Self-Study Problems / Exam Preparation

- Explain the colour changes observed for the nickel complexes shown in **Figure 1**, which are the following
    - $[Ni(H_2O)_6]^{2+}$aq is green
    - $[Ni(H_2O)_4en]^{2+}$aq is pale blue
    - $[Ni(H_2O)_2en_2]^{2+}$aq is blue/purple
    - $[Ni(en)_3]^{2+}$aq is magenta/violet
  - H_2O is a weaker field ligand than ethylenediamine, this means that water should have a smaller Δ_{oct}, or energy gap between the d-d transitions. The energy gap is related to the wavelength of light absorbed and d-d transitions are in the right part of the (visible) spectrum to influence the colour of complexes.
  - As water ligands are substituted for en in these complexes Δ_{oct} splitting will increase as there is a stronger σ-FO interaction between the TM and the en ligands, the "e_g" MOs will rise in energy. Water is a weak π-donor and the energy of the antibonding "t_{2g}" MO interaction will be reduced on removing water, increasing Δ_{oct}.
  - Using the colour wheel, **Figure 2**
    - $[Ni(H_2O)_6]^{2+}_{aq}$ is green, which means it must absorb in the red part of the spectrum ie low energy region.
    - $[Ni(en)_3]^{2+}_{aq}$ is magenta/violet which means it must absorb in the yellow part of the spectrum, ie a mid energy region.
    - orange sits between yellow and red, and would indicate an intermediate absorption between these two extremes, the transmitted colour is blue

Figure 1 colour changes in Ni complexes.[1]

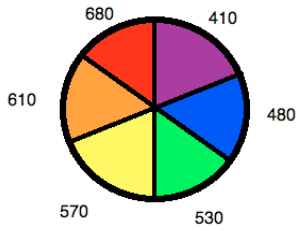

Figure 2 Colour wheel.[2]

- H^- and R^- are appear relatively high in the spectrochemical series (ie as strong field ligands). Use MO diagrams to explain how this occurs, when these ligands have no π*-orbitals.
  - H^- and R^- are strong σ-donors, this means they have σ-orbitals which are relatively high in energy and thus interact more strongly with the dAOs of the metal, raising the energy of the e_g orbitals more than ligands like NH_3 or H_2O, **Figure 3**

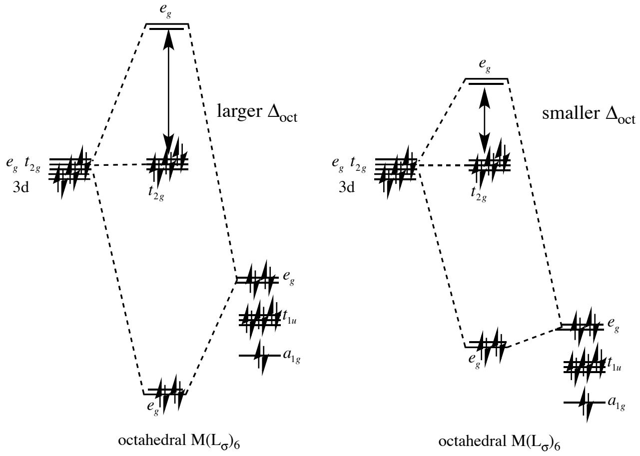

Figure 3 variation in the octahedral splitting parameter

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

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

- Generate the sigma FOs for $6L_{\sigma}$ arranged in an octahedral from a fragment L_4 (equatorial ligands) and L_2 (axial ligands), **Figure 4**

