

Ligand field theory

General considerations with an example - what happens by dissolving Ti^{3+} -ion in water?

- Ti^{3+} is positively charged, the oxygen in the water molecules is partially negatively charged
- => attractive interaction between electrons in the water molecules and Titanium-cation
- => one could expect spherical surrounding of the Ti^{3+} by the water molecules with oxygen pointing in direction of the cation.

but:

- repulsion between outer electrons of the Ti^{3+} and electrons of the oxygen in the water molecules
- => electronic structure of outer electrons (d-orbitals) of the Ti^{3+} is important:
- d-orbitals: three are lying between the axis (d_{xy} , d_{xz} , d_{yz}), two in direction of the axis ($d_{x^2-y^2}$, d_{z^2}).
- => not every direction is energetically equal
- => no spherical but octahedral or tetrahedral coordination should be energetically favored
- **octahedron:** all six atoms lie in direction of the axis
- => repulsion of ligands and electrons in d-orbitals along the axis
- => splitting of the five degenerated energy levels into two different levels, where the lower one contains the three orbitals between the axis and the higher one the other orbitals
- **tetrahedron:** all four atoms lie between the axis
- => repulsion of ligands and electrons in d-orbitals between the axis
- => oppositional splitting in comparison to the octahedral case (three higher and two lower levels)
- difference between the two energy levels is Δ
- the splitting in tetrahedral field is lower than in an octahedral field ($\Delta_{\text{tet.}} = 4/9 \Delta_{\text{oct.}}$)

What can be explained with help of this theory?

example I: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, red-violette, configuration of Ti^{3+} $[\text{Ar}]3d^1$

- in this example Δ is about 243 kJ per mol (500 nm)
- => absorption at about 500 nm (range of blue-green light)
- => red violette is the contrast colour

example II: $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, very weak pink, configuration of Fe^{3+} $[\text{Ar}]3d^5$

- all five d-orbitals are filled half (all with α -spin)
- => excitation should not be possible (forbidden by spin)
- => very weak colour

example III: $[\text{Fe}(\text{CN})_6]^{3-}$, configuration of Fe^{3+} $[\text{Ar}]3d^5$

- magnetic measurements show a significantly lower magnetic momentum than for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- magnetic momentum μ can be calculated according to: $\mu_{\text{mag}} = (n(n+2))^{0.5} \mu_{\text{B}}$, with n = number of unpaired electrons, μ_{B} = magnetic constant
- => $[\text{Fe}(\text{CN})_6]^{3-}$ must contain paired electrons (conflict to Hundt's rule)
- in $[\text{Fe}(\text{CN})_6]^{3-}$ Δ is bigger then the pairing energy of the spins => **low spin complex**
- in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ Δ is lower than the pairing energy of the spins => **high spin complex**
- => splitting (Δ) depends on the ligands (and on the cation what is not further proofed here)
- => spectrochemical series

Jahn-Teller-effect:

- stretching of the two atoms in z-direction in an octahedron leads to an advantage for all orbitals with z-components because the repulsion decreases
- => splitting of the two energetic levels into four levels at all
- => complexes with unsymmetric occupation of the higher level d-orbitals often show this effect, for example Cr^{2+} (d^4 high spin), Mn^{3+} (d^4 high spin), Ag^{2+} (d^9) and Co^{2+} (d^7 low spin).