CRYSTAL FIELD THEORY (CFT)

Crystal Field Theory was proposed by the physicist Hans Bethe in 1929 to describe the bonding in coordination complexes and to rationalize and predict some important properties of coordination complexes (colours, magnetism etc.). This model was based on a purely interaction between the ligands and the metal ion in the complexes with various geometries like octahedral, tetrahedral, square planar etc. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions.

This theory is based on the concept that when the negative charges of the incoming ligands (or the negative ends of dipolar molecules like NH_3 and H_2O) attract the positively charged metal ion, there is also repulsive interaction between d electrons present on the metal ion and the ligands. Certain assumptions are taken while dealing with CFT-

1. The ligands are treated as point charges. In fact, this is not practically true since sometimes the size of ligand particularly when it is sulfur or phosphorus donating ligands, is approximately similar to the size of metal ion.

2. The interactions between metal ion and ligand are treated as purely electrostatic, no covalent interactions are considered. This again is not true, some of the observations cannot be explained without invoking covalent interactions. In isolated gaseous metal ion, all of the five d-orbitals are degenerate.

3. When a hypothetical spherical field of ligand approaches the metal ion, d-orbitals still remain degenerate, but their energy level is raised a bit due to repulsion between the orbitals of metal & ligand. This energy level is called Barycenter. But in the transition metal complexes, the geometry about the metal ions are octahedral, tetrahedral or square planar etc., the field provided by the ligands is not at all spherically symmetrical therefore d-orbitals are unequally affected by the ligands and degeneracy of d-orbitals in metal removed and split into different energy levels **(e.g. t_{2g} or e_g).**

- To understand CFT, one must understand the description of the lobes of d-orbitals given in the figure:

- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.
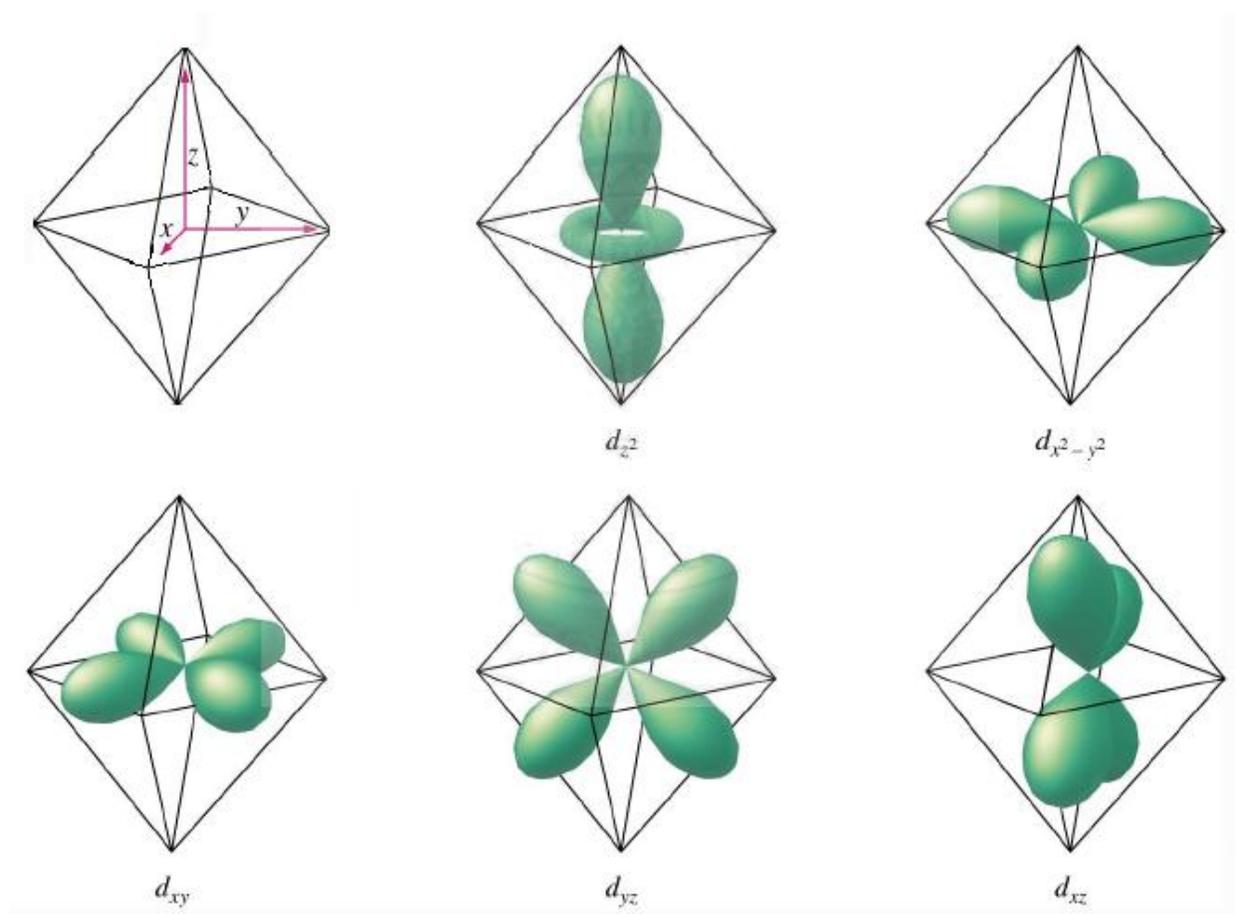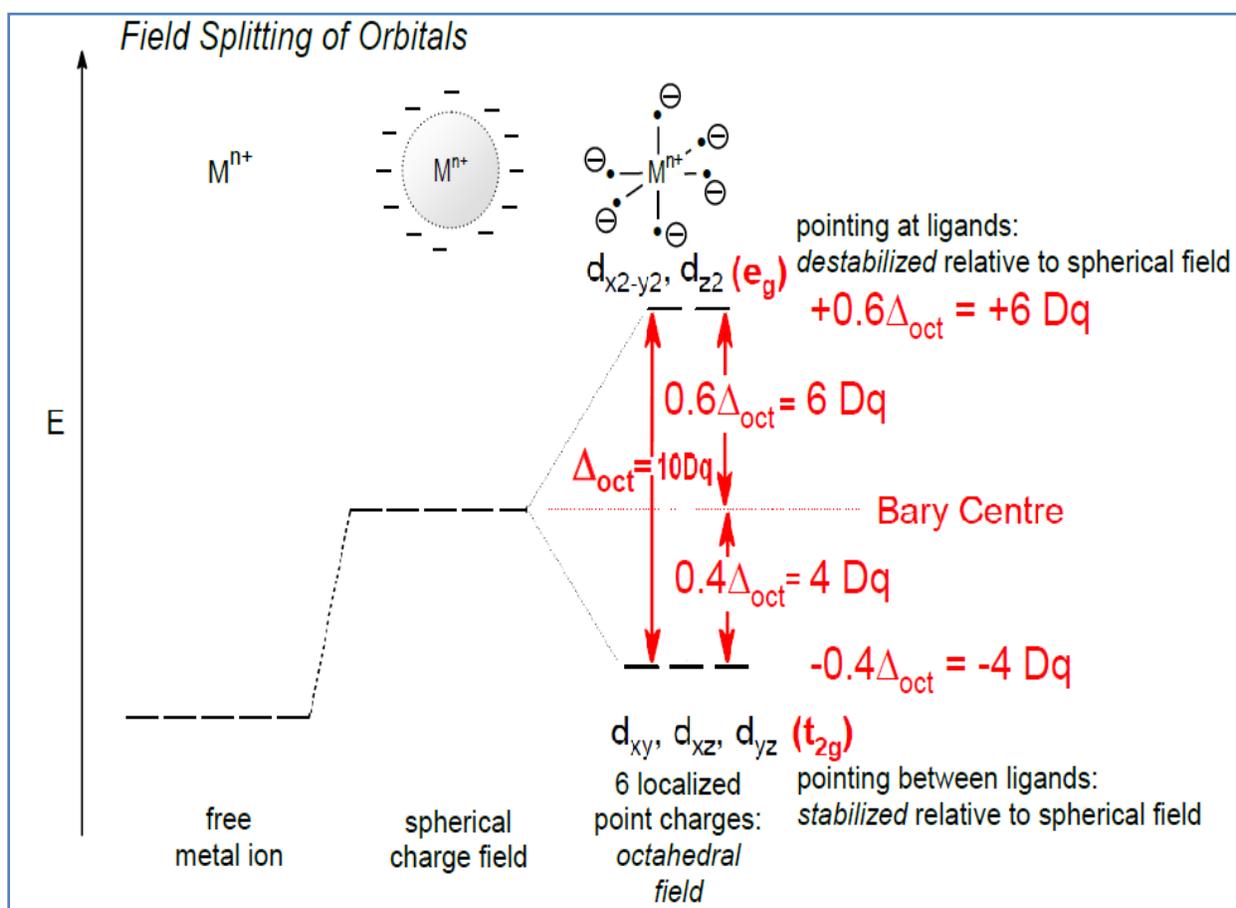

Figure 1: Shapes of d-orbitals

CRYSTAL FIELD EFFECTS ON OCTAHEDRAL COMPLEXES

- In octahedral complexes, the ligands approach along the axes.

