The d^5 *trans*-[Ru^{III}(H$_2$O)$_4$Cl$_2$]$^+$ problem (revised 2/11/03)

The solution to the d^5 *trans*-[Ru^{III}(H$_2$O)$_4$Cl$_2$] problem – assumes trigonal water molecules and D$_{2h}$ symmetry. See inset Figure 1. Assume Cl-Ru-Cl is z axis. Choice of x and y is arbitrary. Using the character Table, the d orbitals transform as x2-y2, z2 as a$_g$; xy, xz and yz as b$_{1g}$, b$_{2g}$ and b$_{3g}$ respectively. Because of repulsion by water and halide lone pairs, and using coordinate axis shown in Figure 1, the angular overlap model would predict the energy order xz > yz > xy   - this is purely based, qualitatively, on the availability of oxygen and chloride lone pairs to repel any electrons in these orbitals. Note the orientations of the trigonal pπ orbital on each oxygen.

For symmetries of sigma bonds (and Ru-L stretching vibrations), carry out operations of group on the Ru-O,Cl bonds- as there is no operation that mixes Ru-Cl with Ru-O you can do this in two steps.

	E	C2z	C2y	C2x	i	xy	xz	yz
σ-Ru-Cl	2	2	0	0	0	0	2	2
σ-Ru-O	4	0	2	2	0	4	2	2
π-Ru-Cl	4	-4	0	0	0	0	0	0
π-Ru-O along x	2	0	0	-2	0	-2	2	0
π-Ru-O along y	2	0	-2	0	0	2	0	-2

Using the formula to reduce the reducible reps to a sum of irreducible reps- one obtains:

σ-Ru-Cl a$_g$ + b$_{1u}$

σ-Ru-O   2a$_g$ + b$_{2u}$ + b$_{3u}$

π-Ru-Cl b$_{2g}$ + b$_{3g}$ + b$_{2u}$ + b$_{3u}$ {this would be e$_g$ + e$_u$ in the higher D$_{4h}$ group}

π-Ru-O along x - b$_{2g}$ + b$_{1u}$ {note these map nicely, as they should on the xz and p$_z$, orbitals}

π-Ru-O along y - b$_{1g}$ + b$_{3u}$ {note mapping on xy and p$_x$ orbitals here and then think that you might have just looked for the mapping to reduce the rep. instead of doing it formally}

Hence create the qualitative MO diagram as shown in Figure 2

Consider transitions from the filled orbitals to the d(b$_{2g}$) orbital. Since this is a π-orbital transitions from the σ-levels will be overlap forbidden. In D$_{2h}$ symmetry, x,y,z transform as b$_{3u}$, b$_{2u}$ and b$_{1u}$ respectively. Multiply b$_{2g}$ by each of these, you obtain b$_{1u}$, a$_u$ and b$_{3u}$ respectively. Therefore ONLY transitions from these levels will yield symmetry

allowed transitions; Recall we want the triple product, i.e. $\langle b_{1u} | r | b_{2g} \rangle$ (where r is one of the aforementioned x,y,z vectors), to contain (result in) a_g.

Thus transitions possible:
From π-chloride $b_{3u} \rightarrow b_{2g}$ polarization along z (b_{3u})
From π-oxygen along y $b_{3u} \rightarrow b_{2g}$ polarization along z (b_{1u}) **BUT this is an in-plane pπ MO orbital, so transition to out of plane xz is overlap forbidden**

From π-oxygen along x $b_{1u} \rightarrow b_{2g}$ polarization along x (b_{3u})

So, we expect two strong LMCT bands from π-chloride and from π-oxygen (along x, with pπ out of the molecular plane). With the former likely to lower energy, {formally negative charged Cl   valence orbitals likely to lie higher than neutral oxygen}
In addition there could be higher energy bands from the σ-b_{1u} and σ-b_{2u} and σ-b_{3u} orbitals to the σ^* antibonding x^2-y^2 and z^2 orbitals. However, note that a transition from the in-plane σ-orbitals to z^2 and a transition from the axial σ-b_{1u} (Cl) to x^2-y^2 will both be overlap forbidden. So we should see two (or really three) strong much higher energy transitions {σ-orbitals lie deeper and there is a 10Dq jump !}
Namely
σ-chloride b_{1u} to a_g (z^2) polarized along z
σ-oxygen b_{2u} and b_{3u} to a_g $(x^2$-$y^2)$ polarized along y and x respectively- they will probably merge into one band

Think about the consequences if the hole in the d shell is in b_{1g} or in b_{3g} instead of b_{2g}. The polarization will surely change- will the number of bands change ??

Feb 11/03
QED