

the tetrahedral geometry is predicted with one unpaired electron. But X-ray study of the complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  reveal that the ligands are arranged in planar arrangement around  $\text{Cu}^{2+}$  ion which can only be possible due to  $dsp^2$  hybridisation of copper ion.

6. VBT fails to explain why square planar complex of copper (II) such as  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  do not behave as reducing agent but  $\text{Co}^{2+}$  ( $d^7$  ion) form inner orbital octahedral complexes which behave as reducing agents. However in both the system, non bonding electron is promoted to higher energy orbital.
7. VBT is unable to explain the thermodynamic or kinetic stabilities of complexes.
8. VBT cannot give an explanation for the rates of reactions and its mechanisms.
9. For some complexes the observed values of magnetic moment do not show agreement with the calculated values of magnetic moments predicted by VBT.
10. VBT could not explain the quantitative correlation between the electronic spectra of complexes and their magnetic moment.

**Crystal Field Theory :** This theory was proposed by Bethe and Van Vleck and was initially proposed for ionic crystals and therefore was given the name crystal field theory. In 1952, Orgel applied this theory to coordination compounds. In crystal field theory, a complex compound consists of a metal ion surrounded by anionic or negative ends of polar ligands which creates an electrostatic field and the bonding between metal and ligand is considered to be purely electrostatic in nature. In this theory the effect of the external electric field set by the ligands on the relative energy levels of the  $d$ -orbitals of the central metal atom is considered which splits the degenerate  $d$ -orbitals into different sets of different energy levels. The nature of splitting decides the distribution of electrons among different sets of  $d$ -orbital and hence provides an explanation for magnetic and spectral properties and is often very useful in the explanation of distorted structures, thermodynamic properties and kinetics.

The five  $d$ -orbitals are degenerate in a free ion *i.e.* all the five  $d$ -orbitals have same energy, although they have different orientations with respect to the cartesian axes  $X$ ,  $Y$  and  $Z$ , the origin of which is the centre of the metal ion. The two  $d$ -orbitals *e.g.*  $dx^2 - y^2$ ,  $dz^2$  (*eg* set) have their lobes extending along the cartesian axes, while those of  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  (*t<sub>2g</sub>* set) lie in between the cartesian axes. A particular stereochemistry places the ligands about the metal ion at certain chosen points with respect to the cartesian axes. The electrostatic field produced by the ligands leads to removal of the degeneracy of the  $d$ -orbitals of the free ion, therefore giving a new energy level of the  $d$ -orbitals. Different stereochemistries give different  $d$ -orbital orderings.

**Octahedral stereochemistry :** In this geometry, six ligands are brought near the positively charged central metal ion along the three cartesian axes  $X$ ,  $Y$  and  $Z$ . There will be net electrostatic attraction between positively charged metal ion and negative charge on ligands, but due to repulsion between the ligand electrons and  $d$ -orbital electrons of the metal, there will be a general increase in the energy of these  $d$ -orbitals. Not all  $d$ -electrons

will be affected equally, those in the  $dx^2 - y^2$  and  $dz^2$  orbitals will be repelled more than those in the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals because these orbitals have their lobes along the axes hence they point towards the ligands whereas the lobes of the orbitals  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  lie in between the cartesian axes. Hence, the repulsions between the ligands and the orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$  are greater than the repulsions between the ligands and  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals.

The three  $t_{2g}$  i.e.  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals are degenerate and same is true about two  $e_g$  orbitals i.e.  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals. Under the influence of ligands, the five  $d$ -orbitals which were initially degenerate in free metal ion are now split into two sets ( $t_{2g}$  &  $e_g$ ). The separation of five  $d$ -orbitals of the metal ion into two sets having different energies is called crystal field splitting. The energy gap between  $t_{2g}$  and  $e_g$  sets is denoted by  $\Delta_0$  or 10 Dq (o-octahedral stereochemistry). The mean value of these perturbed  $d$ -orbitals is taken as zero. This is also called as the baricentre.

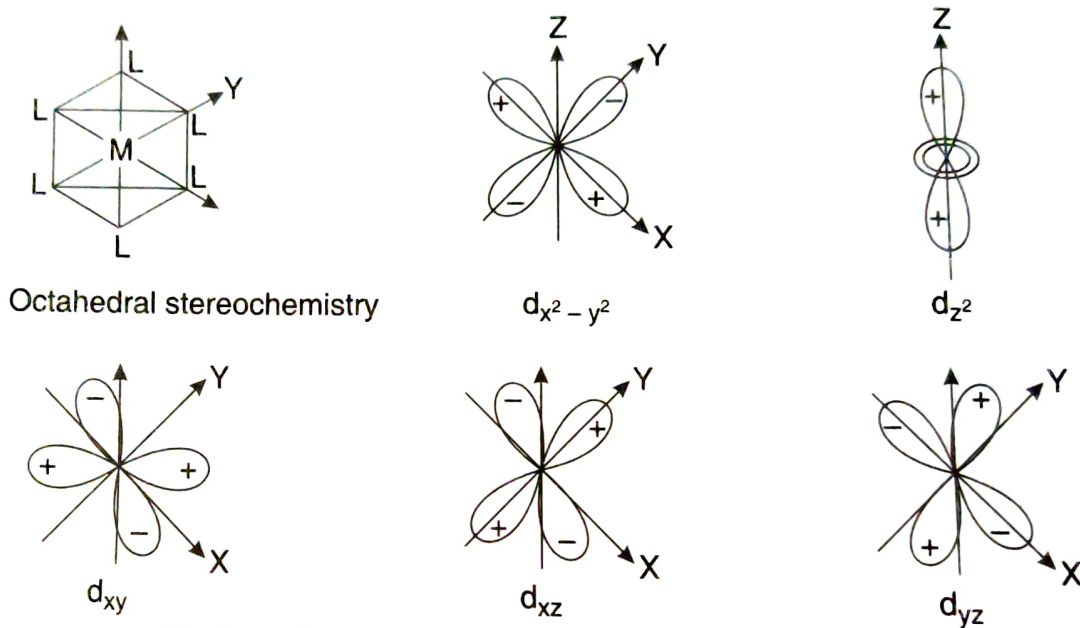


Fig. 7.1 : Shapes and orientations of the five  $d$ -orbitals.

