US05CCHE22 (SEM-V)

Unit-2: CRYSTAL FIELD THEORY

Dr. Trupti Darji

Importance of crystal field theory:

Crystal field theory is a powerful and simple method of understanding and correlating properties of ionic crystals that arise primarily from the presence of the partly filled shells. This theory provides a way of determining by simple electrostatic consideration, how the energies of the metal ion orbital will be affected by the set of surrounding atoms or ligands.this theory works best for 3d series. The splitting of 4f-orbitals are so small that they are not chemically important.

Important features of Crystal Field Theory:

1. The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.
2. The ionic ligands regarded as negative point charges and the neutral ligands are regarded as point dipoles or simply dipoles, i.e. according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.
3. The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e., it does not consider any orbital overlap.
4. According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively charged(cation) and negatively charged(anions or dipole molecule which act as ligand) species.

Grouping of Five d-Orbitals into t_{2g}, and e_g Sets of Orbitals

On the basis of the orientation of the lobes of the five-d-orbitals with respect to coordinates these have been grouped into the following two sets.

1. e_g set of orbitals: d_{x2}, and d_{x2-y2} orbitals:

This set consist of two orbitals which have their lobes along the axes and hence are called axial orbitals. Quite obviously these are **d_{x2}**, and **d_{x2-y2}** orbitals. Group theory calls these orbitals e_g orbitals in which refers to doubly degenerate set.

2. T_{2g} set of orbitals: d_{xy},d_{yz},d_{xz}, orbitals:

This set includes three orbitals whose lobes lie between the axes and are called non-axial orbitals. Group theory calls these orbitals t_{2g}orbitals where in t refers to triply degenerate set.

Crystal Field Splitting of d-Orbitals in Octahedral Complex:

In case of free metal ion all the five d-orbitals are degenerate, i.e., these have the same energy. Now let us consider an octahedral complex, $[ML_6]$ in which the central metal cation, M^{n+} is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in below figure.

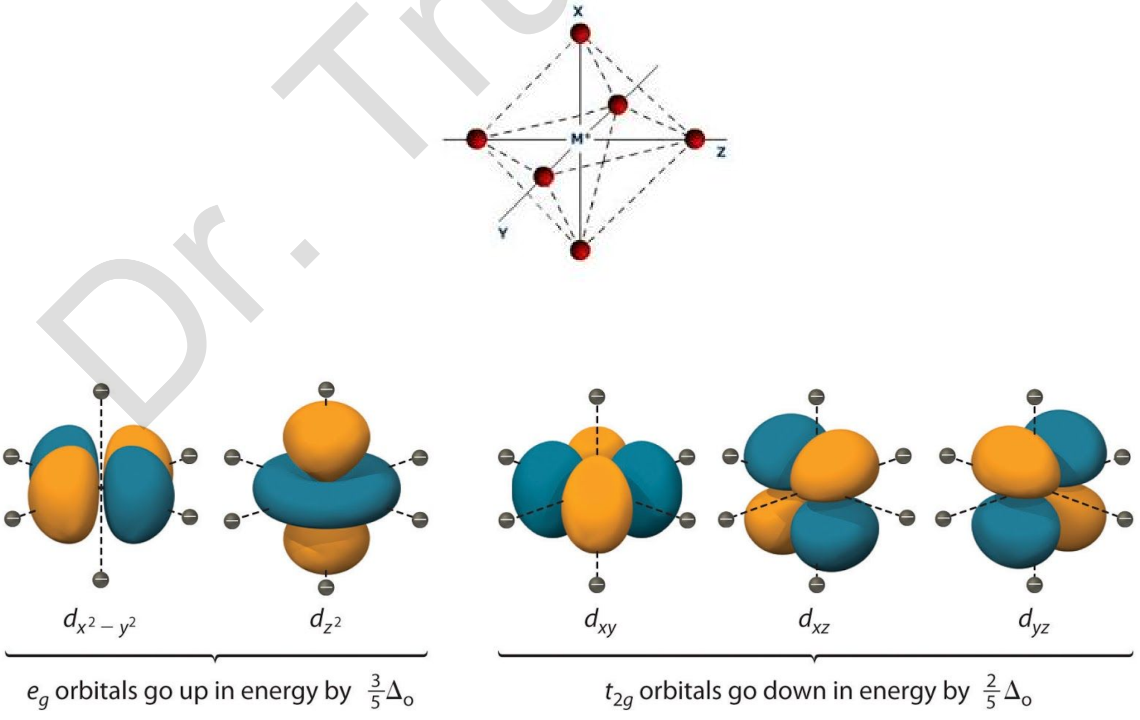

Fig: Orientation of the lobes of five d-orbitals of the central metal atom/ion

Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M" from both the ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. This repulsion will raise the energy of all the five d-orbitals. If all the ligands approaching the central cation are at an equal distance from each of the d-orbitals (i.e., the ligand field is spherically symmetrical), the energy of each of five d-orbitals will raise by the same amount, i.e. all the d-orbitals will still remain degenerate, although they will now have higher energy than before. This is only a hypothetical situation. Since the lobes of the two e_g orbitals lie directly in the path of the approaching ligands, the electron in this orbitals experience greater force of repulsion than those in three t_{2g} orbitals whose lobes are directed in space between the path of the approaching ligands i.e. the energy of e_g orbitals is increased while that of t_{2g}, is decreased (Remember:greater is the repulsion, greater is the increase in energy). Thus we find that under the influence of approaching ligands, the five d-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels viz., t_{2g}, level which is triply degenerate and is of lower energy, and e_g level which is doubly degenerate and is of higher energy.

