Crystal-field theory

This is an early theory of electronic structure of complexes especially for the properties of transition metal ions in ionic crystals. The model of an **octahedral complex** is used, with six ligands placed on the Cartesian axes centered on the metal ion. The ligands interact strongly with the central metal ion.

1. Ligand field splitting parameters

$d_{z^2}, d_{x^2-y^2}$ symmetry type: **e_g (**$3/5\Delta_o$ above the average energy)

- d-orbitals pointing directly along the Cartesian axes and directly at the ligands

=> the electrons are repelled more strongly by the ligands

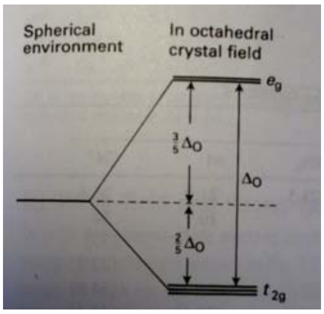
=> orbitals are doubly degenerate

d_{xy}, d_{yz}, d_{zx} symmetry type: **t_{2g} (**$2/5\Delta_o$ below the average energy)

- d-orbitals that point between the ligands

=> electrons are less repelled by the ligands

=> orbitals are triply degenerate



This leads to an **energy diagram** in which the t_{2g} orbitals lie below the e_g orbitals. The separation (energy difference) is called "ligand field splitting parameter" Δ_o (O: stands for octahedral)

2. Spectrochemical series

The ligand field splitting parameter (Δ_o) varies systematically with the kind of ligands. In the spectrochemical series the ligands are arranged in order of increasing energy for the splitting of the d orbitals (higher optical absorption). The values of Δ_o also depend on the metal ion with two important trends: Δ_o increases with increasing oxidation number and increases down a group. Δ_o depends also on the row of the metal ion in the periodic table and normally $\Delta_o(5d) > \Delta_o(4d) > \Delta_o(3d)$.

=> spectrochemical series of ligands:

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py < NH_3 <$ $en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$

=> spectrochemical series of metal ions:

$Mn^{2+} < Ni^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

3. High spin and low spin complexes

low spin complex: species with smaller number of parallel electron spins

high spin complex: species with the greater number of parallel electron spins

Ligand field stabilization energy *(LFSE)* is the net energy of a **$t_{2g}^x e_g^y$ configuration.** It is relative to the average energy of the orbitals with: **LFSE= $(-0.4x+0.6y)\,\Delta_o$**

For the lowest energy configuration the Pauli Exclusion Principle and if possible the Hund's rule have to be respected. The ground state configuration for d^n configurations with n= 1, 2, 3 and also for n= 8, 9, 10 complexes is unambiguous because there is no competition between LFSE and pairing energy. There are two possibilities for d^n configurations with n=4, 5, 6, 7: the high spin and the low spin configuration. The strength of the crystal field (Δ_o) and the spin pairing energy (P) depend on the identity of both metal and ligands and it is not possible to specify a point in the spectrochemical series at which a complex changes from high spin to low spin.

e.g. d^4 elements :

1.) **High spin** : three 3d electrons occupy separate t_{2g} and one electron occupies one of the e_g orbitals -> pairing penalty avoided

LFSE= 3x $(-0,4\Delta_o)+ 0,6\ \Delta_o= -0,6\ \Delta_o$

2.) **Low spin** : all electrons occupy the t_{2g} orbitals so that one of them is occupied from two electrons -> strong coulomb repulsion: “pairing energy” (P)

LFSE= 4x $(-0,4\Delta_o)= -1,6\Delta_o$ **- net stabilization= $-1,6\Delta_o$-P**

Δ_o<P= “weak-field case”: - lower energy is achieved if the upper orbital is occupied: $t_{2g}^3\ e_g^1$ configuration e. g. $[Cr(OH_2)_6]^{2+}$ (high spin complex)

Δ_o>P= “strong field case”: - lower energy is achieved by occupying only the lower orbitals despite the cost of the pairing energy: t_{2g}^4 configuration e.g. $[Cr(CN)_6]^{4-}$ (low spin complex)

4. Color of transition metal complexes

The color of transition metal complexes is related to the excitation of the d-electrons from the t_{2g} state to the e_g state. The splitting of the d orbitals is directly related to the energy of the absorbed light. The color of the complex is the complementary color of the absorbed light.

	$[Ni(H_2O)_6]^{2+}$	**$[Ni(NH_3)_6]^{2}$**
Color of the complex	Green	Blue
Absorbed light	Red	Yellow
Splitting	small	Larger as for $[Ni(H_2O)_6]^{2+}$

References:

P. Atkins, T. Overton, J.Rourke, M. Weller, F. Armstrong, *Shriver & Atkins ‘Inorganic Chemistry*, 5th edition, **2010**, Oxford University Press, Oxford.
E. Riedel, *Anorganische Chemie*, 6. Auflage, **2004**, Walter de Gruyter, Berlin

Further tasks:

I. Apply the crystal-field theory for octahedral complexes on a d^6 configuration. Give a possible example and calculate the LFSE.
II. Explain the difference of high and low spin complexes.