldom presented
  - often only the energy levels and key MOs are presented

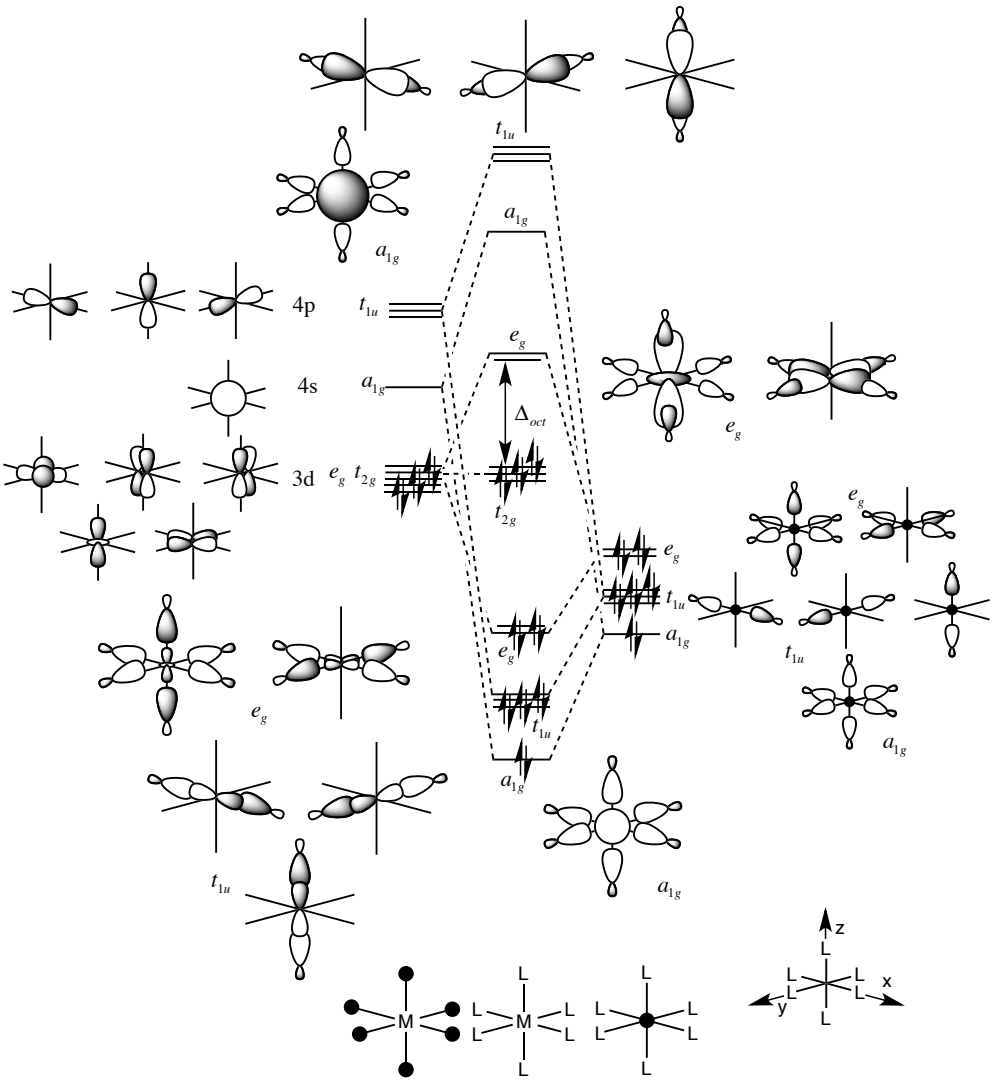

Figure 8 TM ML_6 MO diagram (without annotations)

