

Inorganic Chemistry with Doc M.

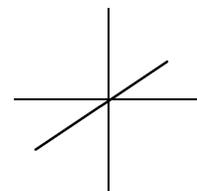
Day 17. Transition Metals Complexes III: Ligand Field Theory (MO Theory)

Topics:

1. Molecular orbital theory and the octahedron
2. The MO energy diagram and Δ_o

1. Octahedral transition metal complexes utilize s, p and d-orbitals in their bonding. For a first row transition metal, these are the 3d, 4s and 4p orbitals (the valence orbitals). Here we will create a molecular orbital diagram that could be used for most octahedral first row complexes. (By simply switching the principle quantum numbers, the diagram will work for second and third row complexes as well.) You will need the O_h character table. We will use the 10-step approach, as guided below, to create a molecular orbital diagram for $ML_6^{+/-n}$.

Step 1. (3 pts) Sketch the ligand group orbitals needed for σ -bonding on a Cartesian coordinate system. Label each circle with a number. Each circle represents the lone pair being donated by the ligand. (Eventually, we will encounter situations where the metal and ligand each donate one to make true covalent bonds, as opposed to coordinate covalent bonds, but the approach is exactly the same.) These six circles will form the SALC sets.



Step 2. Determine the point group symmetry of the set of orbitals drawn and look up its character table. Answer: O_h

Step 3. (4 pts) Determine the *reducible representation*, Γ . Note: it is not necessary to do each and every symmetry operation in order to go on. If any are ambiguous, skip them for now.

| | | | | | | | | | | |
|----------|---|-----------------|-----------------|-----------------|-----------------|---|-----------------|-----------------|--------------|--------------|
| O_h | E | 8C ₃ | 6C ₂ | 6C ₄ | 3C ₂ | i | 6S ₄ | 8S ₆ | 3 σ_h | 6 σ_d |
| Γ | | | | | | | | | | |

Step 4. (5 pts) Determine the irreducible representations. This can be determined from the following formula, used to determine the number of each irreducible representation:

$$n_{\text{irreducible representation}} = \frac{1}{\text{order}} \sum(\Gamma)(\text{coef})(X)$$

where "order" is the sum of the coefficients from along the top of the character table (1 + 8 + 6 + 6 + 3 + 1 + 6 + 8 + 3 + 6 = 48 for the O_h character table below), Γ is the familiar reducible contribution and X is the character for each irreducible component.

| O _h | E | 8C ₃ | 6C ₂ | 6C ₄ | 3C ₂ | i | 6S ₄ | 8S ₆ | 3σ _h | 6σ _d |
|----------------|---|-----------------|-----------------|-----------------|-----------------|---|-----------------|-----------------|-----------------|-----------------|
| | | | | | | | | | | |

You do not need to use this formula (because of the tricks we've learned), but if you did use it because the columns that list how orbitals transform was missing, for example, the calculation would look like this for the first irreducible representation for O_h, namely a_{1g}:

$$n_{a_{1g}} = [(6)(1)(1) + (0)(8)(1) + (0)(6)(1) + (2)(6)(1) + (2)(3)(1) + (0)(1)(1) + (0)(6)(1) + (0)(8)(1) + (4)(3)(1) + (2)(6)(1)]/48$$

