Crystal Field Theory

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Crystal Field Theory (CFT) supersedes valence bond theory as it provides a simple method to explain the **electronic spectra** and **magnetism** of transition metal complexes. CFT is based on the influence of incoming ligands on the **five** d-orbitals in the metal centre; which depends on the number of such ligands and the **geometry** of the compound. According to the shapes and orientation of d-orbitals, they are divided into two groups.

t_{2g} **orbitals** - d_{xy}, d_{yz} and d_{xz} orbitals with lobes (*i.e.* electron density) located between the x, y and z axes.

e_g **orbitals** - $d_{(x^2-y^2)}$ and d_{z^2} orbitals with lobes pointing along the axes.

CFT is based on four main **assumptions**:

a. Ligands are considered as point charges.

b. The bonding between the metal and the ligand is entirely electrostatic.

c. There is no interaction between the metal orbitals and ligand orbitals.

d. In the free metal atom, the d-orbitals have the same energy, *i.e.*, they are degenerate.

CFT for Octahedral Complexes

As e_g orbitals have lobes directed towards the ligands, they are strongly interacting with ligands than the t_{2g} orbitals. Thus, e_g orbitals have higher energy with respect to the t_{2g} orbitals. As a result, the d-orbitals are no longer degenerate; the energy of the two e_g orbitals is raised, while the energy of the three t_{2g} orbitals is lowered by the same amount as shown in Figure 1. The difference in energy between the t_{2g} and e_g levels is denoted by the symbol Δ_o. The term Δ(delta) represents the **crystal field splitting**, and the subscript '**o**' refers to the **octahedral**.
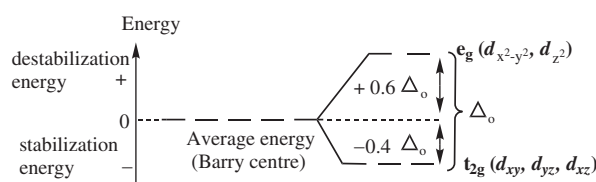
Figure 1: Energy diagram for an octahedral compound

'Δ' depends on the electrostatic field generated by the ligands; thus, some create a **stronger** field than the others. When ligands are arranged in the increasing order of their electrostatic field strength, it is known as the **spectrochemical series**.
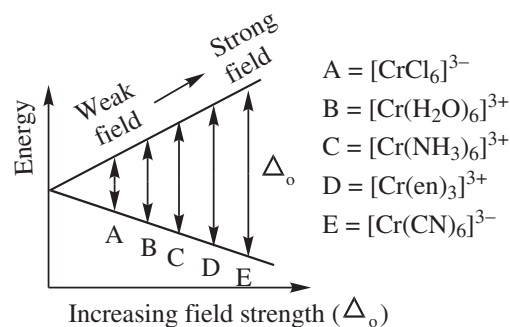
$\longleftarrow$ **Weak field ligands**

$I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < OH^- < EtOH < Oxalate < H_2O < NCS^- < EDTA^{4-} < NH_3 < py < en < bipy < phen$ (1,10-phenanthroline) $< NO_2^- < PR_3 < CN^- < CO$

Strong field ligands $\longrightarrow$

The factors which effect on the crystal field splitting are as follows.

Nature of the ligand - Energy gap Δ varies with the type of ligands as shown below.

A = $[CrCl_6]^{3-}$
B = $[Cr(H_2O)_6]^{3+}$
C = $[Cr(NH_3)_6]^{3+}$
D = $[Cr(en)_3]^{3+}$
E = $[Cr(CN)_6]^{3-}$

Figure 2: Effect of ligand fields on Δ_o

The charge on the metal - Δ increases with increasing of the charge on the metal ion; as the central ion with a higher charge can polarize the ligand to a great extent, thereby it increases the electrostatic field.

Position of metal centre within the Group - Δ_o increases as the row number increases within the Group; $\Delta_o(3d) < \Delta_o(4d) < \Delta_o(5d)$.

