Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (T. Y. B. Sc.)

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Unit: 2 - Spectra and Magnetic Properties

Module Name: Effect of Crystal Field Splitting on Properties of Octahedral Complexes: Magnetic

Module No: 16

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Notes

Effect of Crystal Field Splitting on Magnetic Properties of Octahedral Complexes:

Crystal Field Splitting (CFS) can successfully explain the Magnetic Properties of Complexes. Accordingly , it gives the following information

i) Explains if a compound is DIAMAGNETIC OR PARAMAGNETIC

ii) Calculation of Magnetic Moment of a magnetic substance

iii) The magnetic properties are then determined from the Magnitude of CFS in an Octahedral Complex (Δo)

I. Diamagnetic and Paramagnetic substances

Diamagnetic substances do not have any unpaired electrons. They are repelled by magnetic field and do not have permanent magnetic dipole moment.

Example: Water, wood, Glass, Organic Compounds and metals like pure Au, Cu, Zn, *etc*

Paramagnetic substances have unpaired electrons. They are attracted by magnetic field and have a magnetic dipole moment. The greater the number of unpaired electrons, greater is the magnetic moment of the substance. ***Example*** : CuO, FeO, Fe_3O_4, *etc.*

Crystal Field Splitting in an Octahedral Complex

In Crystal Field Splitting, the *d- orbitals* of the central metal atom tend to split into two energy levels in presence of ligands.

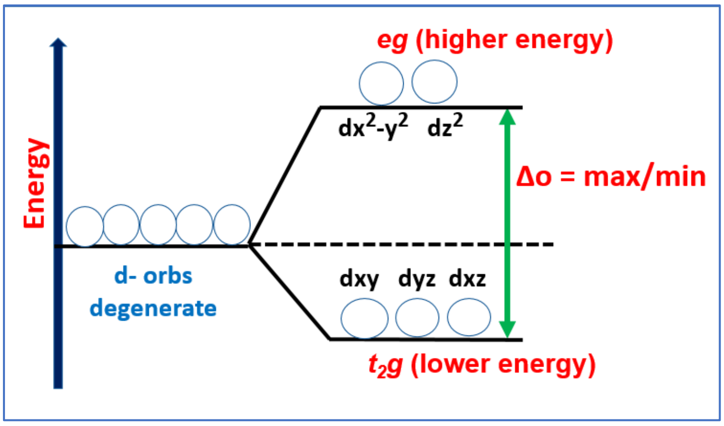
The two energy levels are

- The lower energy *t_2g level*
- The higher energy *eg level*

The energy difference between t_2g and *eg levels* is called as **Crystal Field Stabilisation Energy (CFSE)**

The Magnitude of CFS (Δo) then depends upon the strength of the ligands which causes either maximum or minimum Crystal field splitting.

Crystal Field Splitting diagram of an Octahedral Complex:



The magnitude of 10Dq (Δo) and the distribution of the electrons in metal *d*-orbs are thus dependent / influenced by the strength of LIGAND FIELD

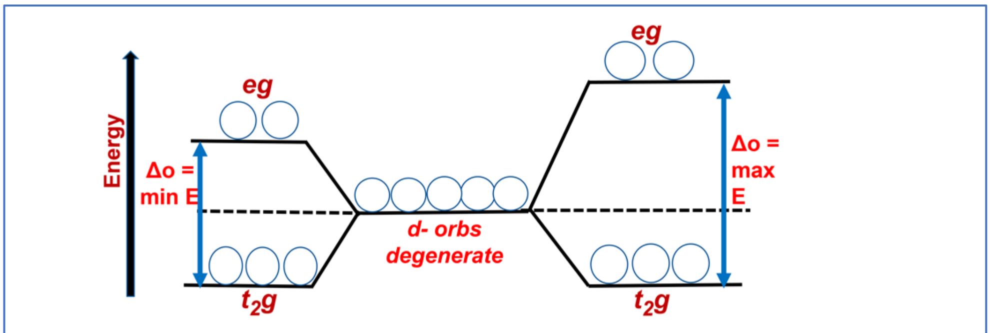
2. NATURE and STRENGTH of LIGANDS

Depending upon their field strength, the ligands are arranged in the order of their increasing splitting power. This arrangement of ligands is called Spectrochemical Series and is given as;.

$I < Br < S^{2-} < SCN^{-} < Cl < NO < F < OH^{-} < H_2O < NCS^{-} < NH_3 < en < dipy < phen < \tilde{N}O^{2-} < CN^{-} < CO$.

The ligands on the right side of the series provide the STRONGEST FIELD (HIGH Δ) and are the most effective in forcing the metal ions to form low spin complexes. The ligands on the left provide WEAK FIELD (LOW Δ) and usually form high spin complexes.

CFS diagram showing d-orbital splitting in presence of Weak and Strong Field Ligands in an Octahedral complex:



i) *CFS in Weak Field Oh complex*
Δo = min splitting
Forms HIGH SPIN (HS) complex

ii) *CFS in Strong Field Oh complex*
Δo = max splitting
Forms LOW SPIN (LS) complex

Strong Field Ligands and Weak Field Ligands thus determine the Magnitude of CFS and the electron distribution in the t_2g and *eg* orbitals . Once electrons are filled in the t_2g and *eg* orbitals, the Magnetic Behavior of a complex can be explained.