$\Delta_0$  or 10 Dq is called crystal field splitting energy. It can be shown that the energy of the  $t_{2g}$  orbitals is  $0.4 \Delta_0$  (or 4 Dq) less than that of hypothetical degenerate  $d$ -orbitals i.e. Baricentre and hence, that of  $e_g$  orbitals is  $0.6 \Delta_0$  (or 6 Dq) above that of hypothetical degenerate  $d$ -orbitals. Thus, the  $t_{2g}$  set loses an energy equal to  $0.4 \Delta_0$  ( $= 4 Dq$ ) and hence get stabilised by  $0.4\Delta_0$  ( $= 4 Dq$ ) while  $e_g$  set gains an energy equal to  $0.6 \Delta_0$  (or 6 Dq) and hence  $e_g$  set get destabilised by an energy amount of  $0.6\Delta_0$  ( $= 6 Dq$ ).

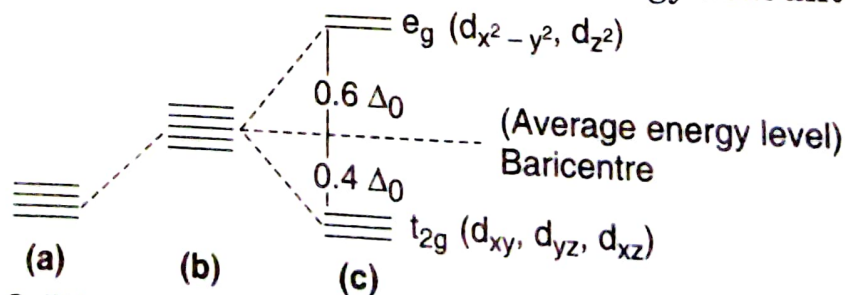


Fig. 7.2 : Splitting of  $d$ -orbitals in octahedral geometry (a)  $d$ -orbitals in free ion (b) Average energy of  $d$ -orbitals in a spherical ligand field (c) Splitting of  $d$ -orbitals in octahedral stereochemistry

In above figure 7.2, we have taken into consideration only the effect of the point negative charge or point dipoles on the  $d$ -orbitals of the metal ion. But when we consider the complex as a whole as a cluster of metal ions and ligands and also take into consideration the destabilising effect by the dipoles or charge on other filled spherical electron shells, we have to get a situation as shown in figure 7.2.

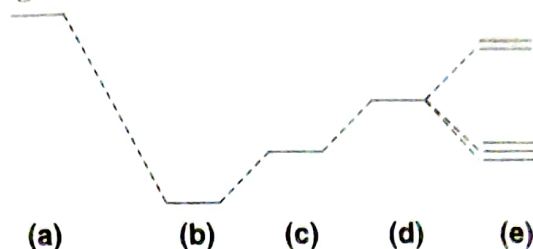


Fig. 7.3 : Different stabilising and destabilising effects in a coordination complex : (a) Free ion (b) Attraction between metal ion and ligands (c) Destabilisation of filled shells (d) Destabilisation of  $d$ -orbitals (e) splitting of  $d$ -orbitals.

The  $s$ -orbital does not undergo any splitting. However, its energy is increased by the point dipoles. The three  $p$ -orbitals are located along a particular cartesian axis with lobes on either side of the metal ion nucleus *i.e.*  $p_x$  in  $X$ -axis,  $p_y$  in  $Y$ -axis and  $p_z$  in  $Z$ -axis. In an octahedral stereochemistry, all the three  $p$ -orbitals will be equally destabilised and hence no splitting will take place.

**Tetragonal Elongation and Square Planar Stereochemistry :** If the two *trans* ligands (1, 6 positions) placed along the  $z$ -axis of an octahedron are taken away from the metal ion so that their distance from the metal cation is slightly more than that for the other four ligands lying in the  $xy$  plane, we find a tetragonal structure. During this tetragonal elongation, the  $dz^2$  orbital as also the two other orbitals with  $z$ -component, *e.g.*,  $d_{xz}$ ,  $d_{yz}$  becomes more stable. Since splitting has to maintain the presplitting baricentre *i.e.* the average value for complex, the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals becomes less stable. The orbitals  $d_{xz}$  and  $d_{yz}$  are degenerate and thus have equal energy. Thus, under the influence of the ligands in tetragonal complex, the order of energy of various  $d$ -orbitals can be written as :