Step 9 Analysis: The Octahedral Splitting Parameter

IMPORTANT

- looking at the energy level diagram (**Figure 6**) or MO diagram (**Figure 8**)
  - the 3 lowest energy sets of MOs (a_{1g}, t_{1u} and e_g) are ligand based MOs and are dominated by ligand contributions
  - the t_{2g} MOs are non-bonding dAOs
  - and the 3 highest energy sets of MOs (e_g, t_{2u} and a_{1g}) are metal based MOs and are dominated by metal d, p and s AO contributions
- the octahedral splitting parameter (Δ_{oct}) relates to the **d-manifold** of orbitals, and is defined as the energy gap between the **primarily dAO based MOs**, in this case the <u>non-bonding</u> t_{2g} and the <u>antibonding</u> e_g MOs
- the size of the octahedral splitting Δ_{oct} depends on the strength of the interaction between the ligands and the metal e_g FOs, we already know this depends on $\Delta\varepsilon$, S_{ij} and H_{ij}
  - for example, the higher the energy of the ligand σ-like FO the better the energy match and the larger the interaction increasing Δ_{oct}, **Figure 9**

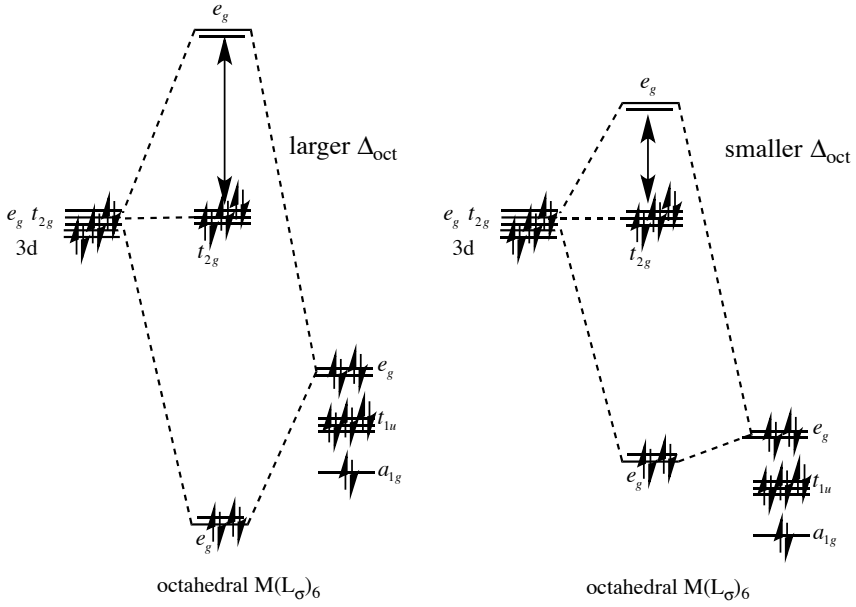

Figure 9 variation in the octahedral splitting parameter

- there are a very large number of complexes that can be treated qualitatively using a σ-donor octahedral MO diagram, a few examples are:
  - L=NH_3: $[Co(NH_3)_6]^{2+}$, $[Rh(NH_3)_6]^{3+}$ and $[Ir(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$
  - when TM ions are solvated in water they often form hydrated octahedral complexes with L=H_2O, $[M(H_2O)_6]^{n+}$ for example: $[Ti(H_2O)_6]^{3+}$ (d^1), $[V(H_2O)_6]^{3+}$ (d^2), $[Cr(H_2O)_6]^{3+}$ (d^3), $[Mn(H_2O)_6]^{2+}$ (d^4), $[Fe^{III}(H_2O)_6]^{3+}$(d^5), $[Fe^{II}(H_2O)_6]^{2+}$ (d^6), $[Co(H_2O)_6]^{3+}$(d^6) , $[Ni(H_2O)_6]^{2+}$(d^8), $[Zn(H_2O)_6]^{2+}$(d^{10})
  - a series of exchange complexes can occur with hydrated complexes, for example; $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5Cl]^{2+}$, $[Cr(H_2O)_4Cl_2]^{1+}$, $[Cr(H_2O)_3Cl_3]$, $[Cr(H_2O)_2Cl_4]^{1-}$, $[Cr(H_2O)_3Cl_5]^{2-}$ and $[CrCl_6]^{3-}$
  - the mixed hydrates can create some interesting isomers, for example $[Cr(H_2O)_4Cl_2]Cl{\bullet}2H_2O$ and $[Cr(H_2O)_5Cl]Cl_2{\bullet}H_2O$
  - mixed σ-donor ligand complexes can also occur: $[Co(H_2O)_2(NH_3)_4]^{3+}$, $[CoCl_2(en)_2]^{+}$, $[CoCl_2(NH_3)_4]^{+}$ and $[Cr(NH_3)(H_2O)_4Cl]^{2+}$