- The d-orbitals where electron density is oriented along the axes, $d_{x^2-y^2}$ and d_{z^2} are repelled much more by the ligands while the orbitals d_{xy}, d_{xz}, d_{yz} having electron density oriented in between the axes are repelled lesser by the ligands.

- Two sets of orbitals eg (doubly degenerate set) and t_{2g} (doubly and triply degenerate) are formed due the repulsion between metals and ligands orbitals.

Field Splitting of Orbitals

pointing at ligands:
d_{x2-y2}, d_{z2} (e_g) *destabilized* relative to spherical field

$+0.6\Delta_{oct}$ = +6 Dq

$0.6\Delta_{oct}$= 6 Dq

Δ_{oct}= 10Dq

Bary Centre

$0.4\Delta_{oct}$= 4 Dq

$-0.4\Delta_{oct}$ = -4 Dq

d_{xy}, d_{xz}, d_{yz} (t_{2g})

6 localized   pointing between ligands:
point charges: *stabilized* relative to spherical field
octahedral
field

E

free   spherical   M^{n+}
metal ion   charge field

a, b = singly degenerate labels   g = gerade (symmetrical about origin)
e = doubly degenerate   u=ungerade (unsymmetrical about origin)
t = triply degenerate

Figure2: Splitting of d-orbitals in Octahedral Field

- The energy gap between eg and t2g is called **crystal field splitting energy** and it is denoted by Δ_o or Δ_{oct} or $10Dq$, where Δ represent **Crystal field splitting energy,** "o" in Δo is for octahedral.
- Because the overall energy is maintained, the energy of the three t_{2g} orbitals are lowered or stabilised by 0.4 Δo and the energy of the two e_g orbitals are raised or repelled by 0.6Δo with respect to hypothetical the spherical crystal field or Bary Centre.

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The Dq notation has mathematical origins in CFT but Δ_o is preferred because of its experimentally determined origin. The size of Δ_o can be measured easily using UV-Vis spec. Example: $[Ti(OH2)6]^{3+,}$ hexaaquatitanium(III) ion (Ti=d1). The complex absorbs light of the current wavelength (energy) to promote the electron from the t_{2g} level to the e_g level.(20300cm^{-1} =493/520 ?nm) *1kJmol^{-1}=83.7cm-1, Δ_o =20300/8.7 = 243kJmol^{-1}* *The single d electron occupies an energy level 2/5 Δ_o which is below the average energy of the d orbitals because of the CFSE of the d-orbitals.* *CFSE=2/5x243=97kJmol^{-1}* *As a result the complex is stable*	
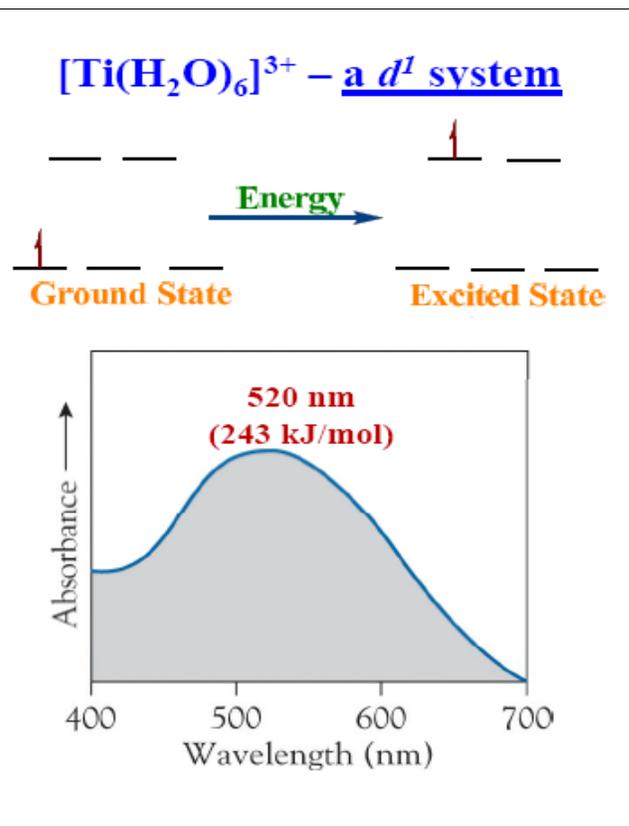
CRYSTAL FIELD STABILIZATION ENERGY (**CFSE**)

- The energy difference between the distribution of electrons in a particular crystal field and that for all electrons in the hypothetical spherical or uniform field levels is called the **crystal field stabilization energy** (CFSE) [This is the measure of the net energy of occupation of the d orbitals relative to their mean energy, Bary Centre].