$$d_{yz} = d_{xz} < d_{xy} < dz^2 < dx^2 - y^2$$

If the two *trans* ligands on the  $z$ -axis are completely removed, we find a square planar geometry for complex compounds. As a consequence of which a further rise in the energies of  $dx^2 - y^2$  and  $d_{xy}$  orbitals takes place and orbitals, all which have  $z$ -component becomes more stable  $d_z^2$ ,  $d_{xz}$  and  $d_{yz}$ . As the lobes of  $d_{x^2-y^2}$  orbitals lie along the axes *i.e.* point towards the ligands, this orbital has highest energy in square planar geometry. The lobes of  $d_{xy}$  orbital lie between the ligands but are coplanar with them. Hence this orbital  $d_{xy}$  is next highest in energy. The lobes of  $d_z^2$  orbital point out of the plane of the square planar complex, but the collar or belt around the centre of the  $d_z^2$  orbital lies in the plane of the molecule. Hence  $d_z^2$  orbital is next highest in energy. The orbitals  $d_{xz}$  and  $d_{yz}$  orbital are lowest in energy because the lobes of the orbitals point out of the plane of the complex. Hence the order of energy of  $d$ -orbitals is

$$d_{xz} = d_{yz} < d_z^2 < d_{xy} < d_{x^2-y^2}$$

**Note :** The terms  $D$  and  $q$  quantities came from mathematical derivation of the electrostatic model. They depend on the charge on the metal ion, the radial distribution of the valence  $d$  electrons and the metal-ligand distance. The factor of 10 in  $Dq$  introduces (specially) for a single electron in an electrostatic potential of octahedral geometry.

The crystal field splitting in square planar complex is represented by  $\Delta_{sp}$  which yields the total square planar splitting from the lowest  $d_{xz}, d_{yz}$  orbital pair to the highest  $dx^2 - y^2$  orbital and is given by

$$\begin{aligned} \Delta_{sp} &= [E(dx^2 - y^2) - E(d_{xz}, d_{yz})] \\ &= [E(dx^2 - y^2) - E(d_{xy})] + [E(d_{xy}) - E(dz^2)] + E(dz^2) - E(d_{xz}, d_{yz})] \quad \dots(7.1) \end{aligned}$$

$$= \Delta_1 + \Delta_2 + \Delta_3 \quad \dots(7.2)$$

The value of  $\Delta_{sp}$  has been found to have greater value than  $\Delta_0$

$$\Delta_{sp} = 1.3 \Delta_0$$

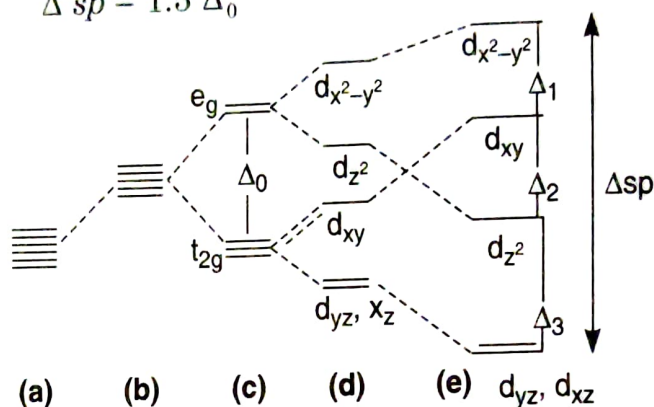


Fig. 7.4 : Splitting of  $d$ -orbitals in tetragonal and square planar stereochemistry of complexes.

(a) Free ion

(b) Shifts in energy due to spherical ligands field

(c) Splitting in octahedral stereochemistry

(d) Splitting of  $d$ -orbitals in tetragonally distorted structure

(e) Splitting of  $d$ -orbitals in square planar stereochemistry.

(e) Splitting of

**Tetrahedral Stereochemistry :** Both the octahedron and tetrahedron can be inscribed in a cube. The splitting pattern for tetrahedral complexes is just the opposite of the splitting pattern of the octahedron. In order to find the  $d$ -orbital splitting in a tetrahedral crystal field, we place the metal ion at the centre of a cube while the four ligands occupy the four alternate corners of the cube. None of the four ligands experiences any of the five  $d$ -orbitals, face to face. However, the lobes of the two  $d$ -orbitals, i.e.,  $dx^2 - y^2, dz^2$  ( $e$  set) are half the diagonal of a face of the cube away from the nearest ligand while the lobes of other three  $d$ -orbitals e.g.  $d_{xy}, d_{yz}, d_{xz}$  i.e.  $t_2$  set are half the edge of a face of the cube away. Thus, the  $dx^2 - y^2$  and  $dz^2$  orbitals now become more stable while  $d_{xy}, d_{yz}$  and  $d_{xz}$  orbitals become less stable. Moreover, there are four ligands and those too in no way in full face position, the total splitting is much smaller than that observed in case of octahedral stereochemistry.  $\Delta_t = 4/9 \Delta_0$ . Like the octahedral complex the relative stabilising effect of the  $e$  set ( $dx^2 - y^2, dz^2$ ) will be  $-6 D_{qt}$  and the relative destabilising effect of the  $t_2$  set ( $d_{xy}, d_{yz}, d_{xz}$ ) will be  $+4 d_{qt}$

$$0.4 d_{qt} = 0.18 \Delta_0, \quad 0.6 d_{qt} = 0.27 \Delta_0$$

Crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex  $\Delta t = 4/9 \Delta_0$ . This energy is too small that it is not able to force the electrons to pair up in tetrahedral geometry. Hence, tetrahedral complexes are generally high spin complexes.

**Trigonal Bipyramidal Stereochemistry :** In this stereochemistry lobes of the  $d_{z^2}$  orbital lies along the  $z$ -axis and hence the  $dz^2$  orbital directly faces two ligands lying on the  $z$ -axis. None of the other  $d$ -orbitals face to face with any of the equatorial ligands. But the  $d_{xy}$  and the  $d_{x^2-y^2}$  orbitals are equally distant with respect to the equatorial ligands and thus form a doublet set *i.e.* are degenerate. The remaining two orbitals *i.e.*,  $d_{xz}$  and  $d_{yz}$  form the most stabilised set *i.e.* have lowest energy.