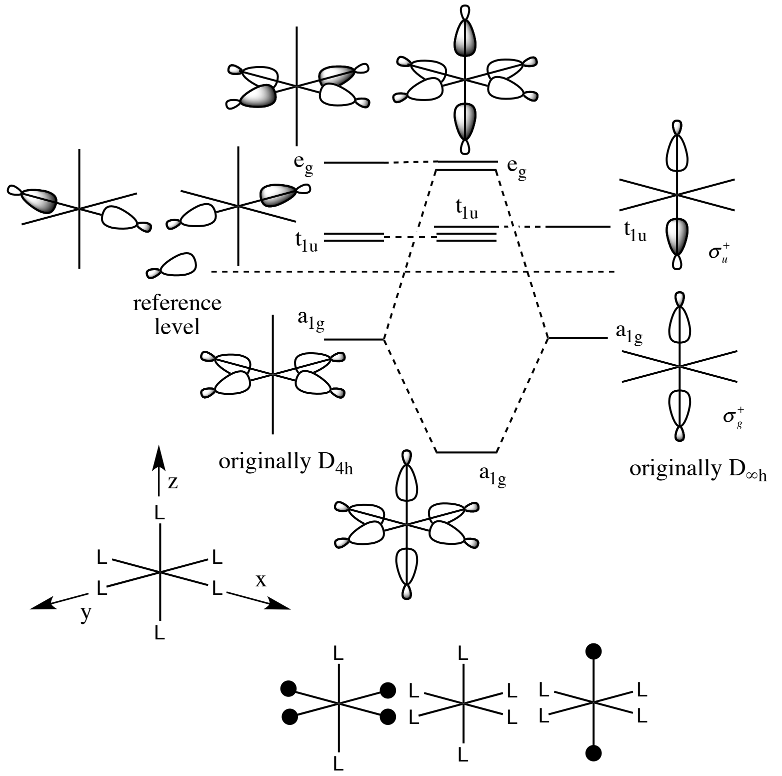

Figure 4 Forming the 6L fragment orbitals

  - the L_4 and L_2 fragments are assumed known
  - because these fragments are not identical we need to determine their symmetry under the O_h point group
  - L_2 fragments originally belong to the $D_{\infty h}$ point group:
    - bonding L_2 FO is totally symmetric in $D_{\infty h}$ this is σ_g^+ in O_h this is a_{1g}
    - antibonding L_2 FO is p_z like in $D_{\infty h}$ this is σ_u^+ in O_h this is one of a degenerate set t_{1u}
  - L_4 fragments originally belong to the D_{4h} point group:
    - totally bonding L_4 FO is totally symmetric in D_{4h} this is a_{1g} in O_h this is a_{1g}
    - 2 degenerate L_4 FO are p_x and p_y like in D_{4h} this is e_u in O_h this is one of a degenerate set t_{1u}
    - antibonding L_4 FO is dx^2-y^2 like in D_{4h} this is b_{1g} in O_h this is one of a degenerate set e_g
  - combining FOs of the same symmetry, that is the a_{1g} MOs we form a bonding antibonding pair, then we need to determine the symmetry of the formed MO under the O_h point group
    - bonding MO for L_6 is totally symmetric a_{1g}
    - antibonding MO for L_6 is dz^2 like which is one of a degenerate set e_g
  - we then need to decide where they sit in terms of energy
    - determine a reference line for a single sigma L orbital
    - the fragment bonding orbitals will lie below this line
    - in L_2 the FO splitting will not be large because the orbitals are two bonds apart
    - in L_4 only the totally bonding FO will lie below the reference
    - the p type combination will lie just above the reference, there are only two orbitals interacting and they are far apart
    - the 4 and 5 component fragments are more antibonding due to the closer through space interactions

- Annotate a C_{4v} MO diagram identifying the short cuts used to determine the new symmetry labels of the fragment orbitals, **Figure 5**

