



# WILSON COLLEGE, MUMBAI

DEPARTMENT OF CHEMISTRY

UNDERGRADUATE SEMESTER -VI

INORGANIC CHEMISTRY

MODULE I

TOPIC: THEORIES OF THE METAL - LIGAND BOND

DR SAKINA.Z. BOOTWALA

HEAD OF DEPARTMENT

<b>SUBJECT</b>	<b>CHEMISTRY</b>
<b>Paper No and Title</b>	Inorganic Chemistry –II
<b>Module No</b>	Module- I
<b>Title</b>	Crystal field theory &Effect of crystal field on metal valence electrons in various geometry

## TABLE OF CONTENTS

1. Learning Outcomes
2. Limitation of the valence bond theory
3. Crystal Field Theory
4. Crystal Field Splitting
5. Effect of Crystal Field on metal valence electrons in various geometry
6. Summary

## Learning Outcomes

After studying this module, you shall be able to

- Know about Crystal field theory and spectroscopic term of d-orbitals
- Know about Crystal field splitting in various geometries from coordination number 2 to 6.

## Limitation of the VBT:

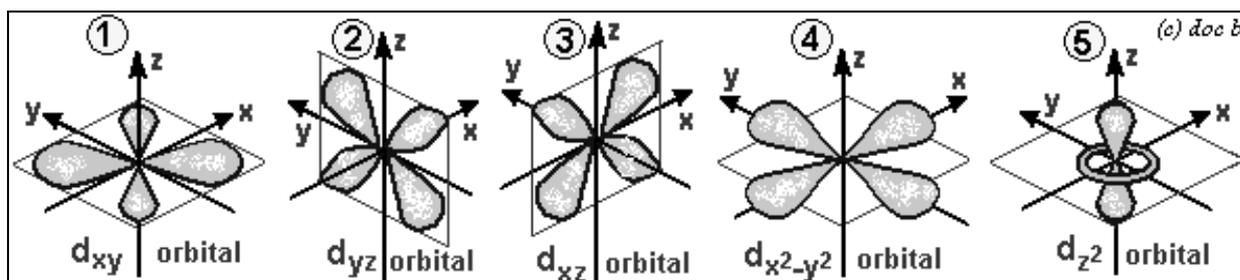
1. It describes the bonding in coordination compound qualitatively
2. It fails to account for various magnetic, electronic and spectroscopic properties of complexes
3. It offers no possibility of predicting or explaining magnetic behaviour beyond specifying the number of unpaired electrons and correlation of this fact with stereochemistry is often poor and even seriously misleading. For example, it was assumed that all square planar nickel (II) complex formed by  $dsp^2$  hybridization were diamagnetic whereas all tetrahedral nickel (II) complexes formed by  $sp^3$  hybridization are paramagnetic. The recent x-ray diffraction studies reveal that square planar nickel (II) complex can be paramagnetic.
4. The theory requires promotion of one electron to a vacant orbital of higher energy. This requires a large amount of energy, the absorption of such a large amount of energy is unfavourable.
5. It is unable to amount for or predict even the relative energies of different structures.
6. It does not take into account the splitting of 'd' orbitals.
7. It fails to explain the formation of inner orbital and outer orbital complexes

### Crystal field theory :

1. Crystal field theory views complexes on the basis of ionic model.
2. CFT considers the metal which forms the centre of the complex as positive ion and the surrounding ligand ions like  $F^-$  and  $Cl^-$  as point charges.
3. If the ligands are dipole molecules like  $H_2O$  and  $NH_3$  then they are considered as point dipoles with their negative ends directed towards the central metal ion. .
4. Therefore, on the basis of CFT, metal – ligand bonding is considered as purely electrostatic or ionic.
5. Apart from forces of attraction, repulsive forces also develop between *d* electrons of metal and the surrounding **negative** field.
6. CFT is mainly concerned with the interaction of the *d-orbitals* of central metal with the surrounding ligands that produce crystal field effects.

### CRYSTAL FIELD SPLITTING :

1. In an isolated gaseous metal ion, all the five *d*- orbitals are **degenerate**, i.e. have the same energy.
2. If a spherically symmetrical field of **negative** charges is placed around the metal ion, the *d-orbitals* remain **degenerate**, but their energy will be raised as a result of repulsion between the **negative** field and the electrons of the d orbitals.
3. This **degeneracy** of *d* -orbitals is possible only when all the ligands are at equal distance from each of *d-orbitals*, which is however only a hypothetical situation.