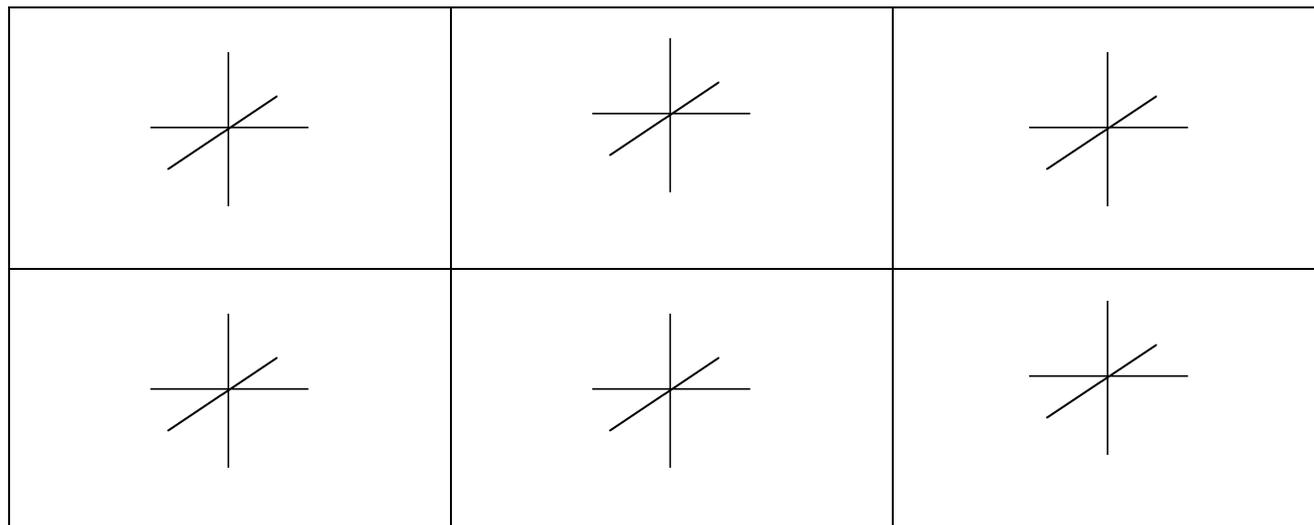
$$= 1$$

$$n_{a_{2g}} = [(6)(1)(1) + (0)(8)(1) + (0)(6)(-1) + (2)(6)(-1) + (2)(3)(1) + (0)(1)(1) + (0)(6)(-1) + (0)(8)(1) + (4)(3)(1) + (2)(6)(-1)]/48$$

$$= 0$$

Continuing on, determine how many e_g irreducible representations are present, and so on. Using the formula or making educated guesses, finish determining what the irreducible components are for the SALC orbitals in an octahedral arrangement.

Step 5. (6 pts) Sketch each of the 6 SALCs (no orbitals from the metal!) with appropriate symmetry labels. Shade in the appropriate lobes of the SALC sets. Complete the table on the next page summarizing how the atomic orbitals are deployed to form the SALCs.



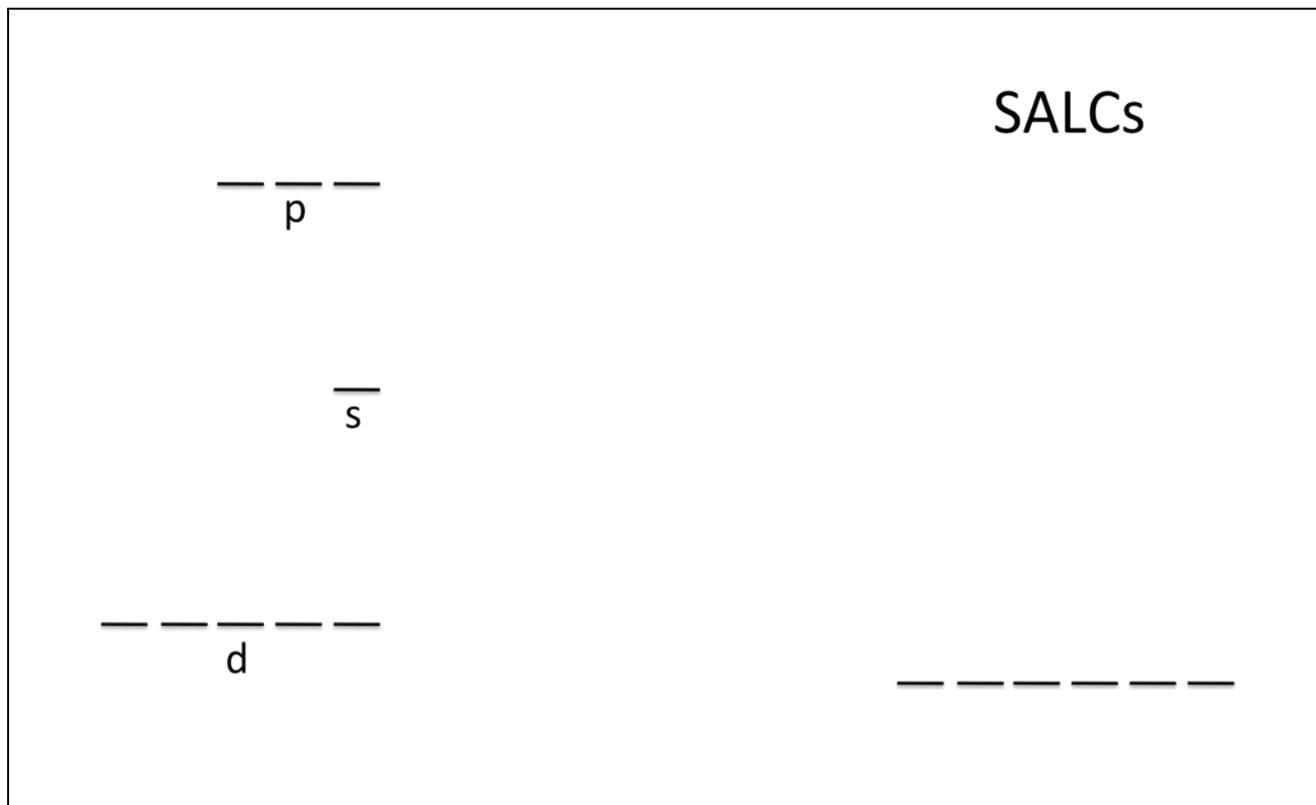
| (symmetry) | AO #1 | AO #2 | AO #3 | AO #4 | AO #5 | AO #6 | Total: |
|---------------|-------|-------|-------|-------|-------|-------|--------|
| SALC () | | | | | | | =1 |
| SALC () | | | | | | | =1 |
| SALC () | | | | | | | =1 |
| SALC () | | | | | | | =1 |
| SALC () | | | | | | | =1 |
| SALC () | | | | | | | =1 |
| Total: | =1 | =1 | =1 | =1 | =1 | =1 | |