In other words the degeneracy of the five d-orbitals is removed under the influence of the ligands. The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting or energy level splitting, This concept of crystal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by Δ_0 or 10Dq where 0 in Δ_0 indicates an octahedral arrangement of the ligands round the central metal cation. This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g}, and e_g sets of orbitals of the central metal cation. Δ_0, or 10Dq is called crystal field splitting energy. With the help of simple geometry it can be shown that the energy of t_{2g} orbitals is 0.4 Δ_0 (=4Dq) less than that of hypothetical degenerate d-orbitals and, hence that of e_g orbitals is $0.6\Delta_0$, (= 6Dq) above that of the hypothetical degenerate d-orbitals: Thus, we find that t_{2g} set loses an energy equal to 0.4 Δ_0, (4Dq) while e_g, set gains an energy equal to $0.6\Delta_0$, (= 6Dq). The loss and gain in energies of t_{2g} and e_g, orbitals is shown by negative (-) and positive (+) signs respectively. Δ_0 is generally measured in cm^{-1}

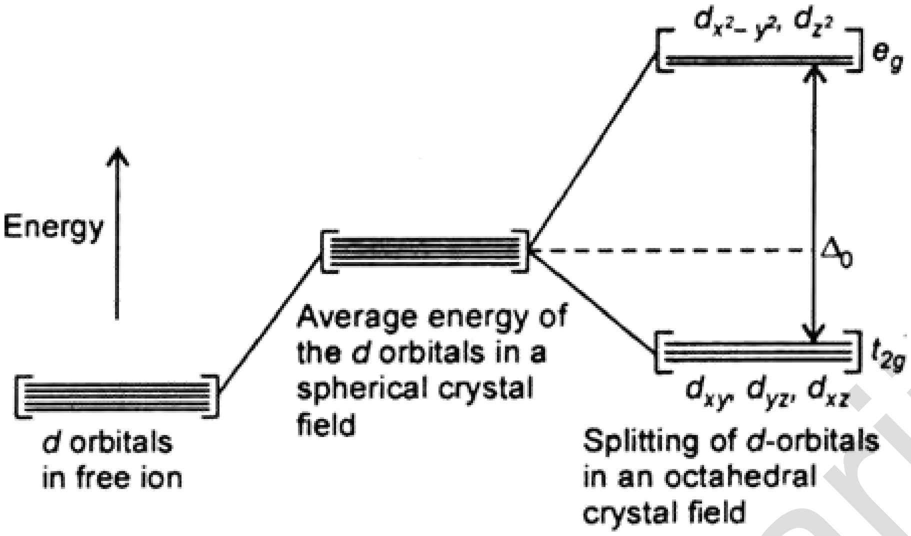

Fig: Splitting of five d-orbitals in octahedral complex

Distribution of d^x Electrons in t_{2g}, and e_g Orbitals in Octahedral Complexes (x = 0 to 10)

Distribution of d^n electrons (x = 0 to 10) in t_{2g} and e_g orbitals in octahedral complexes is represented by $t_{2g}^p\ e_g^q$ configuration in which p and q are the electrons present in t_{2g} and e_g orbitals respectively. Obviously $p + q = x$.

A. Distribution of d^x electrons in high spin (HS) octahedral complexes:

HS octahedral complexes are also called spin free complexes. Since these complexes contain weak field ligands, these complexes are also called weak field or low field complexes. Since the ligands in HS complexes are weak, the energy difference between t_{2g} and e_g sets of orbitals in HS complexes is relatively small and hence all the five d-orbitals of t_{2g} and e_g sets can be supposed to be of the same energy (degenerated).

Consequently distribution of d^x electrons in t_{2g} and e_g orbitals in HS complexes takes place according to Hund's rule which states that electrons will pair up only when each of the five d-orbitals is at least singly filled. Thus in weaker field the first three electrons enter t_{2g} level, 4th and 5th electrons (two electrons) go to e_g set,6th, 7th and 8th electrons (three electrons) occupy t_{2g} set and 9th and 10th electrons (last two electrons) go to e_g set. (See the Table)

B. Distribution of d^x electrons in low spin (LS) octahedral complexes

LS octahedral complexes are also called spin paired complexes. Since these complexes contain strong field ligands, these complexes are also called strong field or high field complexes. Since the ligands in LS complexes are strong, the energy difference between t_{2g} and e_g orbitals is relatively large and hence all the five d-orbitals are not of the same energy.