- however there are also other reasons (based on MO theory) for some ligands to show large Δ_{oct}, these involve the ability of the ligands to donate or accept electrons via a π-type interaction! We will discuss these next lecture.
- first however, we are going to examine how Δ_{oct} and the σ-donor octahedral MO diagram connects with experimental chemistry, in particular UV-vis spectroscopy

Spectroscopy and the Octahedral Splitting Parameter

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- you already know that d-d transitions give rise to the colour of many TM complexes. Light is absorbed exciting an electron from the $t_{2g} \rightarrow e_g$ MOs. The remaining transmitted light gives rise to the observed colour.
- for example, Ti in $[Ti(H_2O)_6]^{3+}$ has a single electron in the t_{2g} level and an excitation to the e_g antibonding dAO-based MO gives this complex a violet colour, **Figure 10**

Figure 10 d-d transition for d^1 $[Ti(H_2O)_6]^{3+1}$

- d-d transitions are formally forbidden by the selection rules thus the intensity for these absorptions is low
  - the **Laporte selection rule** can be stated in two forms, (a) only transitions where the orbital angular momentum changes by ±1 are allowed, thus only transitions s→p or p→d or d→f are allowed, OR (b) that a transition can only occur between states of different parity, thus g→g and u→u transitions are forbidden, both formulations result in d→d transitions $t_{2g} \rightarrow e_g$ being forbidden.
  - the **spin selection rule** requires that the spin multiplicity does not change on a transition
- d-d transitions give broad spectra this is due to metal ligand vibrations, we can think of these as affecting the MO overlap and shifting the energy levels, giving a range of energies over time and a broad spectrum, **Figure 11**

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Figure 11 Absorption spectrum of $[Mn(H_2O)_6]^{2+}$.[2]

[1] Coordination Chemistry slides from Dr. Mimi Hii (2013-14)

[2] Downloaded from http://en.wikipedia.org/wiki/Tanabe–Sugano_diagram, Dec 8 2014

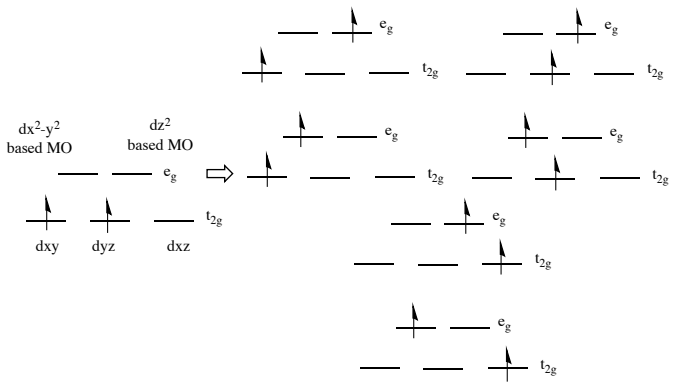

Figure 12 possible d-d transition final states

- initial and final states of the transition can also be different, for example, starting from a d^2 ground state the final electronic configuration can have one electron in any of dxy, dyz or dxz MOs and the excited electron can be in either of dz^2 or the dx^2-y^2 based MOs

treated in my course "Spectroscopy & Characterisation"