Geometry of the complex - For example, the splitting of t_{2g} and e_g levels in octahedral and tetrahedral complexes is quite opposite (see Figures 1 and 4).
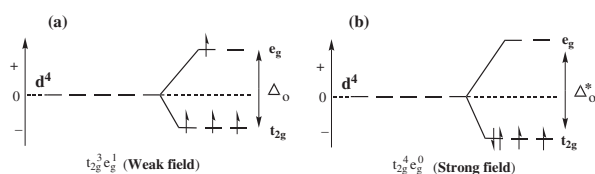
Crystal Field Stabilization Energy

The overall energy of a set of electrons in t_{2g} and e_g levels is known as crystal field stabilization energy (CFSE). **CFSE = [0.6m-0.4n]Δ_o** for $t_{2g}^n.e_g^m$ configuration, *i.e.*, for $t_{2g}^1.e_g^0$, CFSE = -0.4Δ_o; for $t_{2g}^2.e_g^0$, CFSE = -0.8Δ_o and for $t_{2g}^3.e_g^0$, CFSE = -1.2Δ_o. For example, Ti^{3+} ion ($t_{2g}^1.e_g^0$) in $[Ti(H_2O)_6]^{3+}$ is stabilized by an energy amounting to 0.4Δ_o. All possible $t_{2g}^n.e_g^m$ configurations for weak and strong fields are given in Table 1.

For d^4-complexes, two electron distributions ($t_{2g}^4.e_g^0$ and $t_{2g}^3.e_g^1$) are possible (see Figure 3). The electron distribution is determined by the **pairing energy** (PE) (*i.e.* the energy required to pair two electrons in an orbital) and the strength of the crystal field (Δ_o).

(a) The $t_{2g}^3.e_g^1$ configuration is favored when PE>Δ_o. These complexes are known as 'high-spin' or 'weak-field' complexes.

(b) The $t_{2g}^4.e_g^0$ configuration is favored when $\Delta_o^* >$ PE. These complexes are known as 'low- spin' or 'strong-field' complexes.

Note that $\Delta_o<$ PE$<\Delta_o^*$

Figure 3: Energy level diagrams for a d^4 configuration for weak field and strong field ligands

Total Stabilization Energy (**TSE**) = CFSE + m x Pairing Energy (**PE**); m = number of orbitals with paired electrons. For $t_{2g}^5.e_g^0$ configuration,

TSE = CFSE + 2 PE = -2Δ_o + 2PE

Similarly, for the configurations $t_{2g}^6.e_g^0$ and $t_{2g}^6.$

e_g^1, total stabilization energies are -2.4Δ_o+3PE and -1.8Δ_o+3PE, respectively.

CFT for Tetrahedral Complexes

In tetrahedral complexes, t_{2g} orbitals situated between x, y and z axes, and strongly interact with incoming ligands than e_g orbitals. Therefore, t_{2g} orbitals become less stable due to their closeness to the ligands, while e_g orbitals become more stable (see Figure 4).
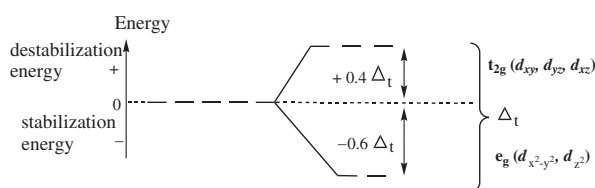
Figure 4: Energy level diagram for a set of five *d*-orbitals in the prescence of a tetrahedral crystal field

Note that $\Delta_t \approx 0.5\Delta_o$ where 't' refers to **tetrahedral**.

Tetrahedral complexes are favored when;

- Ligands are large and bulky
- Ligands are weak field where Δ_t is quite small
- Electronic configuration of the metal centre is d^0, d^5 or d^{10}.

For both octahedral and tetrahedral complexes, CFSE is zero for d^0, d^5 and d^{10} configurations. But for all other configurations, the octahedral CFSE is greater than that of the tetrahedral CFSE; thus octahedral complexes are more stable than tetrahedral complexes.