The order of energy of various  $d$ -orbitals is

$$d_{xz} = d_{yz} < d_{xy} = d_{x^2-y^2} < d_{z^2}$$

**Square pyramidal stereochemistry :** In the square pyramidal geometry, one ligand along the  $z$ -axis is removed from the octahedral geometry. Hence the  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$  orbitals with  $z$ -component becomes more stable as compared to octahedral complex.

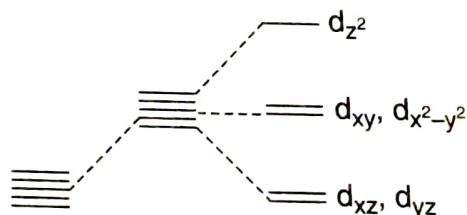


Fig. 7.6 : Splitting of  $d$ -orbitals in trigonal bipyramidal stereochemistry.

The lobes of the  $d_{z^2}$  orbital experiences only one ligand hence the repulsion will be less *i.e.*  $d_{z^2}$  orbital is next highest in energy. The lobes of the  $d_{xy}$  orbital lie between the ligands but are coplanar with them hence this orbital is next highest in energy. In a square pyramidal complex, it can be easily understood that the  $d_{x^2-y^2}$  orbital will be the least stable, this orbitals has highest energy. In this connection, in the square pyramidal complex oxovanadium (IV) complex, a very strong vanadium-oxygen multiple covalent bond is only  $\sim 1.7 \text{ \AA}$  while the other equatorial bond lengths are  $\sim 2.3 \text{ \AA}$  as in the case of  $[\text{VO}(\text{H}_2\text{O})_4]\text{SO}_4$ . Since the ligand in the  $z$ -direction is present in nearer than the equatorial ligands,  $d_{z^2}$  orbital will be most destabilised, next comes the  $dx^2 - y^2$  orbital followed by  $d_{xz}$ ,  $d_{yz}$  orbitals and then the most stabilised  $d_{xy}$ . This is a case of tetragonal compression along the  $z$ -axis.

$$dxz = dyz < dxy < dz^2 < dx^2 - y^2$$

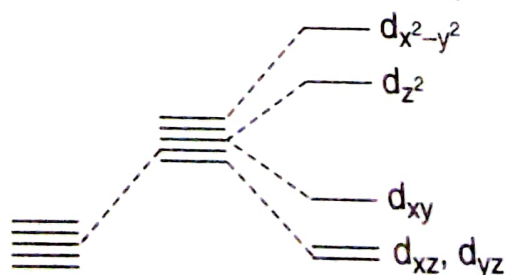


Fig. 7.7 : Splitting of  $d$ -orbitals in a square pyramidal stereochemistry.

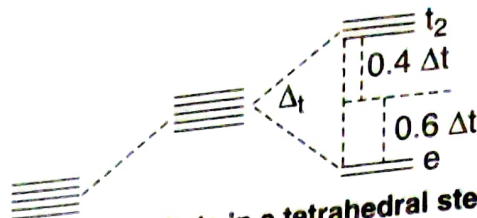


Fig. 7.5 : Splitting of  $d$ -orbitals in a tetrahedral stereochemistry.

## FACTORS AFFECTING THE MAGNITUDE OF $\Delta$ OR $DQ$

The factors affecting the magnitude of  $\Delta$  can be studied under two headings :

- (i) Nature of Metal Cation
- (ii) Nature of ligand
- (iii) Geometry of complex

### 1. Nature of Metal Cation

The influence of this factor can be studied under the following four headings.

**(a) Different charges on the cation of the same metal :** The cations from atoms of the same transition series and having the same oxidation state will have almost the same value of  $\Delta$ . The higher the oxidation state of the central metal cation, larger the value of  $\Delta$  than that cation with lower oxidation state. The reason can be explained as the metal ion with higher oxidation state will polarise the ligands more effectively and thus the ligands would approach such a metal cation more closely and results a greater  $\Delta$  value. The example given below clears that the value of  $\Delta$  for Fe (II) is less than that for the Fe (III) in aquo complex.

$$\Delta_0 \text{ for } [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 10400 \text{ cm}^{-1} \quad 3 d^6$$

$$\Delta_0 \text{ for } [\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 13700 \text{ cm}^{-1} \quad 3 d^5$$

**(b) Different charges on the cations of different metals :** The cation with a higher oxidation state has a larger value of  $\Delta$  than the cation with a lower oxidation state provided that these central metal cations have the same number of  $d$ -electrons and the geometry of the complex will be same.

$$\text{Octahedral complex} \quad \Delta_0 \text{ for } [\text{V}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 12400 \text{ cm}^{-1} \quad 3 d^3$$

$$\text{Octahedral complex} \quad \Delta_0 \text{ for } [\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 17400 \text{ cm}^{-1} \quad 3 d^3$$

This can be explained in terms of greater positive charge on cation and hence a greater attraction. In the example shown above the  $\Delta_0$  value for the  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  is less than that found for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , however the number of  $d$ -electrons are same ( $3d^3$ ).