As a result, the distribution of d^x electrons in t_{2g} and e_g orbitals does not take place in accordance with Hund's rule. This in LS complexes the first six electrons in d^n ion go to t_{2g} orbitals and the remaining four electrons of d_n ion occupy e_g orbitals (S In Table.

H.S.complexes (weak ligand field)	**L.S.complexes (strong ligand field)**
e_g ___ ___ t_{2g} ↑ ___ ___ $d^1 = t_{2g}^1 e_g^0$ (p=1,q=0,n=1,S=1/2,m=0)	e_g ___ ___ t_{2g} ↑ ___ ___ $d^1 = t_{2g}^1 e_g^0$ (p=1,q=0,n=2,S=1/2,m=0)
e_g ___ ___ t_{2g} ↑ ↑ ___ $d^2 = t_{2g}^2 e_g^0$ (p=2,q=0,n=2,S=1,m=0)	e_g ___ ___ t_{2g} ↑ ↑ ___ $d^1 = t_{2g}^2 e_g^0$ (p=2,q=0,n=2,S=1,m=0)
e_g ___ ___ t_{2g} ↑ ↑ ↑ $d^3 = t_{2g}^3 e_g^0$ (p=3,q=0,n=3,S=3/2,m=0)	e_g ___ ___ t_{2g} ↑ ↑ ↑ $d^3 = t_{2g}^3 e_g^0$ (p=3,q=0,n=3,S=3/2,m=0)
e_g ↑ ___ t_{2g} ↑ ↑ ↑ $d^4 = t_{2g}^3 e_g^1$ (p=3,q=1,n=4,S=2,m=0)	e_g ___ ___ t_{2g} ↑↓ ↑ ↑ $d^4 = t_{2g}^4 e_g^0$ (p=4,q=0,n=2,S=1,m=1)
e_g ↑ ↑ t_{2g} ↑ ↑ ↑ $d^5 = t_{2g}^3 e_g^2$ (p=3,q=2,n=5,S=5/2,m=0)	e_g ___ ___ t_{2g} ↑↓ ↑↓ ↑ $d^5 = t_{2g}^5 e_g^0$ (p=5,q=0,n=1,S=1/2,m=2)

e_g ↑ ↑ t_{2g} ↑↓ ↑ ↑ $d^6 = t_{2g}^4 e_g^2$ (p=4,q=2,n=4,S=2,m=1)	e_g ___ ___ t_{2g} ↑↓ ↑↓ ↑↓ $d^6 = t_{2g}^6 e_g^0$ (p=6,q=0,n=0,S=0,m=3)
e_g ↑ ↑ t_{2g} ↑↓ ↑↓ ↑ $d^7 = t_{2g}^5 e_g^2$ (p=5,q=2,n=3,S=3/2,m=2)	e_g ↑ ___ t_{2g} ↑↓ ↑↓ ↑↓ $d^7 = t_{2g}^6 e_g^1$ (p=6,q=1,n=1,S=1,m=3)
e_g ↑ ↑ t_{2g} ↑↓ ↑↓ ↑↓ $d^8 = t_{2g}^6 e_g^2$ (p=6,q=2,n=2,S=1,m=3)	e_g ↑ ↑ t_{2g} ↑↓ ↑↓ ↑↓ $d^8 = t_{2g}^6 e_g^2$ (p=6,q=2,n=2,S=1,m=3)
e_g ↑↓ ↑ t_{2g} ↑↓ ↑↓ ↑↓ $d^9 = t_{2g}^6 e_g^3$ (p=6,q=3,n=1,S=1/2,m=4)	e_g ↑↓ ↑ t_{2g} ↑↓ ↑↓ ↑↓ $d^9 = t_{2g}^6 e_g^3$ (p=6,q=3,n=1,S=1/2,m=4)
e_g ↑↓ ↑↓ t_{2g} ↑↓ ↑↓ ↑↓ $d^{10} = t_{2g}^6 e_g^4$ (p=6,q=4,n=0,S=0,m=5)	e_g ↑↓ ↑↓ t_{2g} ↑↓ ↑↓ ↑↓ $d^{10} = t_{2g}^6 e_g^4$ (p=6,q=4,n=0,S=0,m=5)

Table: Distribution of d' electrons (n = 0 to 10) in t_{2g} and e_g sets of orbitals in HS and LS octahedral complexes

As a result, the distribution of d^x electrons in t_{2g} and e_g orbitals does not take place in accordance with Hund's rule. This in LS complexes the first six electrons in d^n ion go to t_{2g} orbitals and the remaining four electrons of d_n ion occupy e_g orbitals (See Table).

I. p = Total number of electrons in t_{2g} orbital
II. q = Total number of electrons in e_g orbitals
III. x = total number of unpaired electrons in t_{2g} and e_g orbitals
IV. S = Resultant spin = x/2
V. m = Total number of electron pairs in t_{2g} and e_g orbitals
VI. n = p + q where n = 0 to 10

Mean Pairing Energy (P):

Mean pairing energy (P) is the energy which is required to pair two electrons against electron-electron repulsion in the same orbital. P is the pairing energy for one electron pair. Is generally expressed in cm^{-1}. Pairing energy depends on the principal energy level (n) of d-electrons.