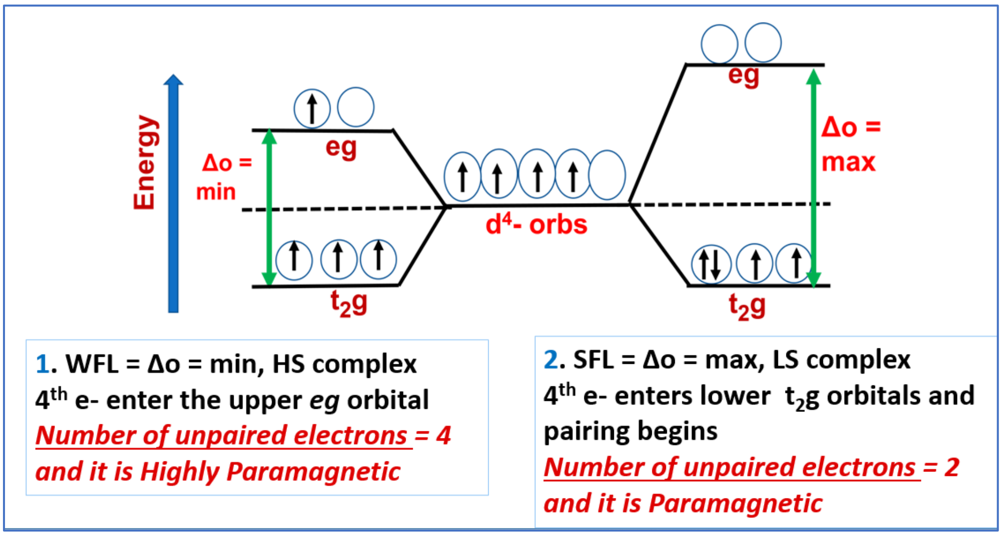
Low Spin Complexes:

Ligands which produce strong ligands, split the d-orbs to a larger extent ie. 10 Dq > P . Therefore, e-s will pair up in lower energy orbs. Such ligands are called as Strong field ligands. E.g. CN^-, CO. And the complexes are called as low Spin complexes / SPIN-PAIRED complexes. (less no. of unpaired e-s). In these complexes, the 4th e- enters the lower t_2g orbital.

High Spin Complexes:

Ligands which produce weak fields split the d-orbs to a small extent ie. 10Dq < P. Therefore, e-s remain unpaired and the 4th e- enters the upper eg orbital. Such ligands are called as Weak field ligands. E.g F-, OH^-, H_2O, etc. And the complexes are called as High spin complexes / SPIN-FREE complexes. (max no. of unpaired e-s). In these complexes, the 4th electron enters the upper eg orbital.

CFS and electron distribution in a d^4 system



1. WFL = Δo = min, HS complex
4th e- enter the upper *eg* orbital
***Number of unpaired electrons* = 4**
and it is Highly Paramagnetic

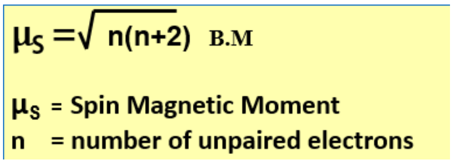
2. SFL = Δo = max, LS complex
4th e- enters lower t_2g orbitals and pairing begins
***Number of unpaired electrons* = 2**
and it is Paramagnetic

3. MAGNETIC MOMENT (μ)

CFS is thus useful in determining the number of unpaired electrons in HS and LS complexes. Magnetic Moment (μ) of a complex can then be found out by using *Spin-Only* formula; *given as*

SPIN MAGNETIC MOMENT (μ_S):

SPIN-ONLY formula considers only the Spin Magnetic Moment of the Central Metal atom caused due to spin of particles. The formula is



$$\mu_S = \sqrt{n(n+2)} \text{ B.M}$$

μ_S = Spin Magnetic Moment
n = number of unpaired electrons

The Orbital Moment is not considered for complexes as the orbital motion of the electrons is considered to be quenched or hindered by the Ligands.

***Examples* :**

- ✓ $[Fe(CN)_6]^{4-}$ is diamagnetic with no unpaired electrons
- ✓ $[Fe(F)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$are strongly paramagnetic with 5 unpaired electrons
- ✓ $[Fe(CN)_6]^{3-}$ is weakly paramagnetic with 1 unpaired electron
- ✓ $[Co(H_2O)_6]^{2+}$ is paramagnetic with 3 unpaired electron

The complex $[Cr(H_2O)_6]^{3+}$ is high spin complex and the number of unpaired electrons are three. Therefore it is paramagnetic complex and μ_s = 3.87 BM. This value agrees well with the observed value of magnetic moment 3.9 BM. For many ions of the transition series, particularly for the first half of the series, μ_s values for high spin complexes agrees with the experimental values.

Thus **Crystal Field Splitting (CFS) can successfully explain the Magnetic Properties of Complexes.**

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