

Inorganic Chemistry with Doc M.

Day 18. Transition Metals Complexes IV: Ligand Field Theory continued

Topics:

1. The three scenarios

2. Scenario 3: π -back bonding

1. The three scenarios for the MO energy diagram.

Scenario #1. Weak field ligands. When Δ_o is small as is the case with weak field ligands (see the Spectrochemical Series from the previous worksheet.), the e_g orbitals are not out of reach from energy considerations. Since the ligands are “good for” $6 \times 2 = 12$ electrons, and the metal cation can have between zero and ten valence electrons, the MO diagram can have between 12 and 22 electrons populating it. Complete the chart. In the third row, list at least two common examples of metals.

d^0	d^1									
12 e^-	13 e^-									
Sc ⁺³										
Ti ⁺⁴										

Scenario #2. Strong field ligands. When Δ_o is larger as is the case with _____ field ligands, the e_g orbitals are generally too high in energy (too antibonding). Populating them is not done very often, although examples exist. As usual, the ligands deliver 12 electrons. This limits the metal cation. It can donate between _____ and _____ electrons. Thus, the range in total electrons in the molecular orbital diagram is between _____ and _____ electrons. Draw a dark vertical line through the table above marking this “cut-off.” Metal ions with more than this number of electrons will have some bonding issues — such as they are easily oxidized.

Scenario 3. π -back bonding.

Certain ligands, specifically those with π -bonding, are capable of a new interaction with transition metal d-orbitals. Let's discover how this works.

Recall the molecular orbital diagram's we created for diatomics back on Day 6 – 8. Sketch such a diagram for cyanide and populate it. Label the HOMO and LUMO.

Next, sketch the Lewis dot structure for cyanide and assign formal charges to each atom. From the standpoint of formal charges, does cyanide coordinate to the metal via the carbon or nitrogen atom?

The lone pair on carbon corresponds to an sp-orbital from the standpoint of Lewis dot and valence bond theory (the theory that brought us hybridization.) It also corresponds to the HOMO in terms of molecular orbital theory. In either case, the electron pair is the Lewis base pair that is donated to the Lewis acid metal. The bond is a coordinate-covalent bond (both electrons from the same donor) and this sort of interaction is called **σ -donation** by the ligand. When we drew the molecular orbital structure for the octahedral metal complex above, the SALC set consisted of six of these σ -donation orbitals. In terms of hybridization, for ammonia the SALCs would be the sp^3 orbitals. What hybrid orbitals would be used for σ -bonding from cyanide to the metal?

Oxygen is transported through the blood by an octahedral Fe^{+2} in hemoglobin. What orbital would be used for σ -donation by a coordinated O_2 ligand?

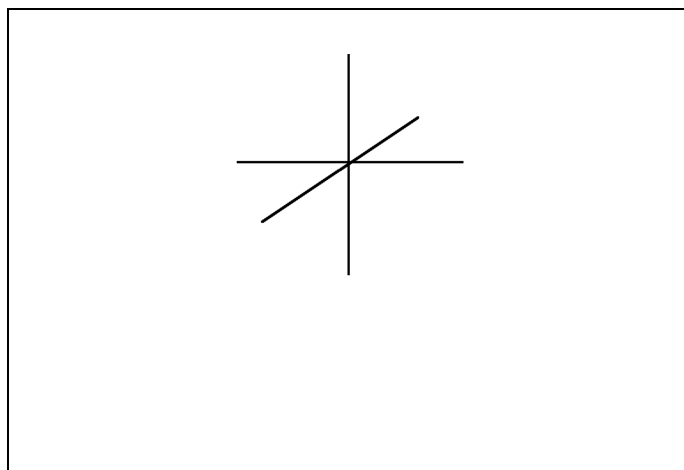
Back to cyanide. The LUMO orbital is the π^* orbital. Sketch it here.

This empty orbital has the right symmetry to overlap with a t_{2g} orbital on the metal. Add this $\pi^* - t_{2g}$ interaction to your π^* sketch in the box above.

Prior to this, the t_{2g} orbitals were non-bonding, but for ligands with π -bonding and thus π^* orbitals, this new interaction is possible. Copy your MO diagram sketched above here, but do not populate it and leave off the t_{2g} non-bonding orbitals.