- As we have seen, the energy difference between t_{2g} and eg orbitals is defined as Δ_o. The energy level of each of the two e_g orbitals would be 0.6 Δ_o above the zero of energy (barycenter) , whereas the energy level of each of the three t_{2g} orbitals would be 0.4 Δ_o below the zero energy.

- Consider the example, the Ti $(H2O)_6$ $^{3+}$ ion . Ti^{3+} has a d^1 electron configuration with the electron occupying t_{2g}, the crystal field stabilization energy (CFSE) is -0.4 Δ_o . For d^2, the CFSE = -0.8 Δ_o and for d^3, CFSE = -1.2 Δ_o. Upon reaching the d^3 configuration, however, the t_{2g} level becomes half-filled and there are no further orbitals of this energy to accept electrons without pairing.

Net energy decrease w.r.t. Barycenter is called Crystal field Stabilisation Energy (CFSE)

$$\text{For } d^1, \text{CFSE} = 1 \times 0.4 = \textbf{0.4 } \Delta_o$$

$$\text{For } d^2, \text{CFSE} = 2 \times 0.4 = \textbf{0.8 } \Delta_o$$

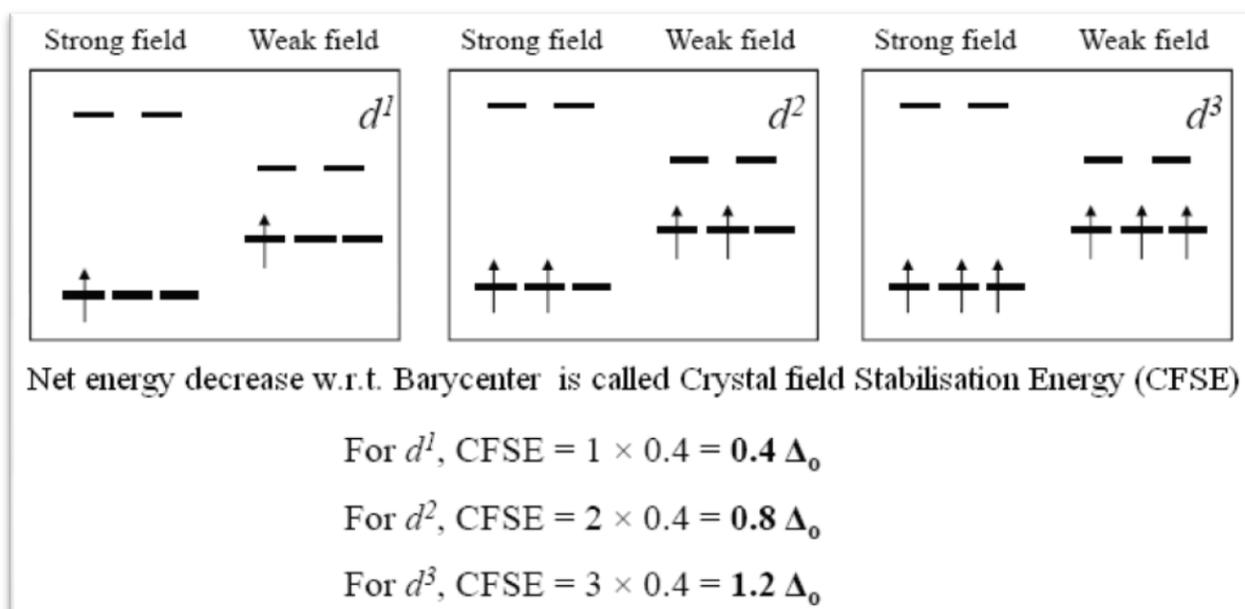$$\text{For } d^3, \text{CFSE} = 3 \times 0.4 = \textbf{1.2 } \Delta_o$$