- each different electronic distribution is referred to as an **electronic state**. The electron Coulomb interactions and correlation within each of these states is different, giving rise to different energies. The different electronic states lead to multiple possible transitions which generate multiple peaks in the UV-vis spectra.
- for example, $[Mn(H_2O)_6]^{2+}$ has a d^5 ground state configuration and has seven d-d bands in its UV-vis spectrum, **Figure 11**
- electronic (UV-vis) spectra allow for the experimental determination of Δ_{oct} and the **spectrochemical series** has been obtained by ranking a large number of complexes according to the empirically determined size of Δ_{oct}
  - a **strong field ligand** substantially raises the e_g MOs leading to a larger Δ_{oct}.
  - a **weak field ligand** has a small effect on the e_g MOs leading to a smaller Δ_{oct}.

spectrochemical series:

$I^- < Br^- < Cl^- < F^- <$
$OH^- < O^{2-} < H_2O <$
$py < NR_3 < NH_3 < en <$
$NO_2^- < CH_3^- < C_6H_5^- <$
$PPh_3 < PR_3 < P(OR)_3 < PX_3$
$< CN^- < CO < NO^+$

- for example, when $NiCl_2 \cdot 6H_2O$ is dissolved in water a variety of nickel coordination complexes can

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Figure 13 (a) Color of various Ni(II) complexes in aqueous solution. From left to right, $[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(H_2O)_6]^{2+}$ (en=ethylene diamine).[3] and (b) colour wheel, absorbance in nm.[4]

[3] http://en.wikipedia.org/wiki/Nickel(II)_chloride, LHcheM, downloaded 1 Dec 2014

[4] image from http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Crystal_Field_Theory/Colors_of_Coordination_Complexes, downloaded 1 Dec 2014

be produced as the H_2O ligands are displaced by en or NH_3 which are stronger field ligands, **Figure 13**

- ignoring the tetrahedral $[NiCl_4]^{2-}$ complex we see that $[Ni(H_2O)_6]^{2+}$ is green and must absorb in the low energy red part of the spectrum (small Δ_{oct}), purple $[Ni(en)_3]^{2+}$ must absorb in the yellow part of the spectrum and blue $[Ni(NH_3)_6]^{2+}$ must absorb in the higher energy orange part of the spectrum (large Δ_{oct}).
- H_2O (abs $\lambda \approx 680$nm) low energy (long wavelength) red part of spectrum, the stronger field ligand NH_3 absorbs at a shorter wavelength (abs $\lambda \approx 610$nm) and the still stronger field ligand en absorbs at an even shorter wavelength (abs $\lambda \approx 570$nm).

Other Factors Influencing the Octahedral Splitting Parameter

- so far we have seen that the better the alignment of the TM dAOs and the ligand σ-bond FOs energy levels the larger Δ_{oct} will be, this alignment will be effected by the character of the metal and ligands involved
- Δ_{oct} does not just depend on the *energy* alignment it will also depend on how well the relevant orbitals *overlap*. These contributing factors are not independent ie a number of properties can effect both the energy and overlap
- thus while the ligands have an important part to play in determining Δ_{oct} they are not the only contributors, the metal also has a role to play
- Δ_{oct} can be influenced by:
  - total charge on the TM complex
  - the oxidation state of the metal
  - the formal charge on the ligand
  - the density of the overlapping FOs
  - the size of the metal
  - the steric limitations of the ligands

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more in your course "TM Coordination & Organometallic Chemistry"

- a higher **oxidation state** is really a higher charge on the central metal which draws in the ligands resulting in better overlap and larger interactions, **Figure 14**
  - for example $\Delta_{oct} = 9400cm^{-1}$ for $[Fe^{II}(H_2O)_6]^{2+}$ but $\Delta_{oct} = 13700cm^{-1}$ for $[Fe^{III}(H_2O)_6]^{3+}$

Figure 14 variation in the octahedral splitting parameter.[5]