Step 6. (3 pts) List all the metal atom's valence orbitals (there are 9: the 4s, the three 4ps and the five 3ds) and assign each one a symmetry label. The first one is done for you.

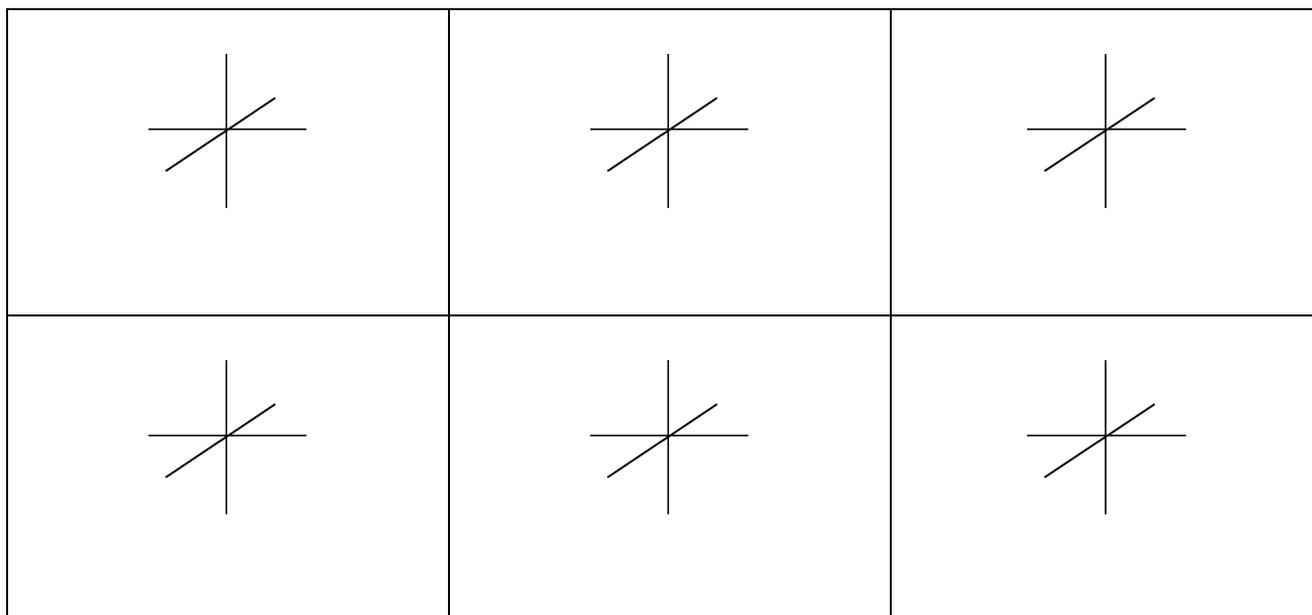
| | | |
|-----------------|--|--|
| 4s (a_{1g}) | | |
| | | |
| | | |