Figure3: Distribution of electrons and CFSE for d^1-d^3 configurations

- For configurations d^4, d^5, d^6 and d^7 two possibilities arise . The determining factor whether high-spin or low-spin complexes arise is the ligand-field splitting parameter. When Δ_o is larger than the pairing energy P for the electrons, the electron pair in the t_{2g} orbitals as far as possible. If the energy required for pairing up the electrons (electrostatic repulsion) is greater than Δ_o, the electrons will be distributed between t_{2g} and e_g levels. In the former case we have the strong-field ($\Delta_o > $ P) arrangement with low-spin complexes, while in the latter we have the weak-field ($\Delta_o < $ P) arrangement with high-spin complexes.
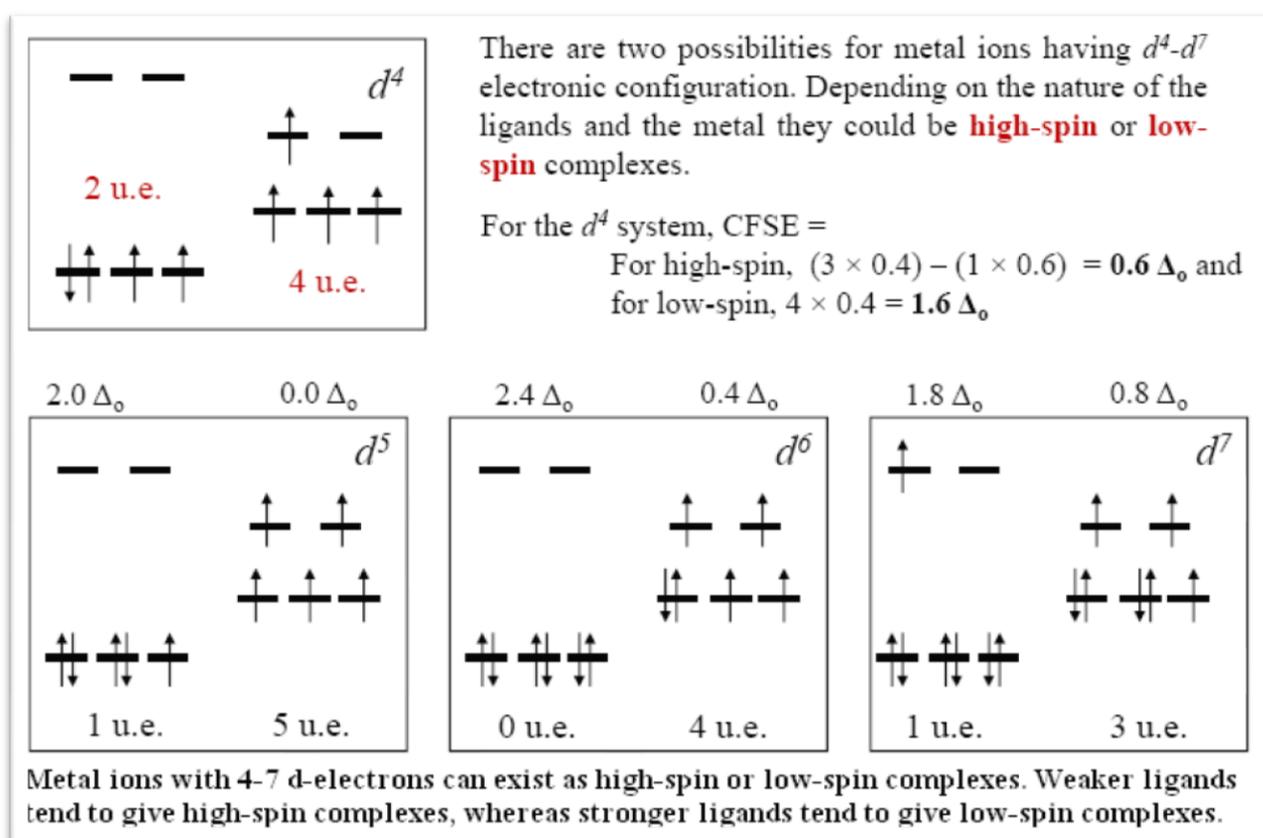
There are two possibilities for metal ions having d^4-d^7 electronic configuration. Depending on the nature of the ligands and the metal they could be **high-spin** or **low-spin** complexes.

For the d^4 system, CFSE =
For high-spin, $(3 \times 0.4) - (1 \times 0.6) = \textbf{0.6}\,\pmb{\Delta_o}$ and
for low-spin, $4 \times 0.4 = \textbf{1.6}\,\pmb{\Delta_o}$

Metal ions with 4–7 d-electrons can exist as high-spin or low-spin complexes. Weaker ligands tend to give high-spin complexes, whereas stronger ligands tend to give low-spin complexes.

