

Chemistry 462

Goals for Chapter 23

Introduction to the Transition Elements: Ligand Field Theory

1. Know the basic properties of the “d-block” or transition metals and transition metal complexes.
2. Understand the three main bonding theories for transition metal complexes: Crystal Field Theory (CFT), Ligand Field Theory (LFT), Molecular Orbital Theory (MO) and the relationships among the three.
3. Understand that, depending on the types of orbitals (symmetry) that the ligands have available to overlap with the d orbitals of a transition metal, the d orbital splitting will be different.
4. Know that the most important Molecular Orbitals in the transition metal ML_6 compounds are the d orbitals, which are filled last. In an octahedral molecule the d orbitals split into two groups: the t_{2g} set (d_{xz} , d_{yz} , d_{xy}) which is lower in energy than the e_g set ($d_{x^2-y^2}$, d_z^2).
5. Know that the d orbital splitting in a tetrahedral geometry, ML_4 , leads to two different sets of d orbitals whose energies are the reverse of the octahedral geometry. In a tetrahedral geometry, the e set ($d_{x^2-y^2}$, d_z^2) is the lowest and the t_2 set (d_{xz} , d_{yz} , d_{xy}) is the higher energy set.
6. Know that the splitting energy between the t_{2g} and e_g sets is called the “octahedral splitting energy” and the common symbols are Δ_o and $10D_q$ (we did not use the latter). The t_{2g} and e_g orbitals in ML_6 represent the Highest Occupied Molecular Orbitals (HOMO's) and the Lowest Unoccupied Molecular Orbitals (LUMO's). In tetrahedral, the e and t_2 levels are the HOMO/LUMO set.
7. Know that π -donors have (a) low energy, filled σ -symmetry group orbitals and (b) higher energy, filled π -symmetry group orbitals that can overlap with metal orbitals that have the same symmetry (recall the possible metal orbitals are the nine valence orbitals d(five), s(one) and p(three) whose energies are in that order). The overlap leads to the t_{2g} and e_g sets of d orbitals with a very small splitting energy Δ_o value.

8. Know that σ -donors have only low energy σ -symmetry group orbitals with which to participate in bonding to the metal which has d, s, and p orbitals whose energies are in that order. Their interaction with the d orbitals leads to an intermediate Δ_o value.
9. Know that π -acceptors have (a) low energy, filled σ -symmetry group orbitals and (b) very high energy, empty π^* -symmetry group orbitals that can overlap with metal orbitals that have the same symmetry. These ligands produce the largest Δ_o value.
10. Know that the tetrahedral molecules produce M.O. energy diagrams similar to the octahedral ones, but that $e < t_2$ in energy and that overall the Δ_t is much smaller than Δ_o for the same metal and ligands (Δ_t is $4/9\Delta_o$).
11. Know that Crystal Field Theory (CFT) arrives at the same d orbital splitting energies found in M.O. theory by assuming that the metal and the ligands are point charges. This is a purely electrostatic bonding theory. The positively charged metal ion without ligands (free ion) has all five d orbitals at the same energy. When point charges (considered to be negative charges of Ligand electrons) are brought around the metal, the orbitals split into two groups (t_{2g} orbitals go down in energy by $2/5\Delta_o$ due to less repulsion of M electrons with L electrons and e_g orbitals go up by $3/5\Delta_o$ in energy).
12. Know that Ligand Field Theory (LFT) is an extension of the concept of Crystal Field Theory, but it allows for covalency considerations in the M-L bonds.
13. Know that High-Spin (H.S.) or Low-Spin (L.S.) Complex refers to the filling of the t_{2g}/e_g and e/t_2 sets with electrons. The Octahedral molecules can be either H.S. or L.S., but tetrahedral is only H.S.
14. Know that the relative amount of the Δ_o and Δ_t values can be used to explain whether a molecule is a High-Spin (H.S.) or a Low-Spin (L.S.) Complex. The choice of whether to be L.S. or H.S. depends on the overall LFSE (Ligand Field Stabilization Energy) for the two different electron configurations (L.S. versus H.S.). One can calculate the LFSE for d^1 - d^{10} configurations by assigning the energy of $-2/5\Delta_o$ for every electron in the t_{2g} set and $+3/5\Delta_o$ for every electron in the e_g set. If there are pairs of electrons, add a P_e term for every L.P.

15. Know that CFT for the tetrahedral geometry predicts the opposite sets of orbitals will be repelled and stabilized by the application of a tetrahedral crystal field. The e set ($d_{x^2-y^2}$, d_{z^2}) is the lowest set and the t_2 set (d_{xz} , d_{yz} , d_{xy}) is the highest.
16. Know that the square planar d orbital splitting can be derived from the octahedral energy diagrams by considering the effect of “pulling two ligands away” along the z direction. This serves to stabilize all orbitals with “z character” and destabilize any orbitals with pure “x and y character”. The limit of pulling away the two ligands is to make an ML_4 square planar compound. Know the diagram that applies to this and that SQUARE PLANAR MOLECULES ARE NEVER HIGH SPIN.
17. Know how to sketch the possible d^1 - d^{10} electronic configurations for an ML_6 (octahedral) and ML_4 (tetrahedral) complex and tell the possible H.S./L.S. configurations whenever applicable. Be able to tell how many unpaired electrons are possible for each type of d^n configuration and H.S./L.S. combination.
18. Know that CFT/LFT can help one to predict properties of transition metal complexes, most importantly for this chapter, magnetism (number of unpaired electrons) and electronic spectroscopy (qualitative determination of how many transitions and whether they will be easy to observe or not).