Calculation of Total Pairing Energy of d^x Ion:

Total pairing energy for electron pairs present in d^x ion = Total number of electron pairs in t_{2g}, and e_g sets of orbitals (m) x Pairing energy for one electron pair (P) = m x P cm^{-1} Here m = Total number of electron pairs in t_{2g} and e_g sets of orbitals and P = Pairing energy for one electron pair (cm^{-1})

Important Points to be Noted from Table-1 :

1. Whether the ligand field is stronger or weaker, for d^1,d^2 and d^3 configuration, the electrons go to the lower energy t_{2g} level , for d^8, d^9 and d^{10} configurations, the first six electrons go to the t_{2g} level and remaining two (in case of d^8 ion), three (in case of d^9 ion) and four (in case of d^{10}) electrons occupy the e_g level. Thus, the distribution of electrons of d^1,d^2,d^3,d^8,d^9 and d^{10} configuration in t_{2g} and e_g levels for both stronger and weaker octahedral ligand field is the same.
2. For each of d^4, d^5, d^6 and d^7 configurations there is a difference in the arrangement of electrons in weak(er) and strong (er) ligand fields.
3. **Number of unpaired electrons (n):**

   High-spin and low-spin complex Weak-field complexes of d^4, d^5, d^6 and d^7 have greater number of unpaired electrons (n) than those of (same ions) strong-field complexes and are thus with a higher value of resultant spin (S). It is for this reason that the weak-field and strong-field complexes are also called spin-free or high-spin (HS) and spin-paired or low-spin (LS) complexes respectively.

   The number of unpaired electrons (ie, the value of the resultant spin, S) in the cases namely D^1 to d^3 and d^8 to d^{10} is the same in both the fields, and it is due to this reason that for these configurations the question of the formation of HS and LS-complexes does not arise. The question does arise for the system d^4 to d^7.

   The paramagnetism of HS-complexes is larger than that of LS-complexes since as is evident from Table-1. HS-complexes have more unpaired electrons (i.e., larger value of S) than the LS-complexes (i.e., smaller value of S).

4. When $\Delta_0 < P$, the electrons tend to remain unpaired and hence high spin (weak field or spin free) octahedral complexes are obtained

   When $\Delta_0 > P$, the electrons tend to pair and hence low spin (strong field or spin paired) octahedral complexes are obtained.

Factors affecting the Magnitude of Δ_0

1. Geometry of the Complex ion.

If we consider the complex ions having the same central metal ion and the same ligands but having different geometry, then the value of Δ_0 depends on the geometry of the complex ion.

It has been found that

$$\Delta_{sp} > \Delta_0 > \Delta_t \quad \text{or} \quad 1.3\,\Delta_0 > \Delta_0 > 0.45\Delta_0$$

Explanation. In octahedral complexes, the splitting of d-orbitals is more than twice as strong as in tetrahedral complexes for the same metal ion and the same ligands. The difference in the value of Δ_{sp}, Δ_0, and Δ_t is because of the following two factors:

A. In octahedral complexes, six ligands are involved while in tetrahedral complexes only four ligands are involved. This results in 33% decrease in the field strength, provided that other factors remain unchanged.
B. In octahedral complexes, the ligands are situated directly in the path of d_{z2} and d_{x2-y2} orbitals (e_g set of orbitals) while in tetrahedral complexes the ligands are not aimed at any of the d-orbitals but exert greater influence on t_2 orbitals (d_{xy}, d_{yz} and d_{xz} orbitals) than on e orbitals (d_{z2} and d_{x2-y2} orbitals). In case of square planar complexes, the degree of splitting is much more than that in tetrahedral complexes.

2. Nature of Ligands: Weaker/Stronger Ligands: SpectroChemical Series.

If we consider complex ions having the same central metal ion and the same geometry but having ligands of different crystal field splitting strength, then the absorption spectra of these complexes show that the position of absorption peaks and hence the value of Δ changes with the change in the magnitude of crystal field splitting power of the ligands. The ligands having higher splitting power (i.e. stronger ligands) to split the d-orbitals of the central metal ion have higher value of Δ while the ligands having lower splitting power (weaker ligands) have lower value of Δ.

Some common ligands have been arranged as follows in the increasing order of their splitting power.

This arrangement is called **spectrochemical** series of ligand.

$I^- < Br^- < NO^-, < Cl^- < SCN^- < F^- < OH^- < C_20_4^{-2} < H_2O < NCS^- <$ edta, gly $<$ py $< NH_2 <$ en $<$ H big $<$ bpy - o-phen $< NO_2^- < CN^- < CO$

3. Nature of the Central Metal Ion:

Following three cases may be studied:

1. **Central metal ions belonging to the same group.** The value of Δ of the complex ions having the same ligands and same geometry but different central metal ions (with the same oxidation state) belonging to the same group of transition series elements increases on descending the group. This statement can also be given as follows:

   A value increases as we move from the first transition series to the second transition series and then to the third transition series or Δvalue increases as we move from the central metal ion with $3d^x$ config- ration to $4d^x$configuration and then again increases on moving from $4d^x$ configuration to $5d^x$ configuration.