Figure4: Distribution of electrons and CFSE for d^4-d^7 configurations

- With d8 , d9 and d10 configurations there is only one possible way for distributing the electrons between the t2g and eg orbitals. The arrangement of electrons in the d-orbitals of ions in octahedral complexes is illustrated in figure 3. Also, for d1 to d10 the resultant CFSE are listed in Table 3.1 , together with the number of unpaired electrons expected for each configuration .
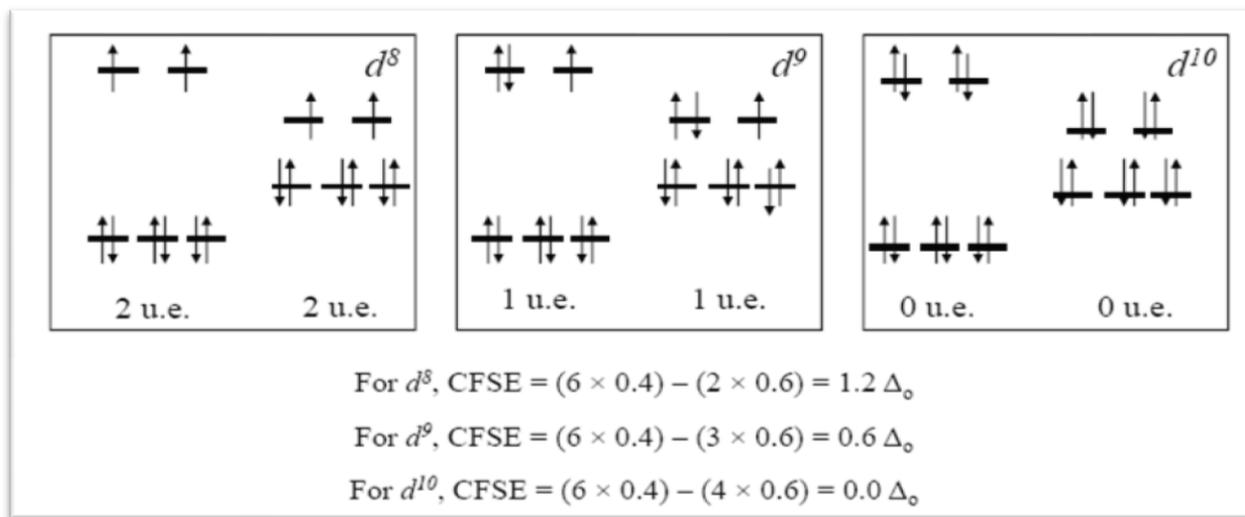

For d^8, CFSE = $(6 \times 0.4) - (2 \times 0.6) = 1.2\ \Delta_o$

For d^9, CFSE = $(6 \times 0.4) - (3 \times 0.6) = 0.6\ \Delta_o$

For d^{10}, CFSE = $(6 \times 0.4) - (4 \times 0.6) = 0.0\ \Delta_o$

Figure4: Distribution of electrons and CFSE for d^4-d^7 configurations

Note: In all the cases the electronic configuration involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons

Table1: Octahedral crystal field stabilization energies (CFSE) for d^n configurations.

Table: Distribution of d-electrons in t_{2g} and e_g sets of orbitals of central metal ion surrounded by ligands in octahedral complexes.
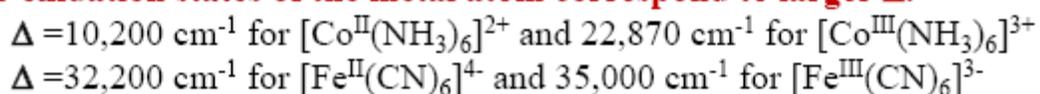
No of electrons	Weak field ligand t_{2g} orbitals			e_g orbitals		CFSE	n	$s=\dfrac{n}{2}$	Strong field ligand t_{2g} orbitals			e_g orbitals		CFSE	n	$s=\dfrac{n}{2}$
$d^1(Ti^{3+})$	↑					-4Dq or -0.4Δo	1	1/2	↑					-4Dq or -0.4Δo	1	1/2
$d^2(Ti^{2+})$	↑	↑				-8Dq or -0.8Δo	2	1	↑	↑				-8Dq or -0.8Δo	2	1
$d^3(V^{2+})$	↑	↑	↑			-12Dq or -1.2Δo	3	3/2	↑	↑	↑			-12Dq or -1.2Δo	3	3/2
$d^4(Cr^{2+})$	↑	↑	↑	↑		-6Dq or-0.6Δo	4	2	↑↓	↑	↑			-6Dq or-0.6Δo	2	1
$d^5(Fe^{3+})$	↑	↑	↑	↑	↑	0	5	5/2	↑↓	↑↓	↑			0	1	1/2
$d^6(Co^{2+})$	↑↓	↑	↑	↑	↑	-4Dq + P or -0.4Δo+ P	4	2	↑↓	↑↓	↑↓			-4Dq + P or -0.4Δo+ P	0	0
$d^7(Co^{3+})$	↑↓	↑↓	↑	↑	↑	-8Dq + 2P or -0.8Δo+ 2P	3	3/2	↑↓	↑↓	↑↓	↑		-8Dq + 2P or -0.8Δo+ 2P	1	1/2
$d^8(Co^{2+})$	↑↓	↑↓	↑↓	↑	↑	-12Dq + 3P or -1.2Δo+ 3P	2	1	↑↓	↑↓	↑↓	↑	↑	-12Dq + 3P or -1.2Δo+ 3P	2	1
$d^9(Cu^{2+})$	↑↓	↑↓	↑↓	↑↓	↑	-6Dq + 4P or -0.6Δo+ 4P	1	1/2	↑↓	↑↓	↑↓	↑↓	↑	-6Dq + 4P or -0.6Δo+ 4P	1	1/2
$d^{10}(Zn^{2+})$	↑↓	↑↓	↑↓	↑↓	↑↓	0Dq + 5P	0	0	↑↓	↑↓	↑↓	↑↓	↑↓	0Dq + 5P	0	0