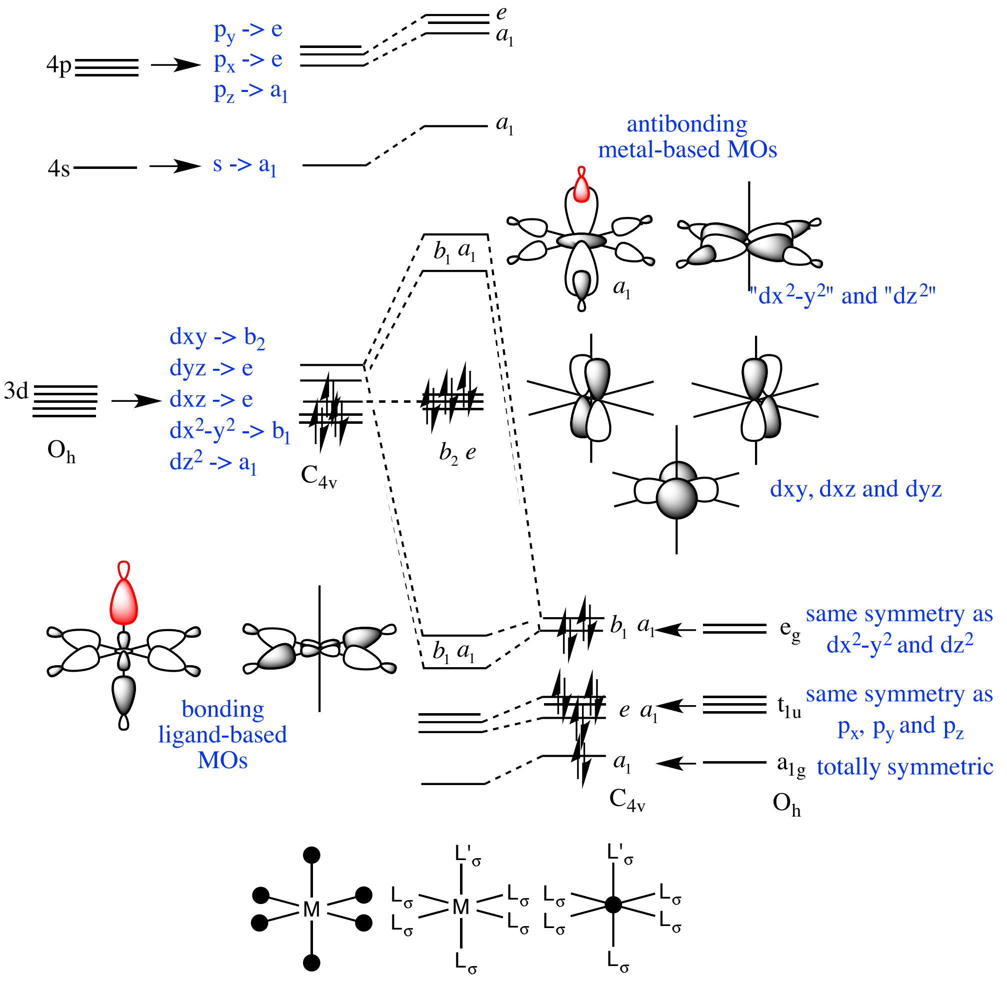

Figure 5 annotated C4v MO diagram

- Which symmetry elements are lost from the D_6 point group to generate the C_{3v} point group?
  - The D_{6h} point group has symmetry operations E, $2C_6$, $2C_3$, C_2, $3C_2$', $3C_2$", i, $2S_3$, $2S_6$, σ_h, $3\sigma_d$ and $3\sigma_v$
  - The C_{3v} point group has symmetry operations E, $2C_3$, and $3\sigma_v$
  - Thus the lost operations are: C_2, $3C_2$', $3C_2$", i, $2S_3$, $2S_6$, σ_h, and $3\sigma_d$

- Determine the 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, **Figure 6**
    - we assume that there is little effect on the orbitals
    - the major change is in the symmetry labels for the FOs and MOs
    - these are determined using the short-cuts

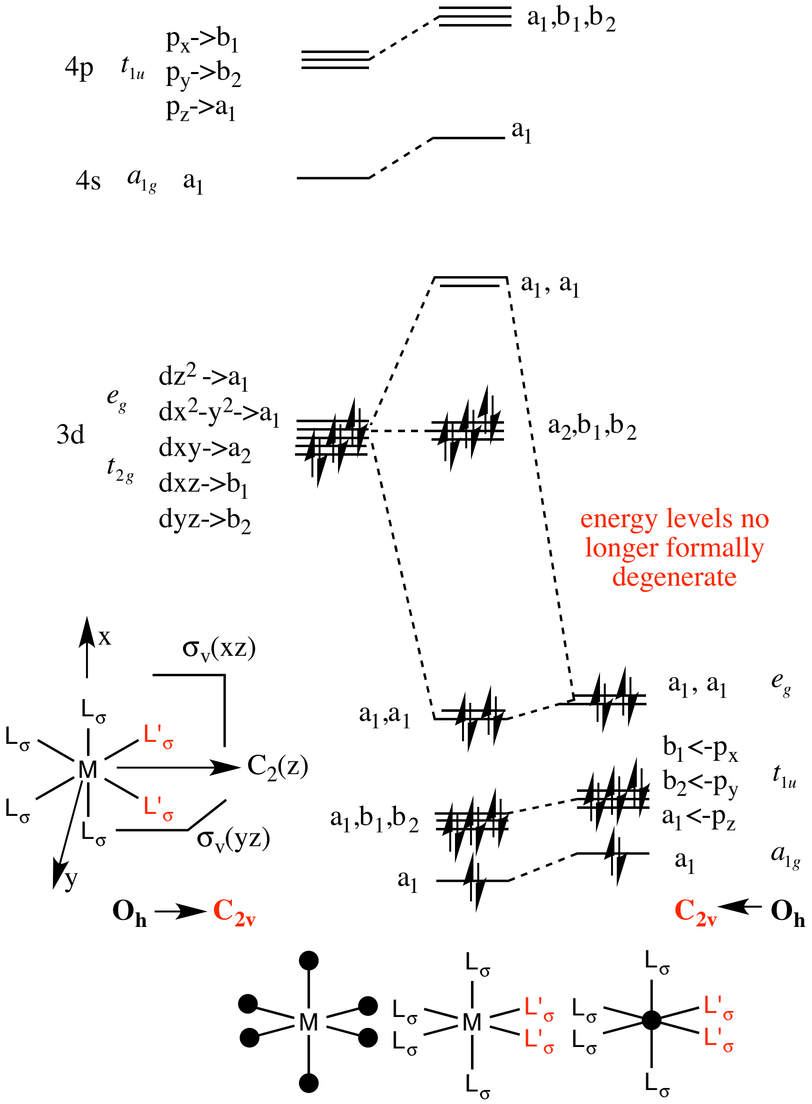

Figure 6 MO diagram for reduced symmetry cis-$M(L'_{\sigma})_2(L_{\sigma})_4$ complex