- **charge effects** on Δ_{oct}
  - you might read that positive charge on the metal will facilitate electron donation from the ligand and a larger Δ_{oct} while a negative charge on the metal will disfavour electron donation.
  - the **reason** for this effect is the lowering of the dAO energies due to the stabilising effect of the positive charge, or the raising of the dAO energies due to the repulsive effect of a negative charge
  - similarly a negatively charged σ-donor ligand has a stronger ligand field, this is because the FO are raised in energy and thus are closer (in energy) to the metal based FOs.
- on **descending a group** Δ_{oct} increases, the 3d AOs are very condensed because there are no inner orbitals of the same angular momentum (3d

[5] Coordination Chemistry slides from Dr. Mimi Hii (2013-14)

contraction), as the radial extent of the dAOs increases from 3d to 4d to 5d overlap with the ligand orbitals improves
  - for example for $[M(NH_3)_6]^{3+}$ where M= Co, Rh and Ir, Δ_{oct} =22900cm^{-1} 34100 and 41000 respectively
- variations with respect to the size of the metal are not as systematic and depend on oxidation state and the d-electron configuration.
  - on moving to the right of the PT the size of the metal decreases due to the increasing nuclear charge (while filling of the same electronic dAO shell). A smaller metal with a more contracted and lower energy dAOs will have reduced energy alignment and reduced overlap and hence a smaller Δ_{oct}.
  - For example, Δ_{oct} $V^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$
- additional **ligand** effects
  - a large bulky ligand may not be able to approach as closely as a smaller ligand and increasing bond distances are a sign of reduced overlap
  - diffuse ligand donor orbitals and the density of the σ- donor can affect the magnitude of the overlap (integral), ie NR_3 vs PR_3 vs AsR_3.

TM Complex with different sigma-donor ligands

IMPORTANT

- if one of the ligands in the octahedral complex is different (L'_σ) from the others (L_σ) then the symmetry is reduced from O_h to C_{4v}, **Figure 15**
- the **underlying σ-framework remains the same**
  - the shape of the orbitals does not change
  - the symmetry labels change and these are easily determined using known short-cuts
- thus we only need to slightly alter the basic O_h MO diagram
  - this is most easily achieved by first working out the drop in symmetry of the fragment orbitals
  - then we can combine orbitals of the same symmetry, the energy changes are small so we use as a guide the basic framework of O_h MOs

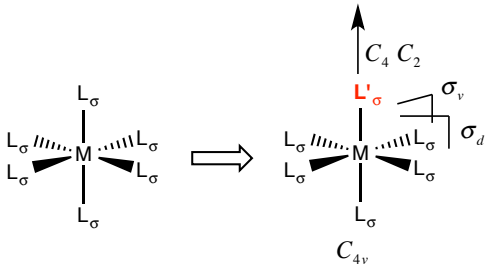

Figure 15 point group reduction and axial definition

In-Class Activity

- determine the new symmetry labels of the metal orbitals (**Figure 16**):
  - hint: use the C_{4v} character table and short-cuts

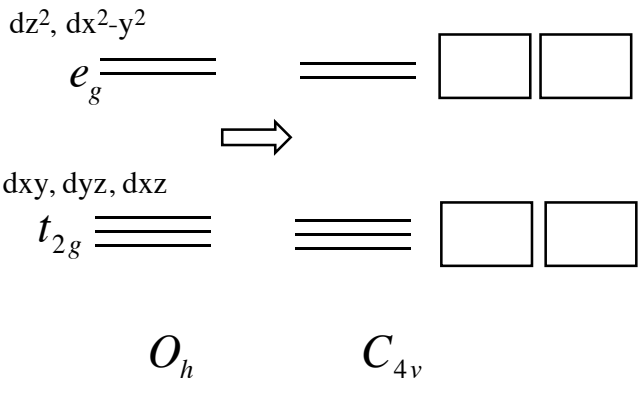

Figure 16 effect of point group reduction on the dAO symmetry labels

- we can similarly determine the new symmetry labels for the ligand σ-orbitals (**Figure 17**)