THE FACTORS AFFECTING CRYSTAL FIELD SPLITTING ENERGY, Δ OR $10Dq$

There are several factors that affect the extent of splitting of the d-orbitals by ligands.

(I) *Oxidation state of the metal .* For a given ,etal , the change of the oxidation state from +2 to +3 would result in a corresponding increase in by 50% . The increased charged of the metal ion will draw the ligands in more closely, hence they will have a greater effect in perturbing the metal d-orbitals.


Higher oxidation states of the metal atom correspond to larger Δ.

Δ =10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$ and 22,870 cm^{-1} for $[Co^{III}(NH_3)_6]^{3+}$

Δ =32,200 cm^{-1} for $[Fe^{II}(CN)_6]^{4-}$ and 35,000 cm^{-1} for $[Fe^{III}(CN)_6]^{3-}$

(II) *Nature of the metal ion involved .* For a given transition series the difference are not great , but within a given group in progressing from 3d -----> 4d ----> 5d the value of increases by 25 - 50%.

In groups, heavier analogues have larger Δ.

For hexaammine complexes $[M^{III}(NH_3)_6]^{3+}$:

$\Delta =$ 22,870 cm^{-1} (Co)

34,100 cm^{-1} (Rh)

41,200 cm^{-1} (Ir)
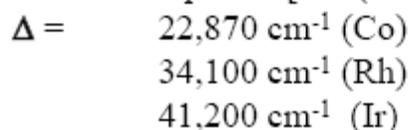
(III) *Geometry of the complex .* The splitting in an octahedral field is about twice as strong as for a tetrahedral field for the same metal ion and the same ligands . In tetrahedral complex the ligands are directed much less efficiently than in octahedral complex

Geometry of the metal coordination unit affects Δ greatly.

Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6:

$\Delta =$ 10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$

5,900 cm^{-1} for $[Co^{II}(NH_3)_4]^{2+}$
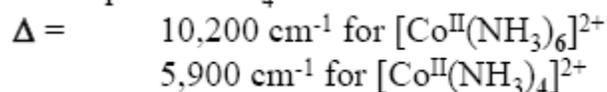
(IV) *Nature and Number of the ligands* . Different ligands cause different degree of splitting.

Nature of the ligands.

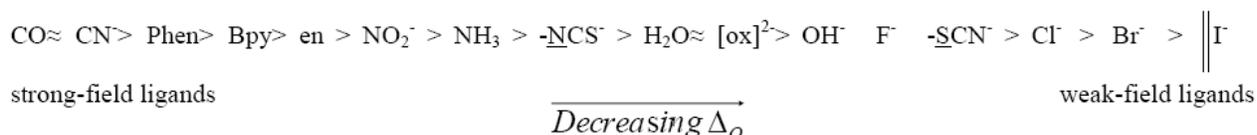For $[Co^{III}L_6]$, Δ in cm^{-1}: 13,100 (F$^-$); 20,760 (H$_2$O); 22,870 (NH$_3$)

For $[Cr^{III}L_6]$, Δ in cm^{-1}: 15,060 (F$^-$); 17,400 (H$_2$O); 26,600 (CN$^-$)