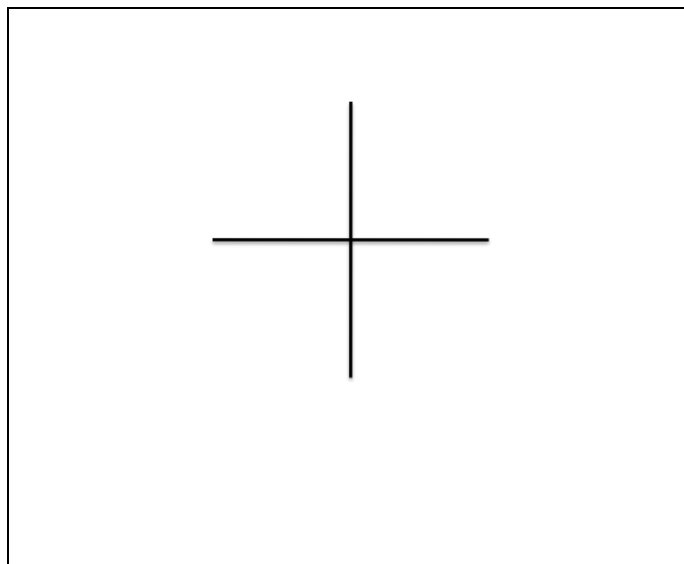
To start, Let's consider the relative energies of the SALC set of σ -donors and the empty π^* orbitals on the ligands. The answer is simple: they are exactly the same as they were in your MO diagram for cyanide above! Relative to the metal's d-orbitals, the π^* orbitals are at about the same energy level as the empty s- and p-orbitals on the metal.

For cyanide and carbon monoxide, there is a triple bond: two p-bonds and two π -antibonds. (For ligands with only a double bond, there is only one p and p^* bond.) Thus, for a SALC set for cyanide, there are $6 \times 2 = 12 \pi^*$ orbitals. Sketch an octahedron, and to the best of your ability, sketch the 12 π^* orbitals that would be used to form the SALC orbitals.



We could go through the usual drill where we perform the octahedral symmetry operations on the 12 π^* orbitals and then use that to produce the irreducible representations, however, it takes a long time and you wouldn't learn anything that you don't already know in terms of procedure. What does come out of this workup, however is a triply degenerate irreducible representation with the same symmetry as the metal's t_{2g} orbitals — and a bunch of other sets that are all non-bonding with s, p and d-orbitals (no additional symmetry-allowed sets.)

The next step, as you recall, was to sketch the MOs and to place them in the energy diagram. Sketch just one of the three equivalent MO drawings (all in one plane) — the result of one of the metals t_{2g} d-orbitals overlapping with four π^* orbitals, all within the same plane. Sketch the MO here.



Is the bonding interaction that you sketched between metal and SALC best described as σ or π in nature?

Suppose the one you sketched featured the d_{yz} orbital and your MO bonding sketch was in the yz-plane (the plane of this paper.) There are two equivalent MO bonding schemes in the d_{xz} and d_{xz} planes. Considering the first one again — the one you sketched, what fraction of each π^* orbital from each ligand participates in each MO? In other words, if we looked at this one t_{2g} SALC set (in the yz plane) and recalling that the contributing atomic orbitals must sum to 1, what fraction of each ligand π^* would you use from each ligand to make the SALC set to overlap with the d_{yz} ?

All together, how many “orbital equivalents” out of the twelve SALCs that we started with are involved in this sort of bonding? The rest of these are non-bonding orbitals.

Finish the MO energy diagram now and populate it for $\text{Fe}(\text{CN})_6^{-4}$.

The π -bonding interaction that we have just explored features electrons from the filled t_{2g} orbitals being distributed out to the ligand's π^* orbitals. Just as we used s-donation to describe the ligand donating electrons to the metal, this π interaction of metal's electrons back to the ligand's π^* orbitals is called **π -back bonding**.

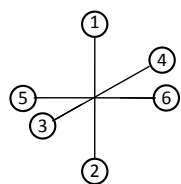
Phosphine and ethane are both capable of π -back bonding. Phosphine uses its empty 3d orbitals. Sketch the interaction between a filled d_{xy} orbital from the metal and phosphine's empty $3d_{xy}$ orbital in an octahedral complex.

The π -back bonding is more important if the ligand has electron withdrawing groups such as fluorine atoms. Thus, PF_3 is better at π -back bonding than is $\text{P}(\text{CH}_3)_3$. So, comparing CN^- and CO , why do you suppose that CO is much better at π -back bonding than cyanide?