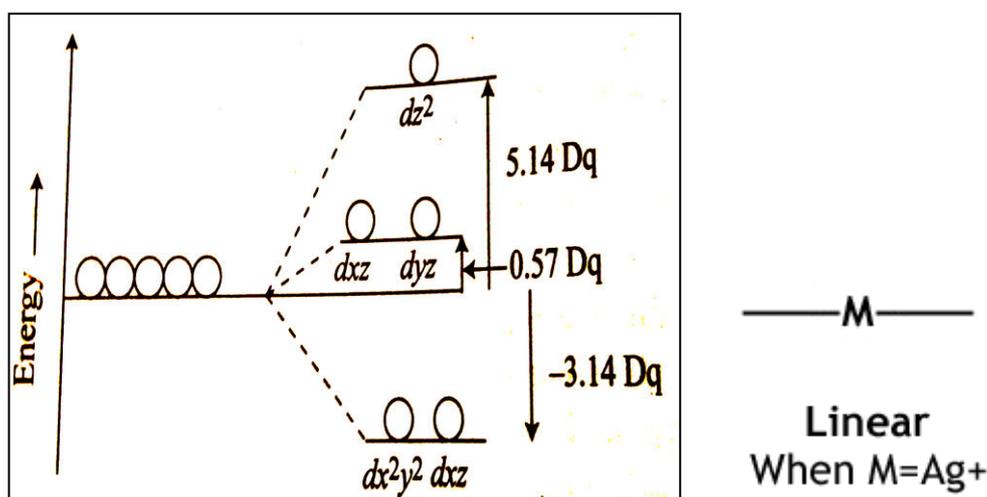


4. In general, the energy of the *d* orbital lying in the direction of the ligands will be raised to a larger extent than that of the orbitals lying in between the ligands.
5. This splitting of the five degenerated orbitals of the free metal ion due to ligand field into groups having different energies is called **crystal field splitting**.
6. This concept of crystal field splitting forms the basis of crystal field theory.
7. The effect of ligand field on the *d-orbitals* of the metal depends upon the nature, direction and number of ligands.
8. Out of the five d orbitals, four d-orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  and  $d_{x^2-y^2}$ ) have four lobes of electron density while the fifth orbital  $d_{z^2}$  has two lobes and a doughnut of electron density around the middle.
9.  $e_g$  orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) are directed along the axes x, y and z.
10.  $t_{2g}$  orbitals ( $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ) are directed in between the axes.

### Effect of crystal field on metal valence electrons in various geometry

1. Coordination number 2;  $[ML_2]$ 
  - a. Where M is a metal and L is a ligand forming a coordinate bond.  
Geometry can be linear or bent structure.

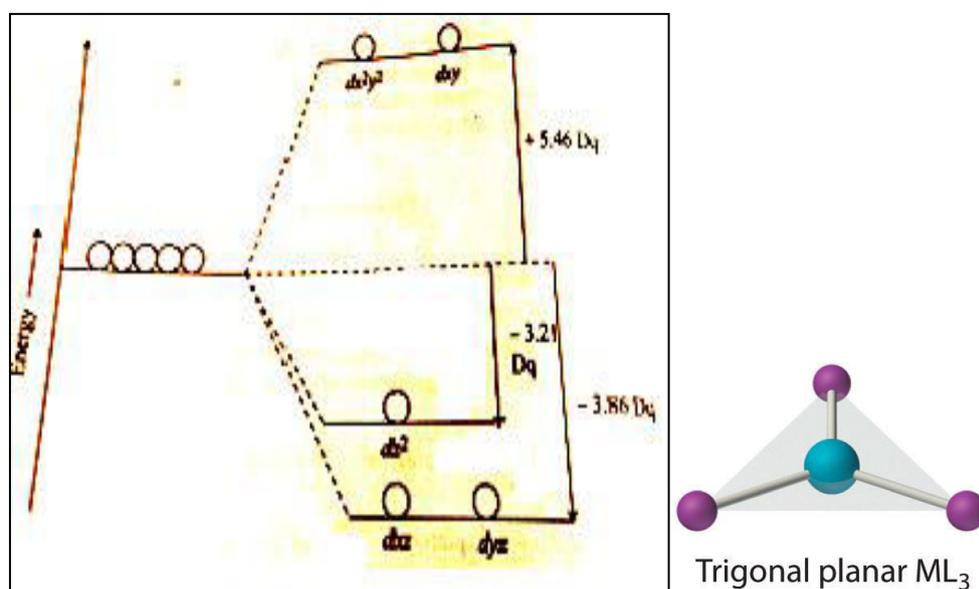
- b. In linear geometry two ligand are present on z-axis at either side, hence it will experience a lots of repulsion and gets destabilize, hence energy of  $d_{z^2}$  increases maximum.
- c.  $d_{xz}$  &  $d_{yz}$  will also get destabilized due to incoming ligands as they are near to z- axis but to a much lesser extent compared to  $d_{z^2}$
- d.  $d_{xy}$  and  $d_{x^2-y^2}$  will be stabilized to conserve the overall d-orbital energy.
- e. The order of energy is  $d_{x^2-y^2} = d_{xy} < d_{xz} = d_{yz} < d_{z^2}$
- f. Splitting pattern of dorbitals in linear complexes is represented as follows e.g  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Au}(\text{CN})_2]^-$