   Thus Δvalue increases with the increase in the value of principal quantum number (n) of d-orbitals of the valence shell of the central metal ion.

2. **Central metal ions of the same metal having different oxidation state.** The value of Δ of the complex ions which have the same ligands and same geometry but their central metal ions are of the same metal with different oxidation state increases with the increase in oxidation state.
3. **Central metal ions of different metals having different oxidation state.** The value of Δ of the complex ions having the same ligands and same geometry, but different central metal ions with different oxidation

states increase with the increase in oxidation state of the central metal ion.

To Calculate the Value of Crystal Field Stabilisation Energy (CFSE) of d^n ion in Octahedral Complexes.

According to CFT, under the influence of the six ligands approaching towards the central metal ion during the formation of an octahedral complex, the d-orbitals of the central metal ion are split into two sets of orbitals viz. Lower the energy triplet t_{2g} and higher energy doublet, e_g sets. t_{2g} set of orbitals is triply degenerate while e_g set is doubly degenerate. The energy gap between these two sets is equal to Δ_0, (or 10Dq), The energy of t_{2g} set is lowered by 2/5 Δ_0 (= $0.4\Delta_{0)}$ or 4Dq while that of e_g set in raised $3/5\Delta_0$ (= $0.6\Delta_0$) or 6Dq relative to the energy of hypotencial degenerate d-orbitals.

Thus, each electrons occupying t_{2g} orbitals decrease the energy of d-orbitals by $-0.4\Delta_0$ (=-4Dq) while that going into e_g orbitals increase its energy by $+0.6\Delta_0$ (=+ 6Dq). – and + signs indicate respectively the decrease and increase in the energy of d-orbitals caused by their splitting under the influence of six ligands. Now let us consider d^x ion having $t_{2g}^p\ e_g^q$ configuration in which p is the number of electrons in t_{2g} set, q is the number of electrons in e_g set and p+q = x

Change in energy (in terms of Δ_0) for $t_{2g}^p\ e_g^q$ configuration

= Loss in energy due to p electrons in t_{2g} set

+ gain in energy due to q electrons in e_g set

$=-0.4\Delta_0$ x No. of electrons in t_{2g} set of orbitals

+ 0.6 Δ_0 x No. of electrons in e_g set of orbitals.

$= -0.4\ \Delta_0 \times p + 0.6\ \Delta_0 \times q$

$= [-0.4p + 0.6q]\ \Delta_0$ ....(i)

Now, since Δ_0 = 10Dq, the above expression can also be written as:

change in energy (in terms of Dq) for the

$t_{2g}^p\ e_g^q$ configuration = [-0.4 p + 0.6q] x 10 Dq ....(ii)

equations (i) and (ii) give the energies of d^x ion having $t_{2g}^p\ e_g^q$ configuration.

The change in energy for d^x ion having t_{2g}^p e_g^q configuration calculated as above is called crystal field stabilisation energy (CFSE) of d^x ion, since it stabilises d-orbitals by lowering the energy which results from their splitting into t_{2g} and e_g orbitals. The derivation of equation (i) and (ii) we have not considered the pairing energy P of d^x ion which is the energy required to pair two electrons against electron-electron repulsion in the same orbital. If the pairing energy of the ion is also involved in the the t_{2g}^p e_g^q configuration of a given d^x ion, then CFSE of the ion is given by the expression:

$$\text{CFSE} = [\,-0.4p + 0.6q\,]\,\Delta_0 + mP \text{ ....(iii)}$$

$$= [\,-4p + 6q\,]\,Dq + mP \text{ ....(iv)}$$

Here m is the total number of paired electrons in $t_{2g}$and e_g sets of orbitals.

Equations (iii) and (iv) have been used to calculate the CFSE value (in terms of Δ_0 and Dq respectively) for d° to d^{10} ions of HS and LS octahedral complexes.

Crystal Field splitting of metal d-orbital in Tetrahedral Complexes:

We know that a tetrahedral complex has tetrahedral geometry. This geometry can be derived from a cube in which the central metal atom/ion (M) is placed at the centre of the cube and the four ligands (L_1,L_2,L_3 and L_4) occupy the four alternate corners of the cube, i.e. the two ligands occupy the diagonally opposite corners of a face of the cube. The three axes viz. x, y and z are directed towards the centres of the face of the cube (See Fig. 1) It may be seen from Figure.1 that the four ligands (L_1,L_2,L_3 and L_4) do not lie directly in the path of the axes. For example the ligands L_1 lies between x and z axes, the ligand L_2 lies between z and y axes, L_3 ligand lies between z and y axes and L_4 ligand lies between y and x axes.