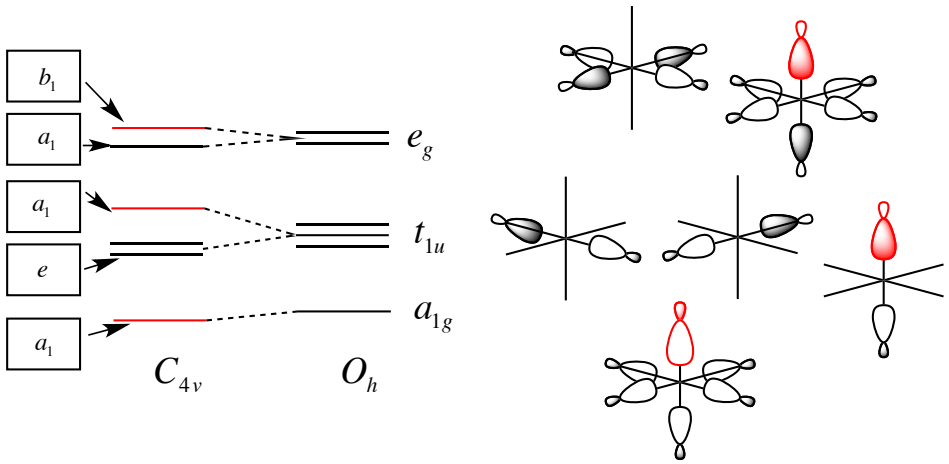

Figure 17 effect of point group reduction on the ligand symmetry labels

In-Class Activity

- now combine the TM dAO and ligand FO components to form the energy level diagram for a C_{4v} TM complex.
- hint: start with an O_h energy diagram and just change the symmetry labels!

Figure 18 The C_{4v} energy diagram

The C_{4v} TM Energy Diagram

- let us now compare the C_{4v} energy diagram with that of O_h, **Figure 19**
  - the energy levels are roughly in the same places
  - the d FOs are degenerate until they feel the effect of the ligands, I've spread them out a bit to illustrate the different symmetries
  - the main effect of the drop in symmetry is to break the degeneracy of some of the energy levels: $e_g \rightarrow a_1$ and b_1, $t_{1u} \rightarrow a_1$ and e

