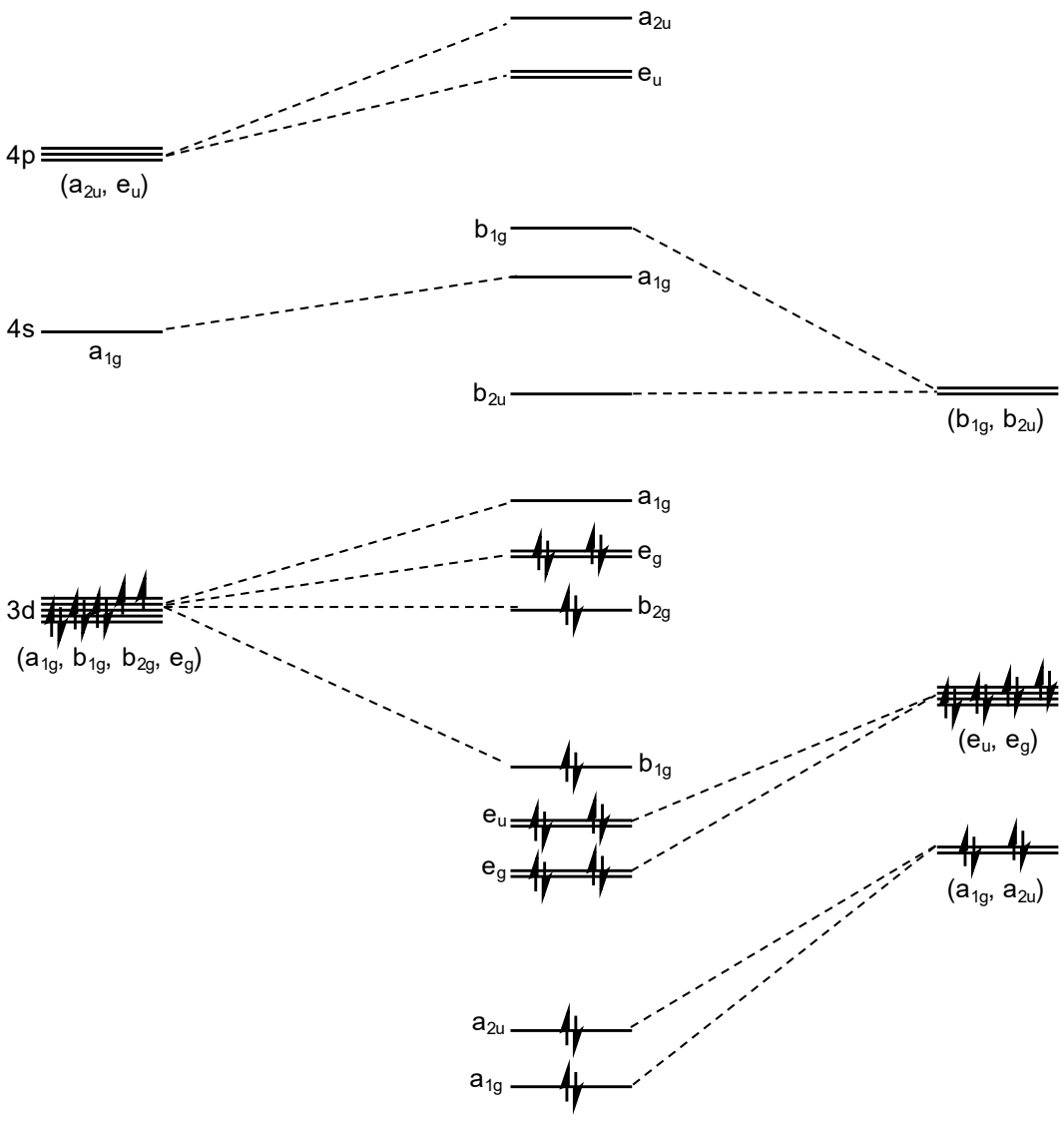
Chem 6330
Problem Set 6 Answer Key

1) MO diagram from PS 6 for $[Ni(cyclobutadiene)_2]^{2-}$



Ni^{2+} - d^8 $[Ni(cyclobutadiene)_2]^{2-}$ 2 x ($cyclobutadiene^{2-}$)

a) Since all of the orbitals are completely filled or completely empty, the symmetry of the ground state would be $^1A_{1g}$, the totally symmetric representation for the D_{4h} point group.