Step 7. (8 pts) Create a MO energy diagram. Start with the correct relative energies! For the metal (sketch AOs on the left side of diagram), the 3d orbitals are lowest in energy providing the metal is a cation, which is almost always the case. The 4s orbital is next lowest in energy and the 4p orbitals are the highest. The ligands have electron pairs and are usually quite content with or without a metal — evidence that the energy of the donating electron pair isn't too high. As a "general" rule, you can sketch the energies of the six SALCs somewhere near

in energy to the lowest of the metal's valence orbitals. I will be checking for labels and for how you connect the atomic and SALC orbitals with lines.



Step 8. (6 pts) Sketch molecular orbital line drawings from overlapping SALCs from Step 5 with the symmetry appropriate AOs from Step 6. Just sketch the bonding interactions — skip the antibonding. You can do it here or, if you prefer, add them to the MO energy diagram above.



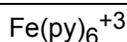
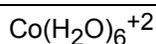
Step 9. (3 pts) Double check to see if you have conserved orbitals.

B. Using the MO energy diagram. Populate the MO diagram (sketched in Step 7, above) for the complex $\text{Cr}(\text{NH}_3)_6^{+3}$.

i. To do so, you should first determine how many electrons are coming from the Cr^{+3} and how many are coming from the six ammonia ligands. Do your math here:

ii. Write the electron configuration here using the notation $(a_{1g})^2 (e_g)^4$ etc.

iii. Write electron configurations for these complexes:



iv. Draw a box around the HOMO and LUMO orbitals in the energy diagram that represents the crystal field orbital energy splitting pattern. Remember this connection! Label Δ_0 .

Review for ACS Final Exam

- The molecular orbitals for octahedral metal complexes are constructed by a linear combination of ligand group orbitals and which atomic orbitals of the metal?
 - $ns + np_x + np_y + np_z + (n-1)d_{x^2-y^2} + (n-1)d_{z^2}$
 - $nd_{xy} + nd_{xz} + nd_{yz} + nd_{x^2-y^2} + nd_{z^2}$
 - $ns + np_x + np_y + np_z$
 - $ns + np_x + np_y + np_z + (n-1)d_{xy} + (n-1)d_{xz} + (n-1)d_{yz}$
 - $np_x + np_y + np_z + nd_{xy} + nd_{xz} + nd_{yz}$
- Rank the d-orbitals from lowest to highest energy for the trigonal prism.
 - $d_{xy} < d_{xz} < d_{yz} < d_{x^2-y^2} < d_{z^2}$
 - $(d_{xy}, d_{x^2-y^2}) < d_{z^2} < (d_{xz}, d_{yz})$
 - $d_{z^2} < (d_{xz}, d_{xy}) < (d_{yz}, d_{x^2-y^2})$
 - $d_{xy} < d_{x^2-y^2} < d_{z^2} < d_{xz}, < d_{yz}$
 - $(d_{xy}, d_{xz}, d_{yz}) < (d_{x^2-y^2}, d_{z^2})$

3. What ligand is a p-acceptor and what is the consequence?

- F^- ; Δ decreases
- F^- ; Δ increases
- NH_3 ; Δ decreases
- NH_3 ; Δ increases
- CO ; Δ increases

4. Which of the following is a characteristic of p-acceptor ligands?

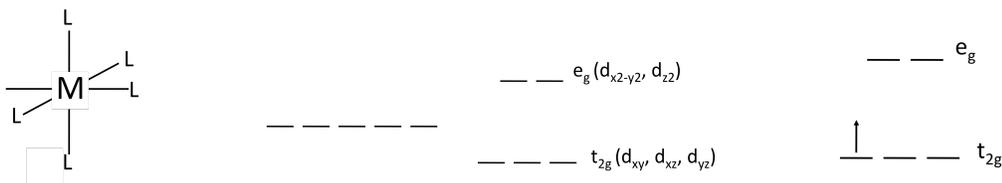
- Δ decreases
- Unusually high oxidation states are stabilized
- The coordination number is always 6
- The ligands have HOMO orbitals with symmetry allowed overlap with empty d-orbitals.
- π -acceptor ligands are also σ -donors.