**(c) Same charge on the metal cation but different number of  $d$ -electrons :** Magnitude of  $\Delta_0$  decreases with the increase of the number of  $d$ -electrons in the metal atoms having the same charge.

$$\Delta_0 \text{ for } [\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 9300 \text{ cm}^{-1} \quad - 3 d^7$$

$$\Delta_0 \text{ for } [\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 8500 \text{ cm}^{-1} \quad - 3 d^8$$

$$\text{Number of } d\text{-electrons} \propto 1/\Delta$$

...(7.3)

Value of  $\Delta_0$  for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ( $3d^8$ ) is less than that obtained for  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ( $3d^7$ )

**(d) Quantum number of the  $d$ -orbitals of the metal ion :**  $\Delta$  increases about 30% to 50% on going from  $3 d^n$  to  $4 d^n$  and by about the same amount again from  $4 d^n$  to

5  $d^n$  complexes i.e. within the same group on going from 3d to 4d to 5d series elements, the  $\Delta_0$  increases. The tendency to form low spin complexes increases on going down the group.

$$\Delta_0 \text{ for } [\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+} = 23000 \text{ cm}^{-1} - 3 d^6$$

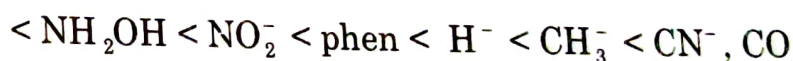
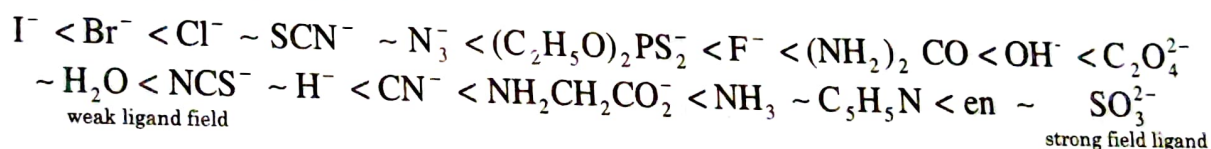
$$\Delta_0 \text{ for } [\text{Rh}^{\text{III}}(\text{NH}_3)_6]^{3+} = 34000 \text{ cm}^{-1} - 4 d^6$$

$$\Delta_0 \text{ for } [\text{Ir}^{\text{III}}(\text{NH}_3)_6]^{3+} = 41000 \text{ cm}^{-1} - 5 d^6$$

## 2. Nature of ligands : Strong and weak ligands and spectrochemical series

For any given central metal cation, the magnitude of  $\Delta$  depends upon the nature of ligands. Some ligands produce strong ligand field around the metal cation and hence stronger ligands have higher splitting power. Some ligands produce weak ligand field around central metal cation and thus weaker ligands have comparatively lower splitting power. Thus, stronger ligands such as  $\text{CN}^-$  give larger value of  $\Delta_0$  and weaker ligands such as  $\text{F}^-$  give a smaller value of  $\Delta_0$ .

The ligands can be arranged in a series on the basis of their increasing splitting power i.e. in the order of their increasing  $\Delta$  value. The series is called spectrochemical series and is given below :



Thus the arrangement of ligands in order of their increasing CFSE ( $\Delta$ ) value is called the spectrochemical series. The order of field strength of the ligands is independent of the nature of metal ion and the geometry of the complex.

## 3. Geometry of the Complex

With the change of the geometry of the complex, the value of  $\Delta$  also changes.  $\Delta$  value for tetrahedral complexes is nearly half of the  $\Delta$  value for octahedral complexes.

$$\Delta_{sp} > \Delta_0 > \Delta_{qt}$$

$$1.3 \Delta_0 \quad \Delta_0 \quad 0.45 \Delta_0$$

while the value of  $\Delta_0$  for square planar complexes is greater than the  $\Delta_0$  value for octahedral complexes.

**Crystal field stabilisation energy (CFSE) :** The energy difference between the two sets of  $d$ -orbitals is called crystal field splitting energy. It is seen that eg orbitals are  $+0.6\Delta_0$  (or  $6D_q$ ) above the average energy level i.e. barycentre and  $t_{2g}$  orbitals are  $-0.4\Delta_0$  (or  $4D_q$ ) below the average energy level in an octahedral ligand field. Thus, each electron occupying  $t_{2g}$  orbitals leads to a decrease in system by  $4\Delta_0$  (or  $4D_q$ ) and hence the system is stabilised to the extent of  $4\Delta_0$  ( $4D_q$ ) compared to the barycentre.

This quantity is called crystal field stabilisation energy.

**Calculation :** The electron occupying a  $t_{2g}$  orbital has an energy of  $-4\Delta_0$  ( $-4D_q$ ) and the electron present in eg orbital has an energy of  $+6\Delta_0$  (or  $6D_q$ ) relative to the barycentre of the  $d$ -orbitals.

Thus, if  $a$  electrons occupy the  $t_{2g}$  orbital and  $b$  electron occupy  $eg$  orbital, then

$$\begin{aligned} \text{CFSE} &= (-0.4 \times a + 0.6 \times b) \Delta_0 \\ &\text{or } (-4 \times a + 6 \times b) Dq \end{aligned}$$

where  $-0.4 \Delta_0 \times a =$  loss in energy due to presence of  $a$  electron in  $t_{2g}$  orbitals.

$+0.6 \Delta_0 \times b =$  gain in energy due to presence of  $b$  electrons in  $eg$  orbitals.

For  $d^1, d^2$  and  $d^3$  configuration, the value of CFSE is same for high and low spin complexes.