In an upcoming worksheet we will learn that if the metal is in a low oxidation state, π -back bonding is more significant. Why is this so?

Day 17 Answers

1. Step 1:

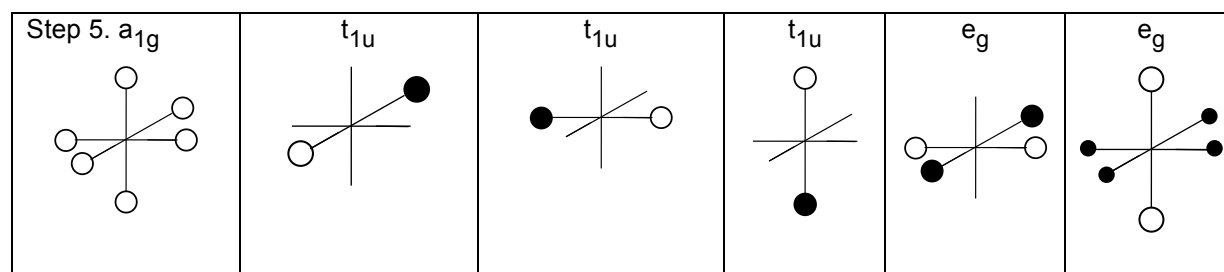


Step 3. (4 pts)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

Step 4. (5 pts):

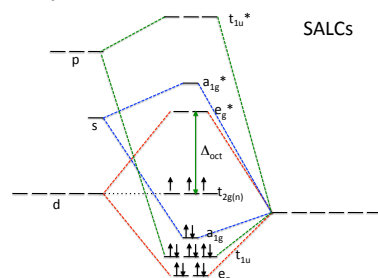
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
E_g	2	-1	0	0	2	2	0	-1	2	0



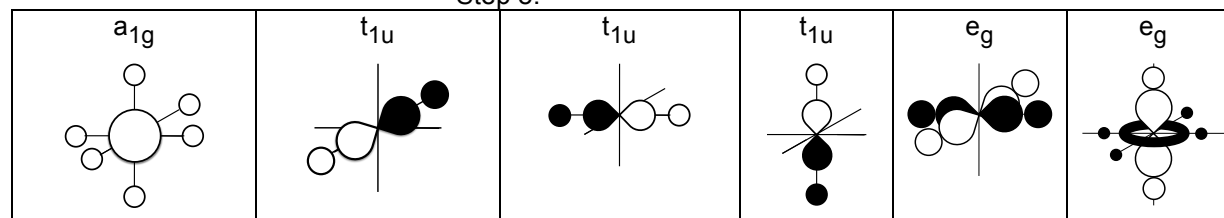
(symmetry)	AO #1	AO #2	AO #3	AO #4	AO #5	AO #6	Total:
SALC (a_{1g})	1/6	1/6	1/6	1/6	1/6	1/6	=1
SALC (t_{1u})	1/2	1/2					=1
SALC (t_{1u})			1/2	1/2			=1
SALC (t_{1u})					1/2	1/2	=1
SALC (e_g)			1/4	1/4	1/4	1/4	=1
SALC (e_g)	1/3	1/3	1/12	1/12	1/12	1/12	=1
Total:	=1	=1	=1	=1	=1	=1	

Step 6. $4s$ (a_{1g}), $4p_x$ (t_{1u}), $4p_y$ (t_{1u}), $4p_z$ (t_{1u}), $3d_{xz}$ (t_{2g}), $3d_{yz}$ (t_{2g}), $3d_{xy}$ (t_{2g}), $3d_{x^2-y^2}$ (e_g), $3d_{z^2}$ (e_g)

Step 7.



Step 8:



B. Using the MO energy diagram. Populate the MO diagram (sketched in Step 7, above) for the complex $Cr(NH_3)_6^{+3}$. See above; i. Cr^{+3} : $[Ar] 3d^3$; ii. $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^3$; iii. Write electron configurations for these complexes: $Co(H_2O)_6^{+2}$: $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^5 (e_g^*)^2$; VCl_6^{-4} : $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^3$; $Fe(py)_6^{+3}$: $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^5$ (assuming the +3 charge and nitrogen ligand results in low-spin; iv. Box should be around the HOMO, t_{2g} , and LUMO, e_g^* . Add the arrow for Δ_O .