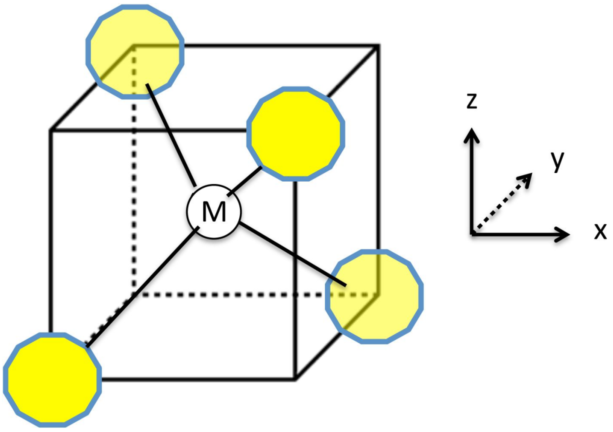

Fig: Position of central metal atom and ligands and representation of axes

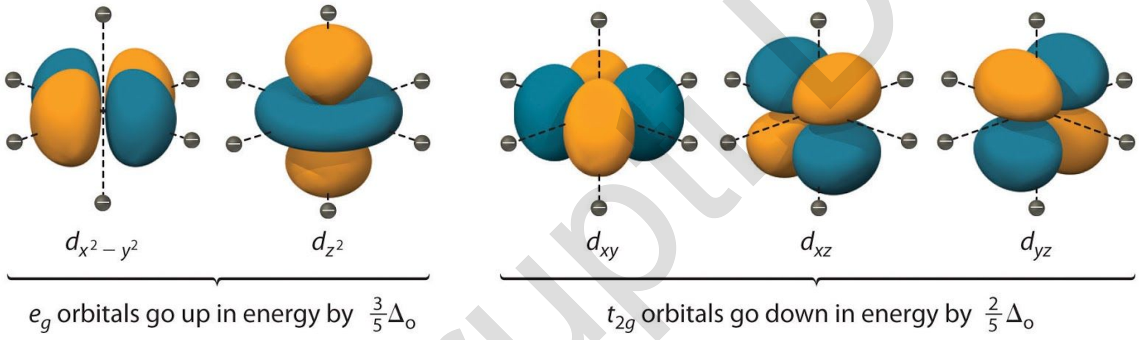

Fig: Orientation of the lobes of five d-orbitals of the central metal atom/ion

In tetrahedral complexes, five d-orbitals of the central metal atom are divided into two groups, viz e and t_2 groups, e set consists of d_{x2-y2} and d_{z2} while t_2 set consist of d_{xy} , d_{yz} and d_{xz} orbitals. The orientation of the lobes of five d-orbitals in a cube has been shown in Fig.2.

Above figure shows that:

1. The lobes of the two orbitals of e set lie along the axes, i.e., the lobes of the two orbitals of e set lie on the bisectors of the angle between pairs of ligands and hence pass through the centre of the faces of the cube. Thus d_{x2-y2} and d_{z2} orbitals lie half a diagonal of a face of the cube away from the two nearest ligands. For example one lobe of d_{z2} orbital along z-axis is placed in between the two nearest ligands viz L_1 and L_2 and the other lobe of d_{z2} orbital is placed

in between L_3 and L_4 ligands. Note that the ligands L_3 and L_4 occupy diagonally opposite corners of a face of the cube.

2. The lobes of the three orbitals of t_2 set lie between the axes, i.e. towards the centre of the edges of the cube. Thus d_{xy} , d_{yz} and d_{xz} orbitals lie just half the side of a face of the cube away from the nearest two ligands. Discussion made at 1. and 2. shows that none of the five d-orbitals points directly towards the ligands.

Calculations have shown that the angle between d_{z2} orbital, metal atom (black circle) and ligand (L_1) is equal to half the tetrahedral angle = 109° 28'/2 = 54°44' and the angle between d_{yz} orbital, central metal atom and ligand L_1 is equal to 35°16' (See Fig.3). The magnitude of these angles suggests that d_{yz} orbital is nearer to the direction of the approaching ligands than d_{z2} orbital.