For  $d^1$  configuration  $t_{2g}^1$

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 1 + 0 \times 0) \Delta_0 \text{ or } (-4 \times 1 + 0 \times 0) Dq \\ &= -0.4 \times \Delta_0 \text{ or } -4 Dq \end{aligned}$$

For  $d^2$  configuration ( $t_{2g}^2$ )

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 2 + 0 \times 0) \Delta_0 \text{ or } (-4 \times 2 + 0 \times 0) Dq \\ &= -0.8 \Delta_0 \text{ or } -8 Dq \end{aligned}$$

For  $d^3$  configuration ( $t_{2g}^3$ )

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 3 + 0 \times 0) \Delta_0 \text{ or } (-4 \times 3 + 0 \times 0) Dq \\ &= -1.2 \Delta_0 \text{ or } -12 Dq \end{aligned}$$

In the presence of weak ligands the energy difference between the two sets of orbitals  $\Delta_0$  is small and  $d$  - electron are distributed according to Hund's rule. Thus in weak ligand field fourth and fifth electron will occupy the  $eg$  orbitals and after then electron pairing will take place.

For  $d^4$  configuration ( $t_{2g}^3 eg^1$ )

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 3 + 0.6 \times 1) \Delta_0 \text{ or } (-4 \times 3 + 6 \times 1) Dq \\ &= -0.6 \Delta_0 \text{ or } -6 Dq \end{aligned}$$

$d^5$  configuration ( $t_{2g}^3 eg^2$ )

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 3 + 0.6 \times 2) \Delta_0 \text{ or } (-4 \times 3 + 6 \times 2) Dq \\ &= 0 \Delta_0 \text{ or } 0 Dq \end{aligned}$$

$d^6$  configuration ( $t_{2g}^4 eg^2$ )

$$\begin{aligned} \text{CFSE} &= (-0.4 \times 4 + 0.6 \times 2) \Delta_0 + P \text{ or} \\ &= -0.4 \Delta_0 + P \text{ or } -4 Dq + P \end{aligned}$$

$d^7$  configuration ( $t_{2g}^5 eg^2$ ) where  $P =$  Pairing energy required to pair electrons against electron-electron repulsion in the same orbital.

$$\begin{aligned} &= (-0.4 \times 5 + 0.6 \times 2) \Delta_0 + 2P \\ &= -0.8 \Delta_0 + 2P \text{ or } -8 Dq + 2P \end{aligned}$$

$d^8$  configuration ( $t_{2g}^6 eg^2$ )

$$\begin{aligned} &= (-0.4 \times 6 + 0.6 \times 2) \Delta_0 + 3P \\ &= -1.2 \Delta_0 + 3P \text{ or } -12 Dq + 3P \end{aligned}$$



$d^9$  configuration ( $t_{2g}^6 eg^3$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 3 \times 6)\Delta_0 + 4P \\ &= -0.6\Delta_0 + 4P \end{aligned}$$

$d^{10}$  configuration ( $t_{2g}^6 eg^4$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 4 \times 6)\Delta_0 + 5P \\ &= 0.0\Delta_0 + 5P \end{aligned}$$

In the presence of strong ligands, the energy difference between two sets of  $d$ -orbitals,  $\Delta_0$  is higher and the distribution of electrons does not follow Hund's rule. Thus in strong ligand field, fourth, fifth and sixth electron will go in to  $t_{2g}$  orbitals and after then electron will center into  $eg$  orbitals.

$d^4$  configuration ( $t_{2g}^4 eg^0$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 4 + 6 \times 0)\Delta_0 + P \\ &= -1.6\Delta_0 + p \text{ or } 16Dq + P \end{aligned}$$

$d^5$  configuration ( $t_{2g}^5 eg^0$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 5 + 6 \times 0)\Delta_0 + 2P \\ &= -2.6\Delta_0 + 2P \text{ or } 20Dq + 2P \end{aligned}$$

$d^6$  configuration ( $t_{2g}^6 eg^0$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 6 \times 0)\Delta_0 + 3P \\ &= -2.4\Delta_0 + 3P \end{aligned}$$

$d^7$  configuration ( $t_{2g}^6 eg^1$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 6 \times 1)\Delta_0 + 3P \\ &= -1.8\Delta_0 + 3P \text{ or } 18Dq + 3P \end{aligned}$$

$d^8$  configuration ( $t_{2g}^6 eg^2$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 6 \times 2) + 3P \\ &= -1.2\Delta_0 + 3P \text{ or } 12Dq + 3P \end{aligned}$$

$d^9$  configuration ( $t_{2g}^6 eg^3$ )





















$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 6 \times 3)\Delta_0 + 4P \\ &= -0.6\Delta_0 + 4P \text{ or } 6Dq + 4P \end{aligned}$$

$d^{10}$  configuration ( $t_{2g}^6 eg^4$ )

$$\begin{aligned} \text{CFSE} &= (-4 \times 6 + 6 \times 4)\Delta_0 + 5P \\ &= -0.0\Delta_0 + 5P \text{ or } \Delta Dq + 5P \end{aligned}$$

The change in value of pairing energy takes place in the first transition series however the pairing energy decreases as we go from top to bottom with in a given group of the periodic table. As we proceed from top to bottom, with the increase in the size of  $d$ -orbitals a greater space will be available for electrons to share, hence pairing energy show a decreasing trend.

Table 7.6 : Crystal field stabilisation energies

<i>d</i> - electron configuration	Strong ligand field (Low spin state)	CFSE ( $\Delta_0$ )	Weak ligand field (high spin state)	CFSE ( $\Delta_0$ )
$d^1$		$-0.4\Delta_0$		$-0.4\Delta_0$
$d^2$		$-0.8\Delta_0$		$-0.8\Delta_0$
$d^3$		$-1.2\Delta_0$		$-1.2\Delta_0$
$d^4$		$-1.6\Delta_0$		$-0.6\Delta_0$
$d^5$		$-2.0\Delta_0$		$0.0\Delta_0$
$d^6$		$-2.4\Delta_0$		$-0.4\Delta_0$
$d^7$		$-1.8\Delta_0$		$-0.8\Delta_0$
$d^8$		$-1.2\Delta_0$		$-1.2\Delta_0$
$d^9$		$-0.6\Delta_0$		$-0.6\Delta_0$
$d^{10}$		$-0.0\Delta_0$		$-0.0\Delta_0$

Simplification of CFSE values are done as pairing energy and electron-electron effects are omitted here.