Answers: A, B, E, E

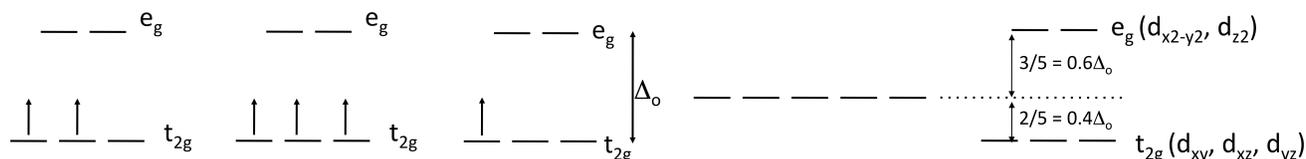
Day 16 Answers

A. The d-orbitals. 1. d_{z^2} ; 2. $d_{x^2-y^2}$; 3. d_{xy} ; 4. d_{xz} ; 5. d_{yz}

B. The energy diagram. (a) yes, less steric repulsion; (b) below:



C. Populating the energy diagram. (a) See above; (b) $(t_{2g})^1 (e_g)^0$; (c) d^2 (e.g. Ti^{+2}) and (d) d^3 (e.g. V^{+2}). Determine the exact fraction of the energy difference...



CFSE for d^1 , d^2 and d^3 ...: for d^1 , CFSE = $0.4 \Delta_o$; for d^2 , CFSE = $0.8 \Delta_o$; for d^3 , CFSE = $1.2 \Delta_o$

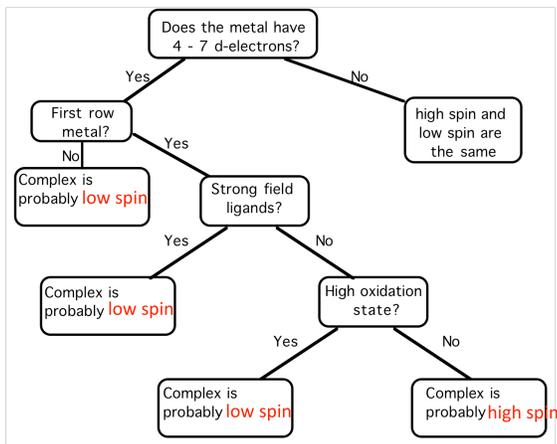
For d^4 , if $P > \Delta_o$, the electron will prefer to occupy the e_g orbital ($t_{2g}^3 e_g^1$). If $P < \Delta_o$, the electron will prefer to occupy the t_{2g} orbital ($t_{2g}^4 e_g^0$). High/low-spin possibilities only occur for d^4 - d^7 electron configurations in an octahedral field.

| | High Spin | | | Low Spin | | |
|----------|------------------|---------------------|-----|------------------|---------------------|-----|
| | config | CFSE | upe | config | CFSE | upe |
| d^0 | $t_{2g}^0 e_g^0$ | 0 | 0 | | | |
| d^1 | $t_{2g}^1 e_g^0$ | $0.4 \Delta_o$ | 1 | | | |
| d^2 | $t_{2g}^2 e_g^0$ | $0.8 \Delta_o$ | 2 | | | |
| d^3 | $t_{2g}^3 e_g^0$ | $1.2 \Delta_o$ | 3 | | | |
| d^4 | $t_{2g}^3 e_g^1$ | $0.6 \Delta_o$ | 4 | $t_{2g}^4 e_g^0$ | $1.6 \Delta_o - P$ | 2 |
| d^5 | $t_{2g}^3 e_g^2$ | 0 | 5 | $t_{2g}^5 e_g^0$ | $2.0 \Delta_o - 2P$ | 1 |
| d^6 | $t_{2g}^4 e_g^2$ | $0.4 \Delta_o - P$ | 4 | $t_{2g}^6 e_g^0$ | $2.4 \Delta_o - 3P$ | 0 |
| d^7 | $t_{2g}^5 e_g^2$ | $0.8 \Delta_o - 2P$ | 3 | $t_{2g}^6 e_g^1$ | $1.8 \Delta_o - 4P$ | 1 |
| d^8 | $t_{2g}^6 e_g^2$ | $1.2 \Delta_o - 3P$ | 2 | | | |
| d^9 | $t_{2g}^6 e_g^3$ | $0.6 \Delta_o - 4P$ | 1 | | | |
| d^{10} | $t_{2g}^6 e_g^4$ | $-5P$ | 0 | | | |