Examination of the D_{4h} character table shows the dipole moment operator ($\vec{\mu}$, xyz) to be A_{2u} (z) and E_u (x,y).

The symmetries and electron configurations of the two lowest lying Laporte-allowed excited states would be:

$(b_{2g})^2(e_g)^3(a_{1g})^0(b_{2u})^1$ E_g x B_{2u} = ^1E_u

$(b_{2g})^1(e_g)^4(a_{1g})^0(b_{2u})^1$ B_{2g} x B_{2u} = $^1A_{1u}$

b) The electronic transitions would be:

$(b_{2g})^2(e_g)^4(a_{1g})^0(b_{2u})^0 \longrightarrow (b_{2g})^2(e_g)^3(a_{1g})^0(b_{2u})^1$ $^1A_{1g} \rightarrow {}^1E_u$

$(b_{2g})^2(e_g)^4(a_{1g})^0(b_{2u})^0 \longrightarrow (b_{2g})^1(e_g)^4(a_{1g})^0(b_{2u})^1$ $^1A_{1g} \rightarrow {}^1A_{1u}$

$$\Gamma_{GS} \times \Gamma_{\mu} \times \Gamma_{ES} \Longrightarrow \text{Must contain } A_{1g}$$

A_{1g} x A_{2u} x E_u = E_g

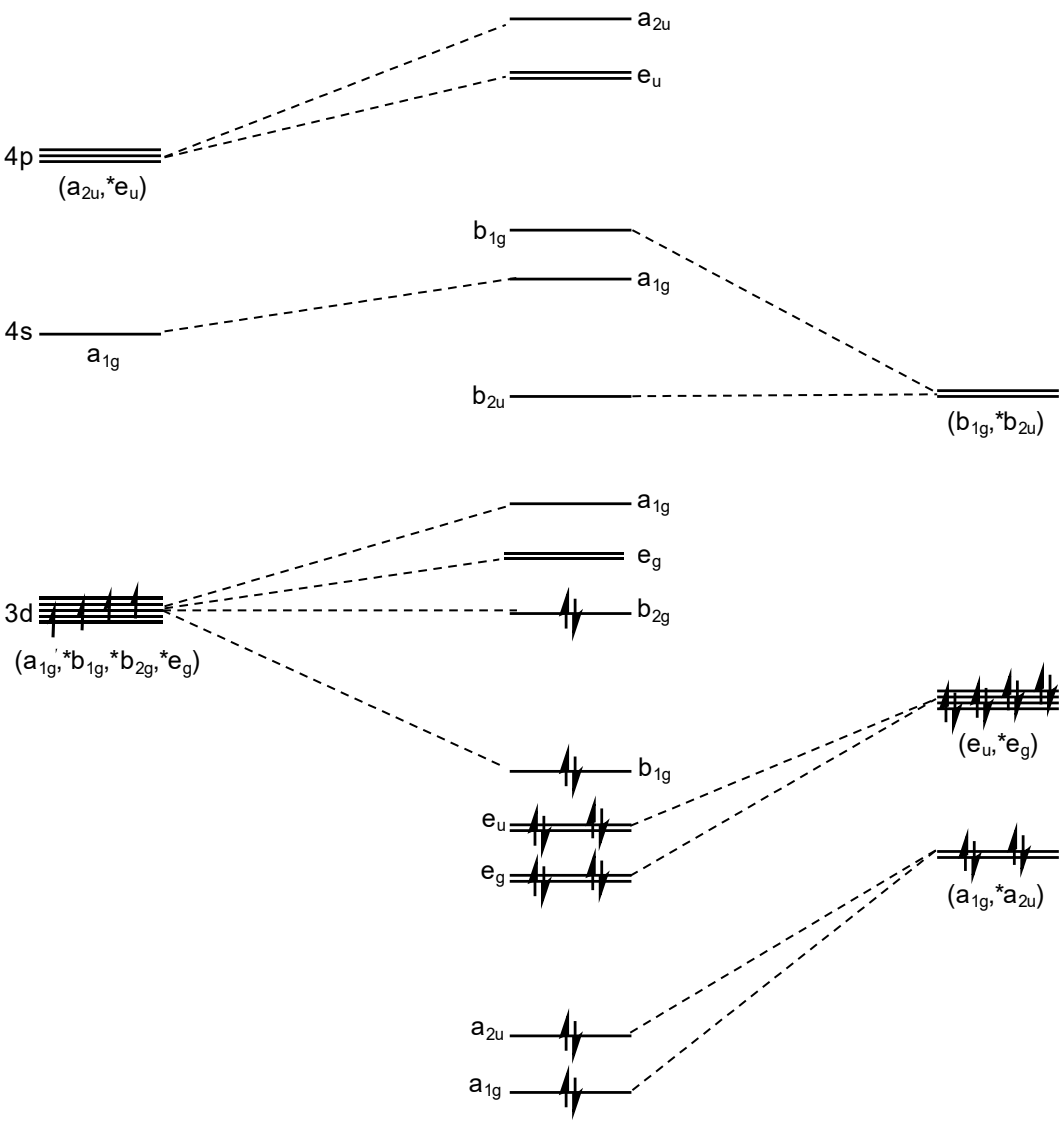
A_{1g} x E_u x E_u = $\boxed{A_{1g}}$ + A_{2g} + B_{1g} + B_{2g} Allowed