## 2. Coordination number 3; $[\text{ML}_3]$

- a. These complexes have trigonal planar structure in which the central metal ion is at the centre of the equatorial triangle with three ligands are at the vertices of the triangle with  $\angle \text{LML}$  bond angle as  $120^\circ$ .
- b. Since the geometry in xy plane, there are no ligands in z-direction, thus orbitals  $d_{z^2}$ ,  $d_{xz}$ , and  $d_{yz}$  will be lowered in energy and thus stabilized.

- c. Also  $d_{xz}$  and  $d_{yz}$  will be stabilized to the greater extent compared to  $d_{z^2}$  orbital. This is because the  $d_{z^2}$  orbital has a central lobe which points towards the ligands in the xy plane while the orbitals  $d_{xz}$  and  $d_{yz}$  have a nodal plane in the xy plane.
- d. Orbitals  $d_{xy}$  and  $d_{x^2-y^2}$  will have highest energy and hence destabilized as these orbitals are in the xy plane in which the ligands are present.
- e. The order of energy is :  $d_{xz} = d_{yz} < d_{z^2} < d_{x^2-y^2} = d_{xy}$

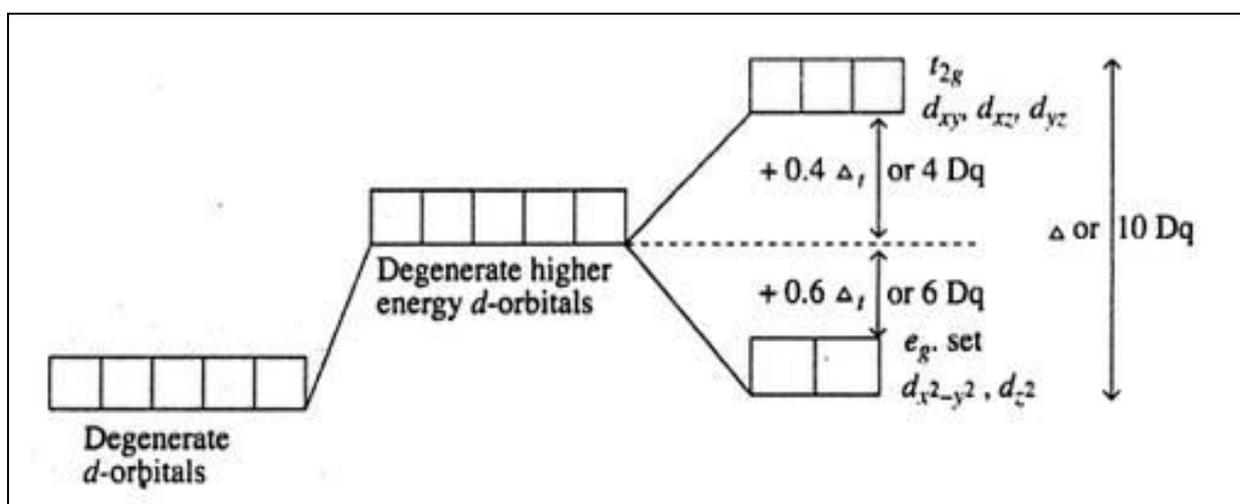
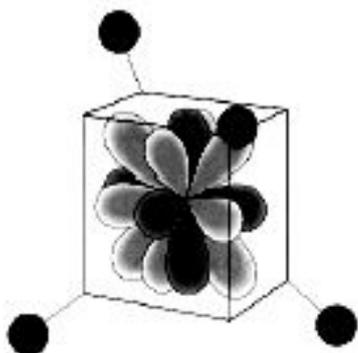