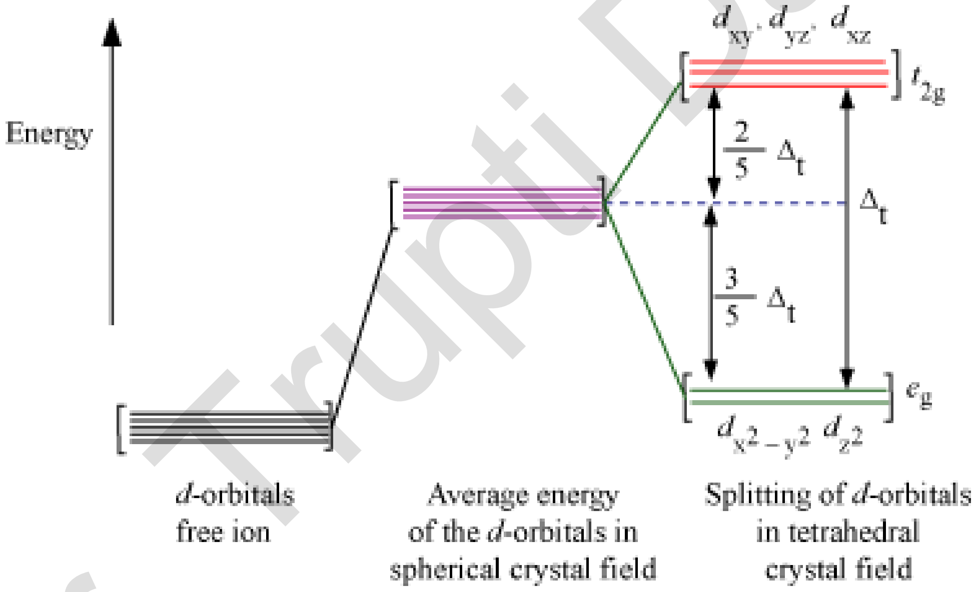

Fig: Splitting of five d-orbitals in tetrahedral complex

In a tetrahedral complex, when the four ligands approach near the central metal atom, the energy of the orbitals of both the sets (e and t_2 sets) increases. Since t_2 orbitals are closer to the direction of the approaching ligands than e orbitals, electrons in t_2 orbitals experience greater repulsion from the approaching ligands than e orbitals. Due to greater repulsion the energy of t_2 orbitals is increased to a larger extent than that of e orbitals. Thus e orbitals are at lower energy level than t_2 orbitals.

In other words we can say that under the influence of four ligands in a tetrahedral complex, five d-orbitals of the central metal atom are split into t_2 and e orbitals. This splitting of d-orbital is opposite to that of d-orbitals under the influence of six ligands in an octahedral complex. t_2 orbitals are raised by 0.4 Δt and e orbitals are lowered by 0.6 Δt from the no splitting state. Here Δt is the energy difference between t_2 and e orbitals.

Relation Between Δ_t, Δ_0, and 10Dq

Calculations have shown that Δ_t is less than Δ_0 for the same metal atom, same ligands and same inter-nuclear distance ($\Delta_t < \Delta_0$) There are two reasons for this:

1. There are only four ligands instead of six in a tetrahedral complex. Thus the ligand field caused by four ligands in a tetrahedral complex is 2/3 of that caused by six ligands in an octahedral complex.
2. The direction of the lobes of d-orbitals in a tetrahedral complex do not coincide with the direction of the ligands approaching towards the central metal atom. This also reduces the Δ_t magnitude of the splitting of d-orbitals in a tetrahedral complex.

Above two reasons suggest that Δ_t should be equal to

$2/3 \times 2/3\Delta_0 = 4/9\Delta_0 = 0.45\Delta_0$

i.e. $\Delta_t = \mathbf{4/9\Delta_0 \quad = \quad 0.45\Delta_0 \quad = \quad 0.45 \times 10\ Dq \quad = 4.5\ Dq}$

This equation also shows that $\Delta_t < \Delta_0$

In case of tetrahedral complexes, since Δ_t is generally less than P ($\Delta_t < P$) the electrons tend to remain unpaired and hence only high spin tetrahedral complexes are known, i.e., low spin tetrahedral complexes are not known.

Distribution of d^x Electrons (x = 0 to 10) of the Central Metal Ion in e and t_2 Sets of Orbitals in Tetrahedral Complexes:

In case of tetrahedral complexes, since Δ_t [Δ_t is the energy difference between t_2 (d_{xy} and d_{yz} and d_{xz} orbitals) and e (d_{x2-y2} and d_{z2} orbitals) sets of orbitals] is generally less than P (P is the energy which is required to pair two electrons in the same orbital against electron-electron repulsion. P is called pairing energy for one electron pair), the electrons tend to remain unpaired in d-orbitals of e and t_2 sets.

In other words we say that in tetrahedral complexes electrons occupy the e and t_2 sets of orbitals in accordance with Hund's rule of maximum multiplicity and hence tetrahedral complexes are HS tetrahedral complexes, i.e. in tetrahedral complexes d^x electrons pair up when each of five d-orbitals of e and t_2 sets is at least singly filled. The pairing of electrons starts from e orbitals, since these orbitals have less energy than t_2 orbitals. On the basis of the above discussion the distribution of d^x electrons in e and t_2 orbitals in tetrahedral complexes (HS tetrahedral complexes) has been shown in below figure.