A_{1g} x A_{2u} x A_{1u} = A_{2g}

A_{1g} x E_u x A_{2u} = E_g

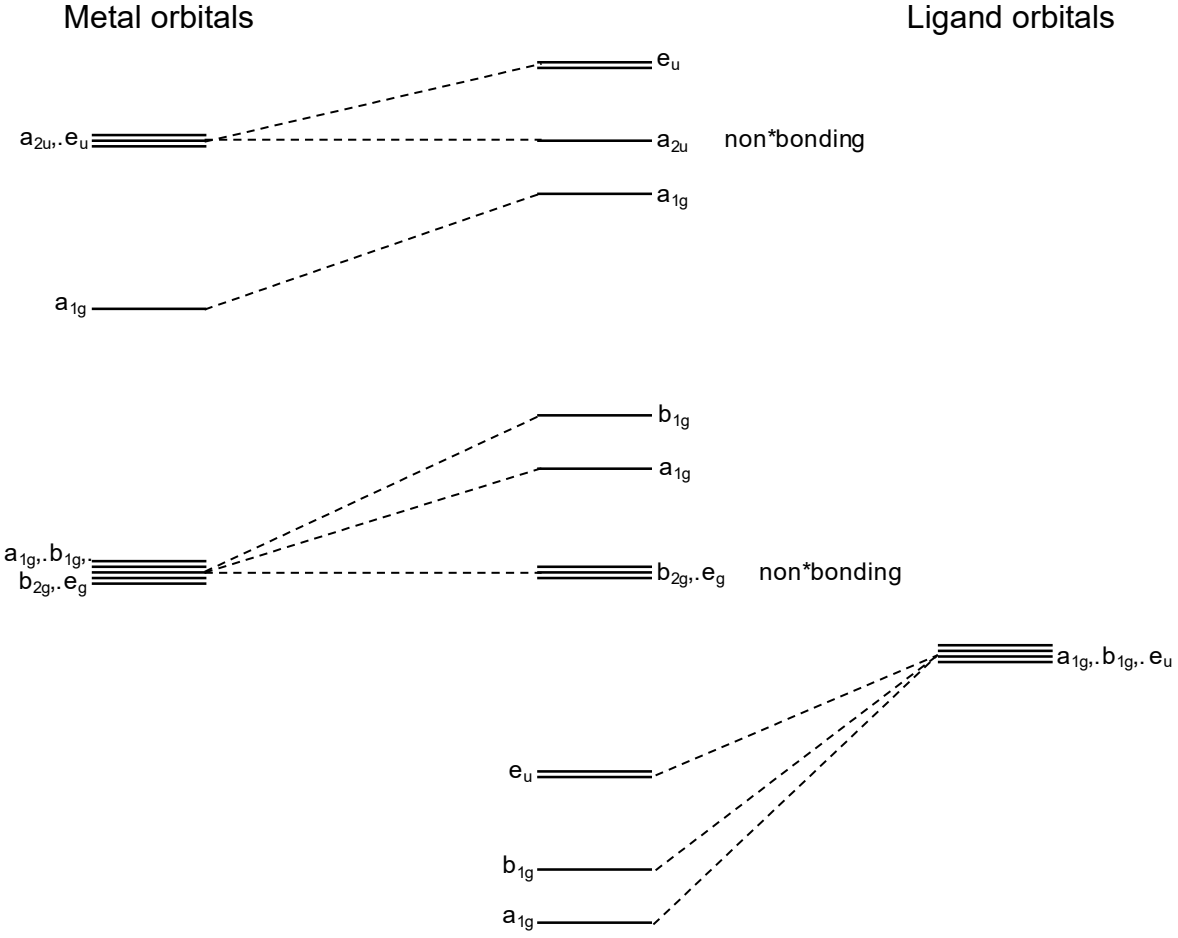
c) These allowed transitions are MLCT transitions and would have ε values in the range of 5,000 – 50,000 $M^{-1}cm^{-1}$. The possible d-d transitions are all Laporte forbidden.