### Distribution of *d*-electrons

1. **When the ligands are weaker** : The ligands with small value of  $\Delta_0$  are called weak ligands such as  $I^-$ ,  $Br^-$ ,  $S^{2-}$  etc.

In this case  $\Delta_0 < P$  [ $P$  = average (or mean) pairing energy] ... (7.4)

Distribution of *d*-electrons takes place according to Hund's rule which states that electrons will pair up only when each of the five *d*-orbitals is singly occupied. In such cases, high spin complexes are formed.

## LIMITATIONS OF CRYSTAL FIELD THEORY

The crystal field theory can successfully explain many properties of transition metal complexes, yet the theory has serious limitations. There are several experimental and semitheoretical arguments that can be interpreted against the concept of splitting of  $d$ -orbitals as a result of pure ionic bonding.

Limitations of CFT can be understood by taking into consideration the following points :

1. CFT emphasises only the metal  $d$ -orbitals and gives no importance to other metal orbitals  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$  and ligand orbitals.
2. CFT does not consider the formation of  $\pi$ -bonding in complexes. The Mossbauer spectra of complexes supports the  $\pi$ -bonding in complexes.

The Mossbauer spectrum of sodium nitroprusside is consistent with a structure in which there is extensive  $\pi$ -bonding between the odd electron in the  $t_{2g}$  set of the  $d$ -orbitals of iron and odd electron on nitrogen (in NO). The filled  $\pi$ -bonding  $\pi$ -antibonding orbital has a large contribution from the nitrogen atomic orbital and the empty  $\pi$ -antibonding orbital has a larger contribution from the iron atomic orbitals. Consequently more of the  $\pi$ -electron density is centred on nitrogen. Due to decreased shielding of the  $s$ -electrons by the  $d$ -electrons, a very high negative  $\delta$  value is obtained.

The very high quadruple splitting is consistent with very extensive  $\pi$ -bonding in the Fe - N - O bond.

3. According to CFT bonds between the metal and ligands are purely ionic in nature with no covalent character but experimental evidences support the covalent character in metal ligand bonds.

### Experimental evidences for metal-ligand covalent bonding in complexes :

The existence of stable complexes formed from uncharged metal atoms and neutral ligands such as metal carbonyls itself suggests that some amount of covalent bonding exists between metal and ligands bonds. Even for complexes formed from metal cation and anionic ligands there is often evidence for electron delocalisation between metal and ligands.

Following evidences have been given to show covalent bonding in complexes.

- (a) **Electron spin resonance spectroscopy** : An unpaired electron not in close proximity with other unpaired electrons or with magnetic nuclei will give single absorption line in the ESR spectrum (parallel alignment to antiparallel alignment transition). The ESR spectra of many complexes show hyperfine splitting pattern that arise due to interaction of the unpaired metal electron with magnetic nuclei on ligands. This clearly indicates that the electron is at least partially delocalised over the ligands.

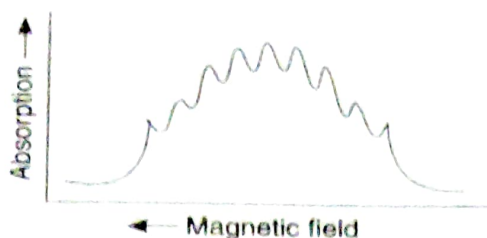


Fig. 7.11 : The ESR spectrum of  $[\text{IrCl}_6]^{2-}$  ion, obtained with the applied magnetic field aligned along one of the Cl — Ir — Cl axes of the complex ion in a single crystal of  $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  containing 0.5% of  $\text{Ir}^{\text{IV}}$  substitutionally replacing  $\text{Pt}(\text{V})$ .

The ESR spectrum of complex ion  $[\text{IrCl}_6]^{2-}$  consists of a quartet because of the hyperfine splitting by the iridium nucleus. Some iridium orbitals and certain orbitals of the  $\text{Cl}^-$  ion overlap. Due to electron delocalisation on the ligand chloride ions, each of these peaks will split into hyperfine lines. Hence it is concluded that the metal ligand bonds have covalent character to some extent.

In the complex bis-salicylaldimine copper complex, appreciable hyperfine splitting of peaks by the ligand takes place indicating the fact that metal ligand bonds have appreciable covalent character and the degree of  $\pi$ -bonding is considerably higher in the plane than out of the plane.