- Depending on the charge (or oxidation state) and nature of metal ion (or metal) and ligand, the strength of the crystal field may be varied from strong to weak.
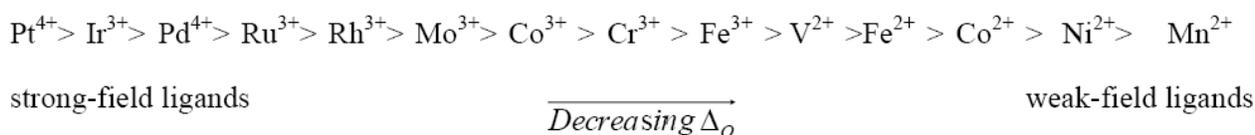
  Δ (strong field) > Δ (weak field)

- It is possible to list ligands or metal ions in order of increasing field strength in a " spectrochemical series " .

i) Spectrochemical series for ligands

$CO \approx CN^- >$ Phen$>$ Bpy$>$ en $> NO_2^- > NH_3 > \underline{N}CS^- > H_2O \approx [ox]^{2-}> OH^-$ F$^-$ $\underline{S}CN^- > Cl^- > Br^- > \| I^-$

strong-field ligands $\qquad\qquad$ weak-field ligands

$$\overrightarrow{Decreasing\,\Delta_O}$$

ii) Spectrochemical series for metal ions

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

strong-field ligands $\qquad\qquad$ weak-field ligands

$$\overrightarrow{Decreasing\,\Delta_O}$$

The value of Δ increases with increasing oxidation number of the central metal ion. The variation of oxidation number reflects the smaller size of more highly charged ions and consequently shorter metal-ligand distances and stronger interaction energies. The value of Δ increases down the group. This reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interaction of the ligands.

Problems

1. **Calculate CFSE for the complex $[Cr(H2O)6]^{2+}$**

Chromium in ground state is $[Ar]3d^5\ 4s^1$, in +2 state, will be a d^4 system with $t_{2g}^2\ e_g^1$ ^{3} ^{1} configuration of   electrons because H_2O is a weak field ligand. CFSE will be therefore

$$-0.4\ \Delta_0 X\ 3+ 0.6\ \Delta_0 = -0.6\ \Delta_0$$
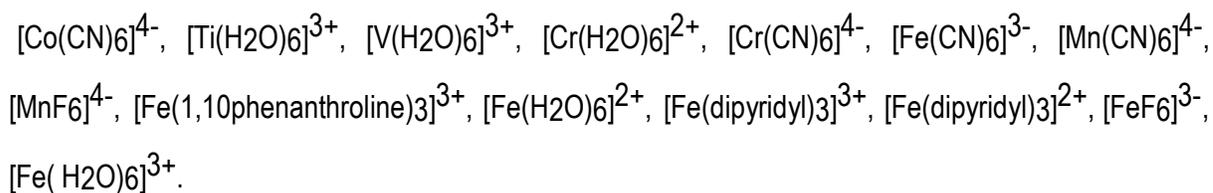
2. Calculate CFSE for $[Fe(CN)6]^{4-}$

Iron in ground state is $[Ar]3d^6\ 4s^2$, in +2 state it will be a d^6 system with $t2g^6\ e_g^0$ configuration of electrons because CN^- is a strong field ligand. Therefore, CFSE be

$$-0.4\ \Delta_0 X\ 6+ 2P = -2.4\ \Delta_0+ 2P$$

Exercise for Practice

1. An aqueous solution of titanium chloride shows zero magnetic moment. Write down its formula assuming it to be an octahedral complex in aqueous solution.

2. Calculate CFSE for the following complexes-

   $[Co(CN)6]^{4-}$, $[Ti(H2O)6]^{3+}$, $[V(H2O)6]^{3+}$, $[Cr(H2O)6]^{2+}$, $[Cr(CN)6]^{4-}$, $[Fe(CN)6]^{3-}$, $[Mn(CN)6]^{4-}$, $[MnF6]^{4-}$, $[Fe(1,10phenanthroline)3]^{3+}$, $[Fe(H2O)6]^{2+}$, $[Fe(dipyridyl)3]^{3+}$, $[Fe(dipyridyl)3]^{2+}$, $[FeF6]^{3-}$, $[Fe(H2O)6]^{3+}$.

3. Give correct order for the energy gap between two sets of d orbitals in the following complexes-

   $[CrCl6]^{3-}$, $[Cr(H2O)6]^{3+}$ $[Cr(en)3]^{3+}[Cr(CN)6]^{3-}$.
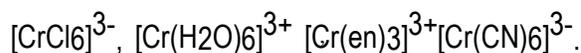
4. Give correct order for energy gap between two sets of d levels in the following complexes –

a. $[Fe (H2O)6]^{2+}$, $[Fe (H2O)6]^{3+}$

b. $[Co(NH3)6]^{3+}$, $[Rh(NH3)6]^{3+}$, $[Ir(NH3)6]^{3+}$