Lecture 5+6+7: Crystal field theory and the spin only formula

1. Draw orbital splitting diagrams for octahedral, tetrahedral and square planar geometries. Draw in the barycentre and label the orbitals, the symmetry of each orbital set, and the appropriate crystal field splitting parameter.

2. Draw and label orbital splitting diagrams for the following complexes. Derive an expression for the CFSEs of the following complexes and state the number or unpaired electrons in each:
   a) \([\text{Co(H}_2\text{O)}_6\text{]}^{2+}\)
   b) \([\text{Fe(phen)}_3^{2+}\) (low spin)
   c) \([\text{NiCl}_4^{2-}\)

3. In which of the following complexes would \(\Delta_o\) be larger and why?
   a) \([\text{Cr(H}_2\text{O)}_6]\text{]}^{2+}\) and \([\text{Cr(H}_2\text{O)}_6]\text{]}^{3+}\)
   b) \([\text{CrF}_6^{3-}\) and \([\text{Cr(NH}_3)_6]\text{]}^{3+}\)
   c) \([\text{Fe(CN)}_6]\text{]}^{3-}\) and \([\text{Fe(CN)}_6]\text{]}^{4-}\)

4. For the following complexes, draw an orbital splitting diagram with the appropriate number of d electrons and calculate the spin-only magnetic moment (don't forget the UNITS).
   a) \([\text{Mn(CN)}_6]^{4-}\)
   b) \([\text{Mn(CN)}_6]^{2-}\)
   c) \([\text{Cr(en)}_3]^{2+}\) (low spin)
   d) \([\text{Fe(ox)}_3]^{3+}\) (high spin)
   e) \([\text{Pd(CN)}_4]^{2-}\)
   f) \([\text{NiBr}_4]^{2-}\)

5. The value of the crystal field splitting parameter is 9 400 cm\(^{-1}\) for \([\text{Fe(H}_2\text{O)}_6]\text{]}^{2+}\) and about 4000 cm\(^{-1}\) for \([\text{FeCl}_2(P\text{Ph}_3)_2]\) (\(\mu_{\text{eff}}\) for both complexes lies between 5.0 – 5.6). Calculate the CFSEs of the two complexes in cm\(^{-1}\) and explain the discrepancy.

6. When \(\text{CoCl}_2\) is dissolved in water, a pale coloured pink solution is obtained. On adding conc. HCl the solution turns an intense blue colour. Suggest structures for the pink and the blue complexes, and draw the appropriate orbital splitting diagrams. What is the reason for the change in colour? Calculate the spin-only magnetic moments of the two complexes you propose.
Tutorial on lecture 8+9: selection rules and LFE

1. A solution of $[\text{Mn(H}_2\text{O)}_6]^{2+}$ has a very faint pink colour while a solution of $[\text{MnBr}_4]^{2-}$ is a more intense green. Draw crystal field splitting diagrams for the two complexes, account for their colours explain why the intensities of the colours are different.

2. Discuss the assumptions on which crystal field theory is based and the experimental evidence for its breakdown.

3. Describe the bonding in $[\text{Ni(NH}_3)_6]^{2+}$ using:
   a) valance bond theory 
   b) crystal field theory 
   c) molecular orbital theory

4. Why is CO a stronger field ligand than PR$_3$?

5. Put the following complexes in order of stability. With the aid of orbital splitting diagrams account for the differences in stability between the complexes.

   $[\text{Zn(EDTA)}]^{2-}$, $[\text{Fe(EDTA)}]^{2-}$, $[\text{Cu(EDTA)}]^{2-}$, $[\text{Ni(EDTA)}]^{2-}$, $[\text{Mn(EDTA)}]^{2-}$