d) Due to cyclobutadiene having a 2- charge, Fe would have to be 4+ to create the neutral complex (Fe^{4+} = d^4), and would have similar transitions as the Ni^{2+} complex. Fe^{2+} would create partially filled degenerate orbitals with a very complex solution.



Fe^{4+} - d^4 $[Ni(cyclobutadiene)_2]^{2-}$ 2 x ($cyclobutadiene^{2-}$)

2) a) σ-only MO diagram



Once again, under D_{4h} symmetry the dipole moment operator has symmetries of A_{2u} and E_u. Since the ground state has A_{1g} symmetry, the excited state must have A_{2u} or E_u symmetry for the transition to be allowed.

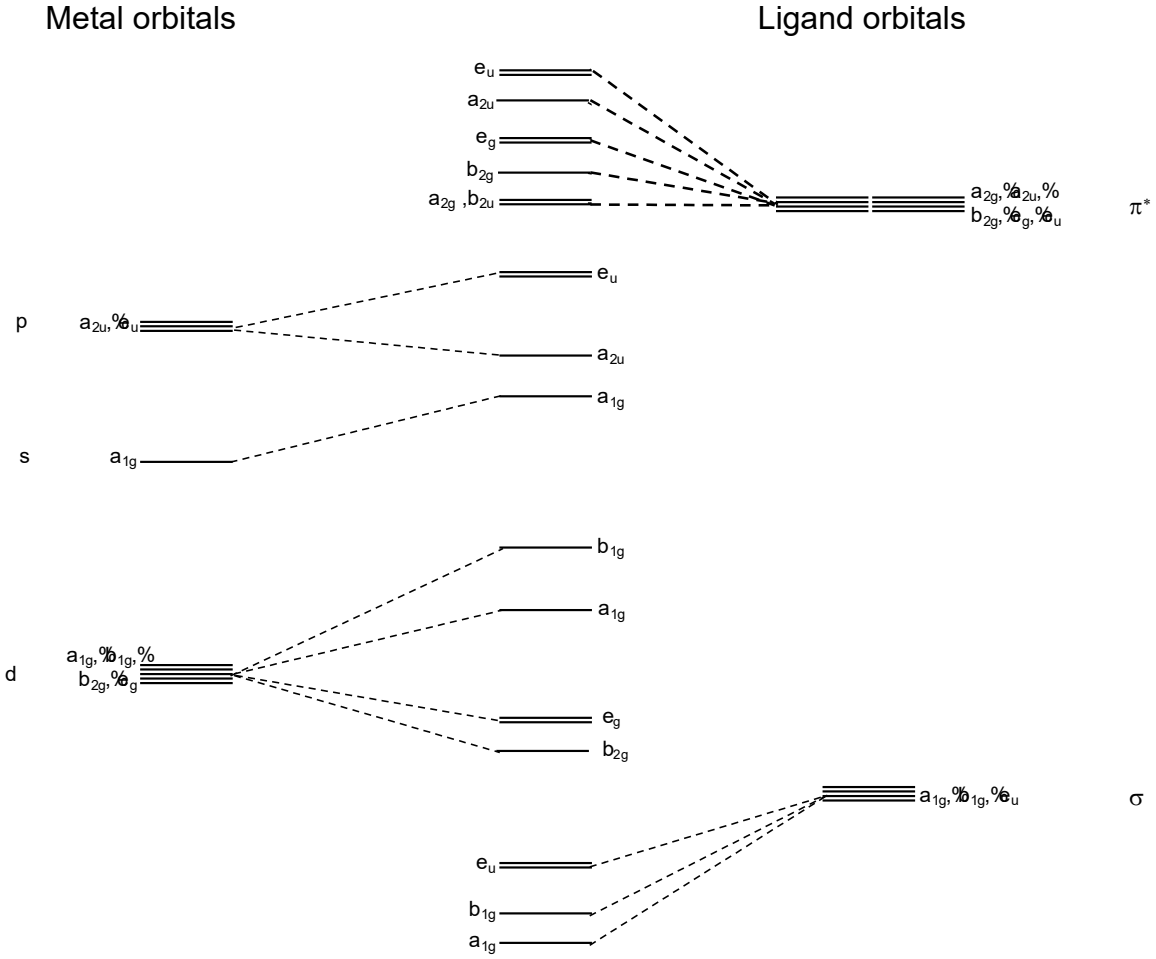
There are several possible low lying allowed transitions:
$(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0 \longrightarrow (a_{1g})^1(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (Excited state has E_u symmetry)