- (b) **Nuclear magnetic resonance spectroscopy** : NMR spectra of complexes such as  $\text{KNiF}_3$  show that metal  $d$ -electrons pass a fraction of time around the fluorine nuclei indicates metal electron delocalisation over the ligand.
- (c) **Nuclear quadruple resonance spectroscopy** : NQR spectrum of some of square planar complexes of Pt (II) and Pd (II) such as  $[\text{Pt X}_4]^{2-}$ ,  $[\text{Pd X}_4]^{2-}$  indicate some covalent character in metal-ligand bonds.
- (d) **Naphelauxtic effect** : It is found that the electron-electron repulsion in complexes is less than that in the free ion. Racah parameter  $B$  is a measure of inter electron repulsion. The lowering of value of  $B$  indicates that the inter electron repulsion value is lower in complex than the free ion. The extent of lowering in the value of  $B$  is a measure of the extent of metal-ligand orbital overlap. Using the data of electronic spectra of complexes, naphelauxtic series for metal and ligands was made which indicates the order of decreasing electron-electron repulsion or increasing naphelauxtic effect *i.e.* (cloud expansion). The observed decrease in electron-electron repulsion that takes place upon bond formation may be given to an effective increase in the distance between electrons that occurs when metal and ligand orbitals overlap to form large molecular orbitals. The ligands that are most effective in making metal electrons delocalises more shows the largest value of the naphelauxtic parameter  $h$ .

$$h = \frac{\text{Inter electronic repulsion for metal in complex}}{\text{Inter electronic repulsion of free ion}}$$

The experimental energy values obtained from electronic spectra of complexes are always lower than that of calculated values. The deviation may be explained as due to presence of covalent character in the M-L bonding. Due to covalent character in the M-L bonding, delocalisation of electron density results in reduced electron-electron repulsion in the complex which has the effect of decreasing the difference in energy states.

**Table 7.14 : The nephelauxtic series of metals and ligands**

Ligand	$h$	Metal	$k$
F <sup>-</sup>	0.8	Mn (II)	0.7
H <sub>2</sub> O	1.0	V (II)	0.1
Urea	1.2	Ni (II)	0.12
Ammonia	1.4	Mo (III)	0.15
Ethelene diammine	1.5	Cr (III)	0.20
Oxalate	1.5	Fe (III)	0.24
Chloride	2.0	Rh (III)	0.28
Cyanide	2.1	Ir (III)	0.28
Bromide	2.3	Co (III)	0.33
Azide	2.4	Pt (IV)	0.6
Iodide	2.7	Pd (IV)	0.7

- (e) **Intensities of  $d-d$  transition** : Another indication that metal ion and ligand orbitals overlap with the effect that the  $d$ -orbitals of the metal ions are not pure metal ion  $d$ -orbitals is given by the intensities of the visible absorption bands due to  $d-d$  transition. The pure  $d-d$  transition is spectroscopically forbidden in the metal complex and thus are very weak. The only mechanism through which these  $d-d$  transitions could enhance intensity would be by interaction of the  $d$ -orbital wave function with vibrational wave functions of the complex ion i.e. vibronic transition and by mixing of  $d$ -orbitals with other metal ion orbitals in those complexes. But these two processes are not sufficient to explain the intensity of the visible absorption bands observed and it is proposed that additional process of overlap and mixing of  $d$ -orbitals with various ligand atom orbitals which is a powerful mechanism for increasing the intensity takes place to a significant degree.
- (f) **Antiferromagnetic coupling** : Another evidence of some orbital overlap between metal ion  $d$ -orbitals and ligand orbitals in compounds that are generally taken as ionic is antiferromagnetic coupling.

Antiferromagnetic substances follow Curie or Curie-Weiss law at high temperature but below Neel temperature show decreasing magnetic susceptibility as the temperature is lowered further. It has been observed by neutron diffraction studies that this effect is not due to pairing of electron spins within individual ions but is due to a tendency of half of the ions to have their magnetic moment lined up in the opposite direction to those of the other half of the ions. Such antiparallel aligning, in which nearest neighbour metal ions separated by an oxide ion collinear with them have opposed moments, can not be explained simply by direct effects. Over the intervening distance, of one magnetic dipole on another, their separation is too great to permit an effect of the observed magnitude. Let us consider an  $M^{2+} - O^{2-} - M^{2+}$  set in which each metal ion possesses an unpaired electron. The oxide ion also has pairs of electrons placed in  $\pi$ -orbitals. If there is overlap between that  $d$ -orbital of one metal ion and  $\pi$ -orbital of the oxide ion, an electron from the oxide ion will move so as to occupy partially the  $d$ -orbital. In so doing, however, it must have its spin opposed to that of  $d$ -electron because of Pauli's exclusion principle. The other  $\pi$ -electron then has its spin aligned parallel to that of  $d$ -electron on the first metal ion. If, it moves to the same extent into the  $d$ -orbital of the second metal ion which already contains that metal ions unpaired  $d$ -electron, the spin of that  $d$ -electron will have to be aligned opposite to that of the entering  $\pi$ -electron and hence opposite to that of the  $d$ -electron on the first metal ion. The net result is that by this intervention of the oxide ion which can only occur because there is some finite, not necessarily large, degree of overlap between metal  $d$ -orbital and oxygen  $\pi$ -orbital, we obtain a system in which the two metal ion  $d$ -electrons were free to orient their spin independently in which they are coupled together with their spins antiparallel. This later state has slightly lower energy at low temperature than has the former, then as the temperature is lowered, the entire metal oxide lattice will tend to drop into it and antiferromagnetism will be observed.

4. CFT is unable to explain satisfactorily for the relative strength of ligands. For example, it gives no explanation as to why  $H_2O$  appears in the spectro chemical series as a stronger ligand than  $OH^-$ . Further ligands are considered as point charges in CFT. The negative ligands should exert more splitting power. But these negative ligands are placed in the lower end of spectrochemical series.

## MOLECULAR ORBITAL THEORY

The CFT provides no explanation for the covalent bonding in complexes and the bonding between metal and ligands as purely ionic is considered. But experimental techniques like NMR, NQR, ESR, Mossbauer suggested some degree of covalent bonding in metal-ligand bond. To include some parameters to adjust the covalent character in bonding in complexes, modified crystal field theory was proposed. This modified form of