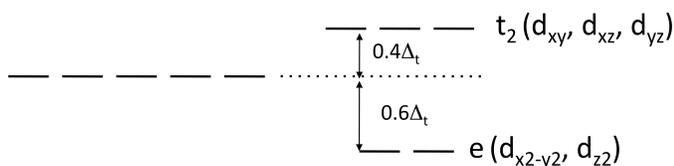
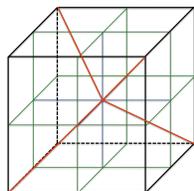
D. Factors affecting Δ_o 2. The nature of the metal ion has an impact on whether the complex will be high- or low-spin. First row metals can be either hs or ls, while 2nd and 3rd row metals are usually ls in an octahedral environment.

3. Calculated Δ_o for $\text{Cr}(\text{CN})_6^{-3} = 17.4 \times 1.7 \times 1000 \text{ cm}^{-1} = 29,600 \text{ cm}^{-1}$; Calculated Δ_o for $\text{Fe}(\text{H}_2\text{O})_6^{+3} = 14.0 \times 1.00 \times 1000 \text{ cm}^{-1} = 14,000 \text{ cm}^{-1}$; Calculated Δ_o for $\text{Ru}(\text{H}_2\text{O})_6^{+2} = 20.0 \times 1.00 \times 1000 \text{ cm}^{-1} = 20,000 \text{ cm}^{-1}$
4. The complex $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ should be high-spin. Wave-numbers are directly proportional to energy, so a pairing energy of $29,875 \text{ cm}^{-1}$ is much greater than Δ_o , so the electrons go high-spin.

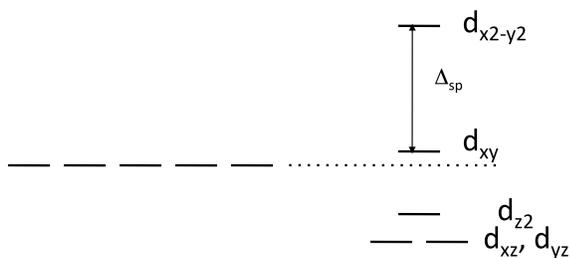
Flowchart:



E. The tetrahedron.

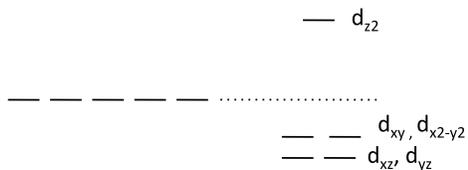


F. The square plane.

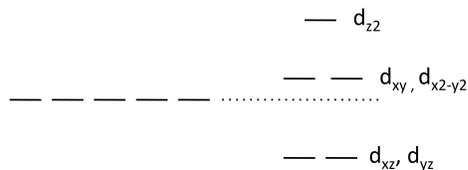


G. Other geometries.

trigonal bipyramid:



pentagonal bipyramid:



Comparing $\Delta_{\text{tetrahedron}}$ to Δ_t : $\Delta_{\text{tetrahedron}}$ in terms of $\Delta_t = 4/9 \Delta_o$; $\Delta_{\text{square pl}} = \Delta_o$. Other geometries that have relatively large Δ values include linear, 2-coordinated, ML_2 , trigonal plane, ML_3 , and the trigonal bipyramid, ML_5 .