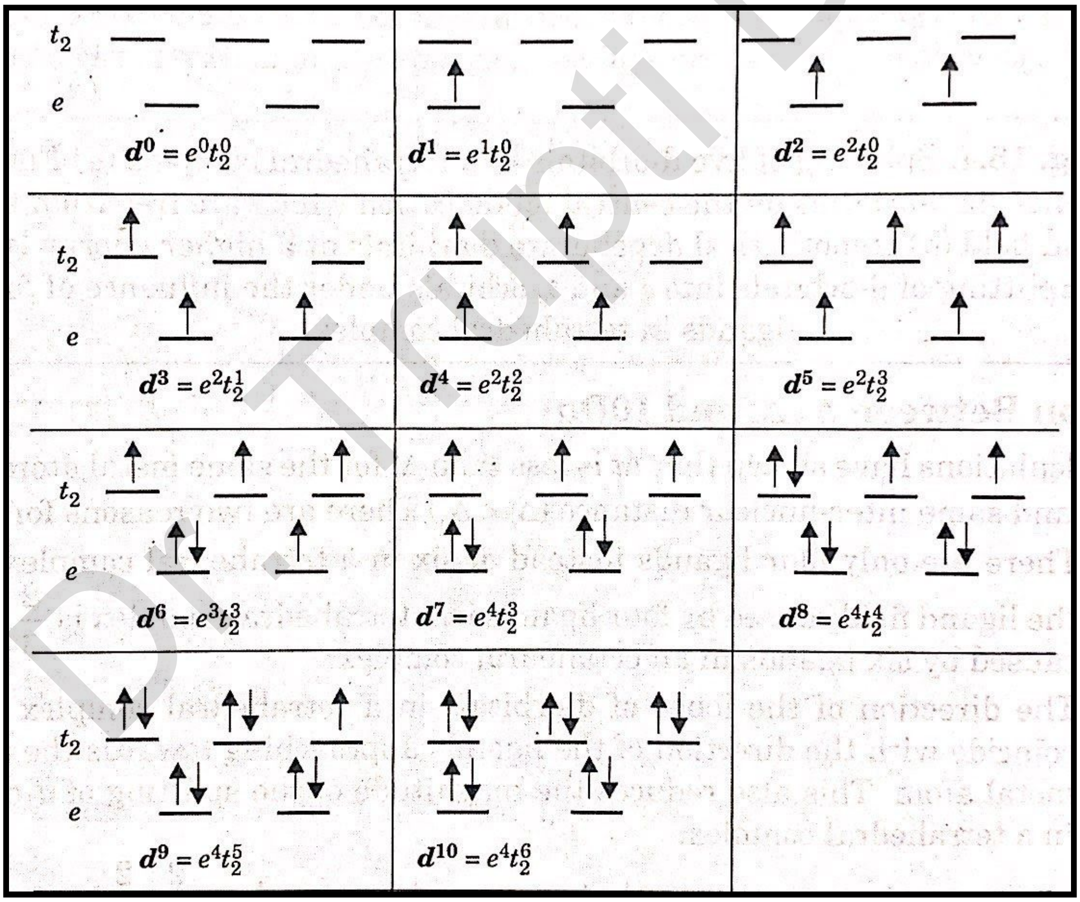

Fig: Distribution of d^x electrons in e and t_2 orbitals in tetrahedral complexes

Calculation of Crystal Field Stabilisation Energy (CFSE) of d^x Ions (x = 0 to 10) in Tetrahedral Complexes

Tetrahedral complexes are always HS complexes, since in these complexes

$P > \Delta_t$.

Thus we calculate CFSE of d^x ions in HS tetrahedral complexes.

According to CFT, under the influence of four ligands approaching towards the central metal ion during the formation of a high spin tetrahedral complex, the d-orbitals of the central metal ion are split into lower energy doublet e orbitals (d_{x2-y2} and d_{z2} orbitals) and higher energy triplet t_2 orbitals(d_{xy} and d_{yz} and d_{xz}orbitals). The energy gap between e and t_2 orbitals is denoted by Δ_t. The energy of e orbitals is lowered by $0.6\Delta_t$ and that of t_2 orbitals is raised by $0.4\ \Delta_t$ relative to the energy of no splitting state. Thus each electron occupying e orbitals decreases the energy of d-orbitals by $-0.6\Delta_t$ while that going to t_2 orbitals increases its energy by $+0.4\Delta_t$, - and + signs indicate respectively the decrease and increase in the energy of d-orbitals caused by their splitting under the influence of four ligands. Now let us consider a d^x ion having $e^p\ t_2^q$ configuration in which p is the number of electrons in e set of orbitals and q is the number of electrons in t_2 set of orbitals and x = p + q.

CFSE for d^x ion having $e^p\ t_2^q$ configuration (x = p+q)

= Loss in energy due to p electrons in e set of orbitals

+ Gain in energy due to q electrons in t_2 set of orbitals.

$= (-0.6\Delta_t \times p + 0.4\Delta_t \times q)$

$= (-0.6 \times p + 0.4 \times q)\ \Delta_t$ ....(i)

Equation (i) gives the value of CFSE in terms of Δ_t

Now since $\Delta_t = 0.45\ \Delta_0$ equation (1) can be written as:

$\text{CFSE} = (-0.6 \times p + 0.4 \times q) \times 0.45\ \Delta_0$....................(ii)

This equation gives the value of CFSE in terms of Δ_0

Now since $\Delta_0 = 10$ Dq, equation (ii) can be written as:

$\text{CFSE} = (-0.6 \times p + 0.4 \times q) \times 0.45 \times 10\text{Dq}$

$= (-0.6\ p + 0.4 \times q) \times 4.5\ \text{Dq}$ ....(iii)

Equation (iii) gives the value of CFSE in terms of Dq.

CFSE values of d^x ions (x = 0 to 10) having $e^p t_2^q$ configuration (x = p + q = 0 to 10) in tetrahedral complexes (HS complexes) have been calculated with the help of equation (i), (ii) and (iii).

Reference book:

Selected topics in Inorganic Chemistry by Malik, Tuli and Madan