CFT for square-planar complexes

Generally, d^8 configurations show square-planar geometry. It can be achieved by removing two axial ligands of an octahedral complex. The energy of the orbitals in the xy plane is increased, which makes d_{z^2} orbital more stable than $d_{x^2-y^2}$. Likewise, d_{xy} becomes less stable than d_{zx} and d_{yz} orbitals as shown in Figure 5. The magnitude of Δ_{sp} is roughly 1.3 times higher than Δ_o.
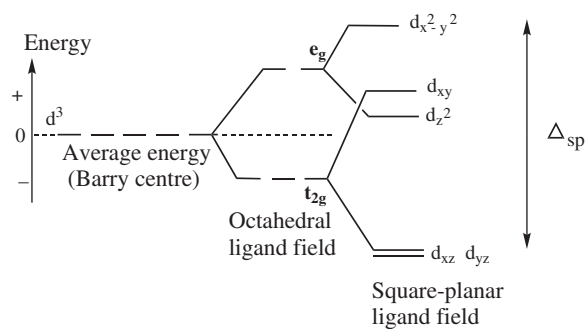
Figure 5: Crystal Field Splitting in a Square-planar complex

Magnetic properties

Total magnetic moment (μ) of an unpaired electron of a paramagnetic complex arises due to its spin about the own axis and its orbital angular momentum. For first-row transition metals, μ is equal to 'spin only' magnetic moment (μ_s), as its orbital angular momentum is negligible. The relationship between μ_s and the number of unpaired electrons 'n' is, $\mu_s = \{n(n+2)\}^{1/2}$. The μ values are given in the Table 1 in Bohr Magneton (BM).

Table 1: Data for an octahedral complex; X = d-electron distribution, Y = number of unpaired electrons n with the μ_s value in brackets

d^n	Strong Field		Weak Field	
	X	Y	X	Y
d^1	$t_{2g}^1.e_g^0$	1(1.73)	$t_{2g}^1.e_g^0$	1(1.73)
d^2	$t_{2g}^2.e_g^0$	2(2.83)	$t_{2g}^2.e_g^0$	2(2.83)
d^3	$t_{2g}^3.e_g^0$	3(3.87)	$t_{2g}^3.e_g^0$	3(3.87)
d^4	$t_{2g}^4.e_g^0$	2(2.83)	$t_{2g}^3.e_g^1$	4(4.90)
d^5	$t_{2g}^5.e_g^0$	1(1.73)	$t_{2g}^3.e_g^2$	5(5.92)
d^6	$t_{2g}^6.e_g^0$	0(0.00)	$t_{2g}^4.e_g^2$	4(4.90)
d^7	$t_{2g}^6.e_g^1$	1(1.73)	$t_{2g}^5.e_g^2$	3(3.87)
d^8	$t_{2g}^6.e_g^2$	2(2.83)	$t_{2g}^6.e_g^2$	2(2.83)
d^9	$t_{2g}^6.e_g^3$	1(1.73)	$t_{2g}^6.e_g^3$	1(1.73)
d^{10}	$t_{2g}^6.e_g^4$	0(0.00)	$t_{2g}^6.e_g^4$	0(0.00)

Color of transition metal complexes

Most transition metal complexes are colored, as they transmit the complementary color of the absorbed light. Excitation of electrons between t_{2g} and e_g levels (or d-d transitions) occurs in the visible region. By analyzing the absorption spectra of these complexes, the size of Δ can be calculated. The possible electron excitations and their intensities are determined by the Laporte and Spin selection rules.

Problems

1.

(a) What are the numbers of t_{2g} and e_g electrons of Cr in $[CrBr_6]^{4-}$? Br^- is a weak field ligand.

(b) Calculate the CFSE and TSE in kJ mol^{-1} if $\Delta_0 = 160$ kJ mol^{-1}.

(c) Calculate the μ_s of $[CrBr_6]^{4-}$.

2.

(a) What is the d-electron configuration of Fe in $[FeBr_4]^{2-}$?

(b) Calculate the CFSE and TSE in kJ mol^{-1} for this anion if $\Delta_0 = 180$ kJ mol^{-1} and PE = 120 kJ mol^{-1}.

(c) Calculate the μ_s of $[FeBr_4]^{2-}$