$(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \longrightarrow (a_{1g})^1(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^1$ (Excited state has E_u symmetry)
$(e_g)^4(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0 \longrightarrow (e_g)^3(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (Excited state symmetry includes A_{2u})

$(e_g)^4(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \longrightarrow (e_g)^3(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^1$ (Excited state symmetry includes A_{2u})

These are all metal-centered transitions (d→p), meaning that the ε values will be around 1,000 $M^{-1}cm^{-1}$.

b) π-acceptor MO diagram:



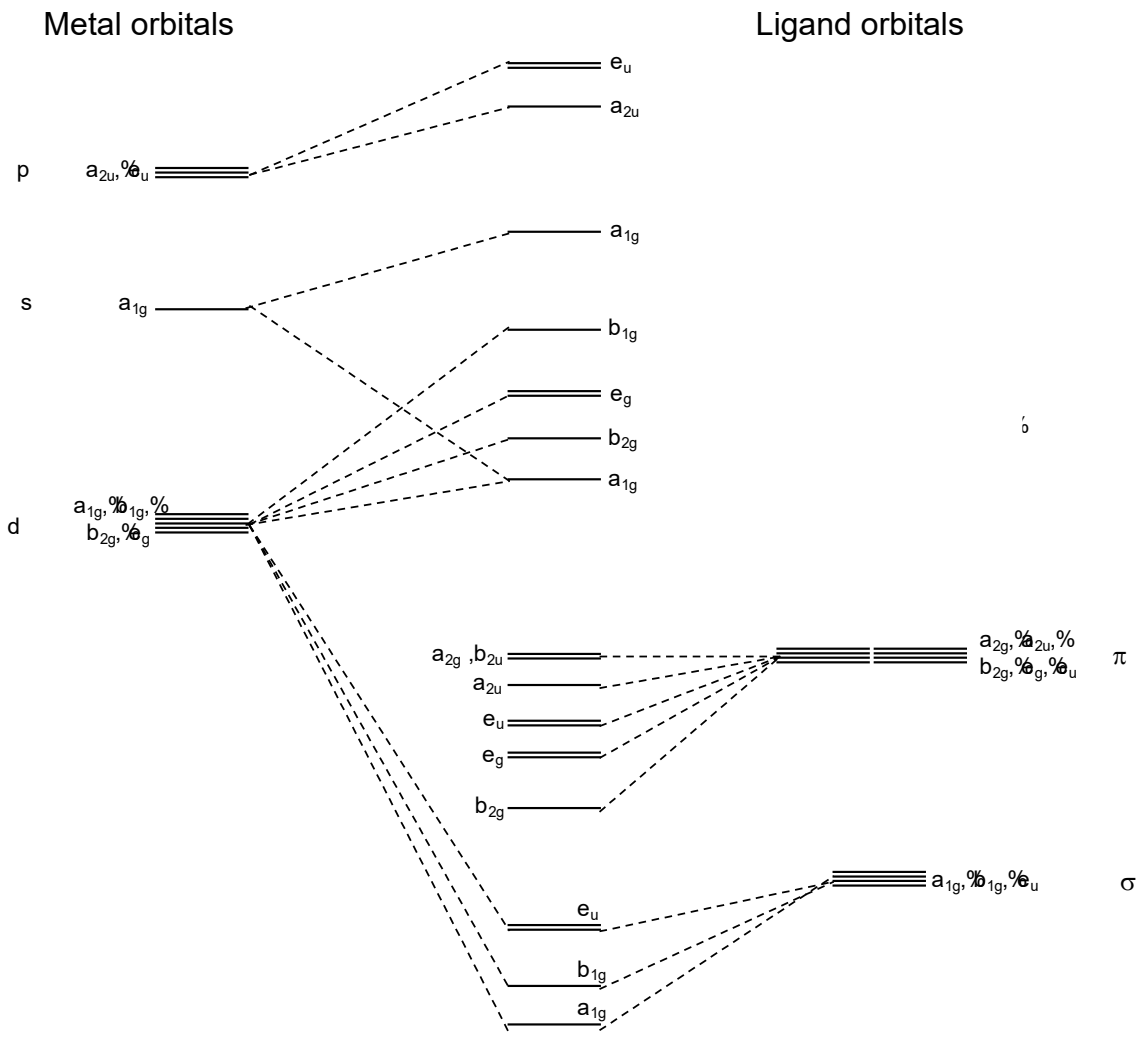
The ground state of this molecule is still A_{1g} and the dipole moment operator still has A_{2u} and E_u symmetry. Now however, there are the ligand π* based orbitals which can be involved in the transitions. There are several possible low lying transitions. These include the same 4 d-p metal based transitions discussed in the σ-only case. There is also now the possibility of the allowed d-π* transitions that would have an expected ε value of around 5,000-50,000 $M^{-1}cm^{-1}$. These include:

$(a_{1g})^2(b_{1g})^0 \dots (a_{2u}(\pi^*))^0 \longrightarrow (a_{1g})^1(b_{1g})^0 \dots (a_{2u}(\pi^*))^1$ (ES = A_{2u})
$(a_{1g})^2(b_{1g})^0 \dots (e_u(\pi^*))^0 \longrightarrow (a_{1g})^1(b_{1g})^0 \dots (e_u(\pi^*))^1$ (ES = E_u)

$(e_g)^4(a_{1g})^2(b_{1g})^0 \dots (a_{2u}(\pi^*))^0 \longrightarrow (e_g)^3(a_{1g})^1(b_{1g})^0 \dots (a_{2u}(\pi^*))^1$ (ES = E_u)
$(e_g)^4(a_{1g})^2(b_{1g})^0 \dots (e_u(\pi^*))^0 \longrightarrow (e_g)^3(a_{1g})^1(b_{1g})^0 \dots (e_u(\pi^*))^1$ (ES includes A_{2u})

$(b_{2g})^2(e_g)^4(a_{1g})^2(b_{1g})^0 \ldots (e_u(\pi^*))^0 \longrightarrow (b_{2g})^1(e_g)^4(a_{1g})^1(b_{1g})^0 \ldots (e_u(\pi^*))^1$ (ES = E_u)

c) π-donor MO diagram:



Once again there are several metal-centered transitions possible. These would include:
$(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \longrightarrow (e_g)^3(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = E_u)
$(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \longrightarrow (e_g)^3(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^1$ (ES includes A_{2u})

$(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \longrightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = A_{2u})
$(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \longrightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = A_{2u})
$(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \longrightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1(e_u)^1$
(ES = E_u)

Now there are also several possible ligand-to-metal charge-transfer transitions. These allowed transitions would be expected to have ε-values around 5,000-50,000 $M^{-1}cm^{-1}$. They include:

$(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0 \longrightarrow (a_{2g})^2(b_{2u})^1(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^1$ (ES = A_{2u})

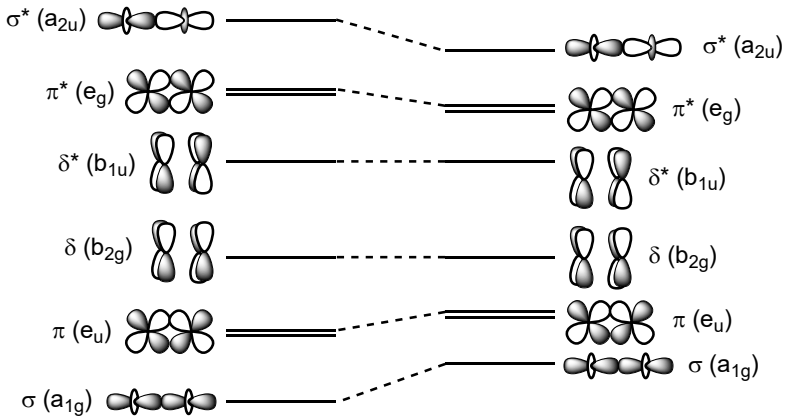
$(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0 \longrightarrow (a_{2u})^1(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^1$
(ES = A_{2u})