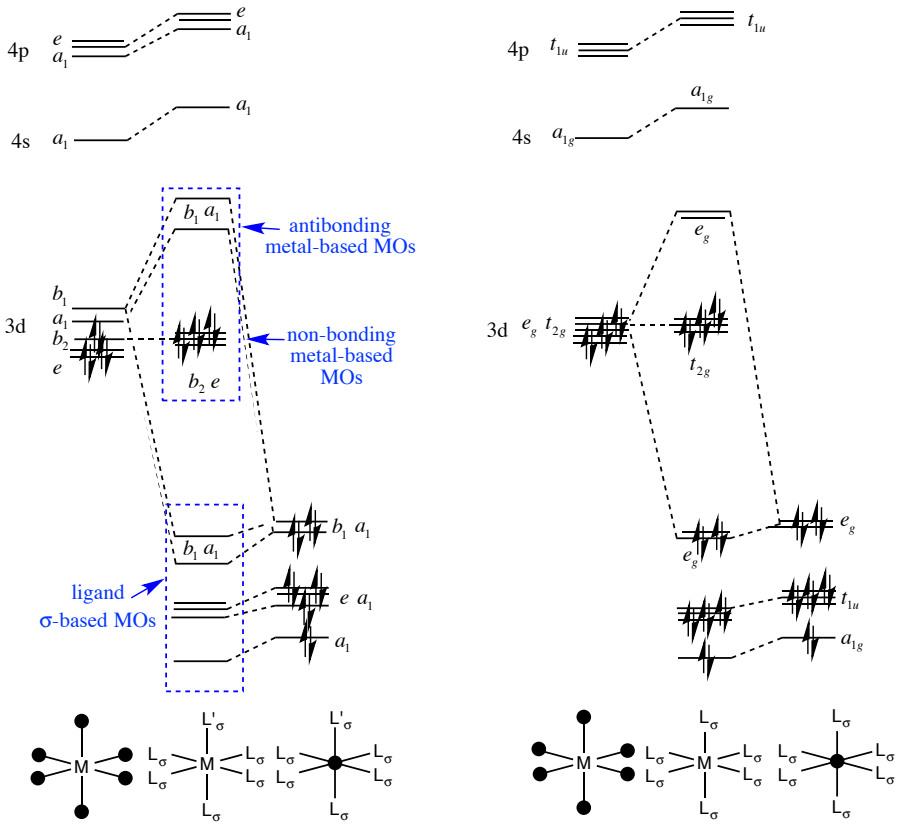

Figure 19 comparing the C_{4v} and O_h energy diagrams

- if we examine the form of the MOs, **Figure 20**
  - the old e_g become the new a_1 and b_1 MOs
  - the a_1 MO has a contribution from L'_σ (in red) but the b_1 MO doesn't
  - the relative ordering of the a_1 and b_1 MOs will depend on the differences between L'_σ and L_σ
- the octahedral splitting parameter is taken as the **maximum splitting of the dAO based MOs**

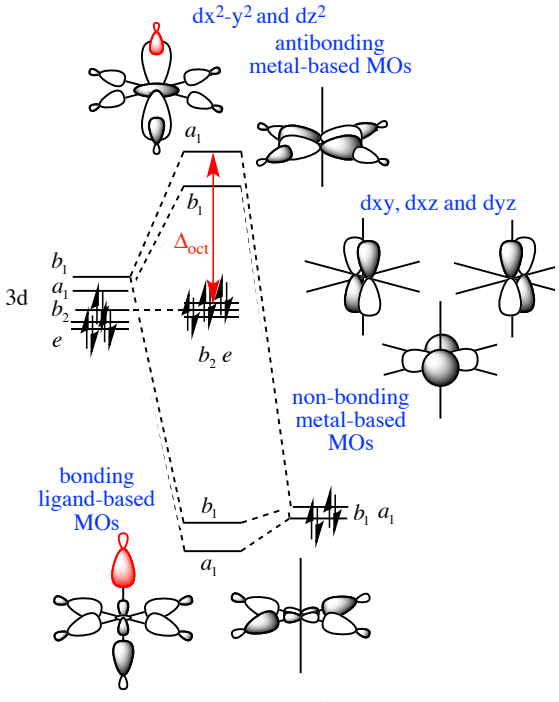

Figure 20 key C_{4v} MOs

Key Points:

- be able to draw the energy level diagram for octahedral transition metal (TM) complexes with σ-bonding ligands
- be able to draw and describe the important MOs for the diagram
- be able to discuss key features of TM energy and MO diagrams, especially features relating to the character of the MOs
- be able to define the octahedral splitting parameter and be able to discuss key properties that impact on or effect the octahedral splitting parameter (such as energy alignment, orbital overlap, symmetry, charge on the complex, TM size and oxidation state)
- be able to draw the energy level diagram for an a lower symmetry transition metal complex with σ-bonding ligands, including square planar complexes

Self-Study Problems / Exam Preparation

- Explain the colour changes observed for the nickel complexes shown in **Figure 21**
- H^- and R^- appear high in the spectrochemical series (ie as strong field ligands). Explain how this occurs, when these ligands have no π*-orbitals.
- Generate the sigma FOs for $6L_\sigma$ arranged octahedrally from a fragment L_4 (equatorial ligands) and L_2 (axial ligands)
- Annotate a C_{4v} MO diagram identifying the short cuts used to determine the new symmetry labels of the fragment orbitals.
- Determine the point group and energy diagram for an "octahedral complex" cis-$M(L'_\sigma)_2(L_\sigma)_4$ where (L'_σ) and (L_σ) are different σ-bonding ligands

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Figure 21 colour changes in Ni complexes.[6]

[6] Image from p16 of Metal Ligand Bonding by R. Janes and E. Moore RSC, Cambridge, 2004.