$(e_u)^4(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0 \longrightarrow (e_u)^3(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^1$
(ES = E_u)

3) a) The lowest energy *allowed* transitions would be:

$(e_g)^4(a_{2u})^0 \longrightarrow (e_g)^3(a_{2u})^1$	($\pi^* \longrightarrow \sigma^*$)	E_u symmetry
$(e_g)^4(a_{2u})^0(b_{2u})^0 \longrightarrow (e_g)^3(a_{2u})^0(b_{2u})^1$	($\pi^* \longrightarrow$ MLσ^*)	E_u symmetry
$(b_{2g})^2(b_{1u})^2(e_g)^4(a_{2u})^0(b_{2u})^0 \longrightarrow (b_{2g})^1(b_{1u})^2(e_g)^4(a_{2u})^0(b_{2u})^1$	($\delta \longrightarrow$ MLσ^*)	A_{2u} symmetry
$(a_{1g})^2(e_u)^4(b_{2g})^2(b_{1u})^2(e_g)^4(a_{2u})^0 \longrightarrow (a_{1g})^1(e_u)^4(b_{2g})^2(b_{1u})^2(e_g)^4(a_{2u})^1$	($\sigma \longrightarrow \sigma^*$)	A_{2u} symmetry

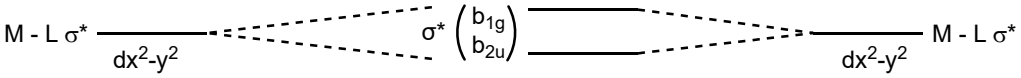
b) If hydroxides bind in the axial positions, they are going to interact with the orbitals that have a component along the z-axis. This means that the orbitals made up of the dz^2, dxz and dyz orbitals would be affected. These orbitals are going to need to use some of their electron density to bond with the hydroxides. This will pull electron density from between the metals, raising the energy of the bonding orbitals slightly and lowering the energy of the antibonding orbitals. The d and d* orbitals, which arise from combinations of the dxy orbitals, will not be affected, as they are not involved in bonding to the axial ligands.

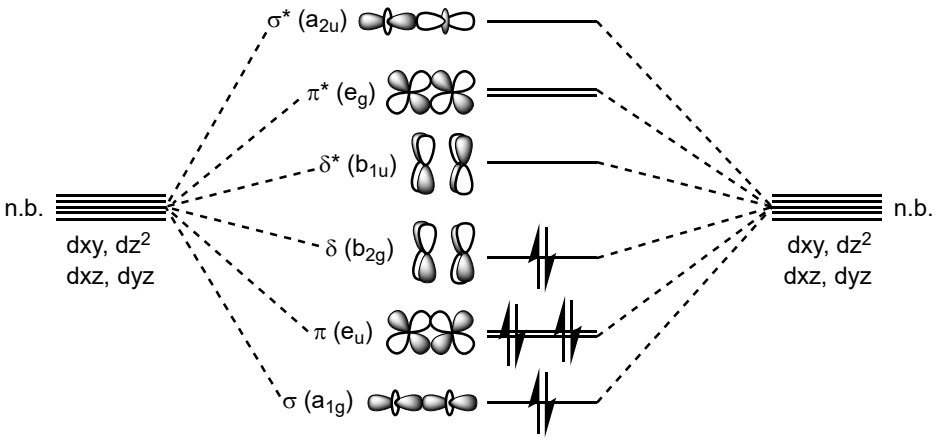


c) This would lower the energy of the $\pi^* \rightarrow \sigma^*$ and $\sigma^* \rightarrow \sigma^*$ transitions, and raise the energy of the transitions to the M-L σ^* orbitals.

d) A stronger σ-donor would have a larger effect on the spectrum. If the donor is strong enough, the orbitals may switch orders and the δ* orbital would become the HOMO. A weaker ligand would have less of an effect.

e) The MO diagram for a d^4 metal would look like:





where the δ and δ* are now the HOMO and LUMO (respectively).

The allowed d-d transitions would be:

$\delta \rightarrow \delta^*$

$\pi \rightarrow \pi^*$

$\sigma \rightarrow \sigma^*$