### 3. Coordination number 4; $[ML_4]$ (geometry tetrahedral & square planar)

#### TETRAHEDRAL GEOMETRY :

- To visualise a tetrahedron placed inside a cube. Four ligands around the central metal atom are considered at the four appropriate corners of a cube, in which the centre of the tetrahedron is taken as the centre of the cube.
- X and Y axes emerge from the sides of the cube and the Z axis from the centre of the top face.

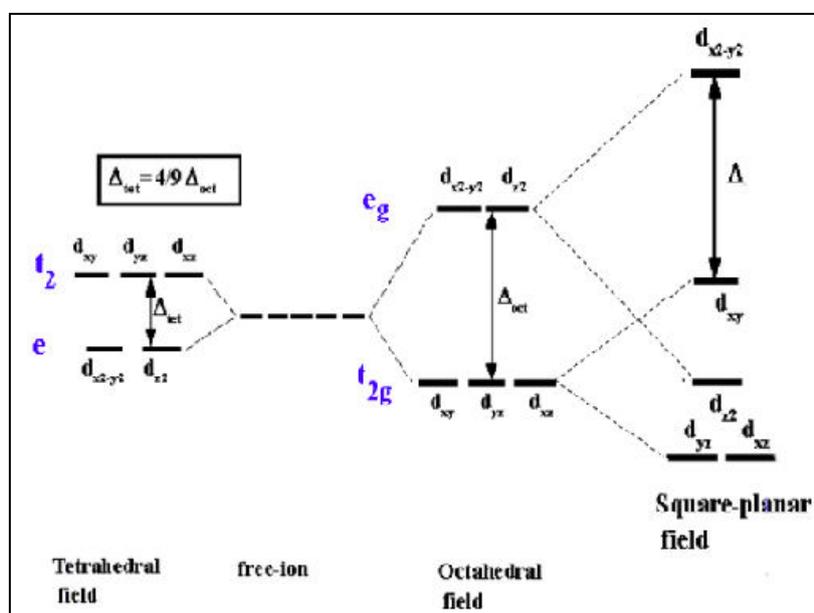
- c. In this arrangement, the **ligands do not directly approach** any of the metal *d* orbitals.
- d. They come closer to the  $t_{2g}$  orbitals, directed at the corners of the cube than to the  $e_g$  orbitals directed at the centres of the face of the cube.
- e. Hence  $t_{2g}$  orbitals will be raised in energy while  $e_g$  orbitals will be lowered.
- f. For maintaining the average energy constant,  $t_{2g}$  orbitals are raised by  $4Dq$  while  $e_g$  orbitals are lowered by  $6Dq$  from the barycentre.
- g. Thus, the energy level scheme for the tetrahedral symmetry is exactly the reverse of that for octahedral symmetry.



- h. It has been observed that the energy separation between the  $e_g$  and  $t_{2g}$  levels  $\Delta_t$ , in tetrahedral symmetry is **smaller** than in octahedral symmetry  $\Delta_o$  ( $10Dq$ ).

## SQUARE PLANAR GEOMETRY

- The square planar arrangement of ligands may be considered to be derived from the octahedral field.
- If two ligands along the Z-axis is removed ,than the four ligands approach the metal ion along X and Y axes
- The ligands field interaction with the metal ion  $d$  -orbital's is will be strongest with  $d_{x^2-y^2}$  (i.e.  $d_{x^2-y^2}$  lying on X and Y axes), lesser with  $d_{xy}$  and the least with  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  due to their orientation with respect to X,Y,Z axes
- The splitting of  $d$  -orbital in square planar field is much larger as compared to splitting in octahedral ligand field.
- The energy difference between  $d_{xy}$  and the highest  $d_{x^2-y^2}$  is called square planar splitting energy and is denoted as  $\Delta_{sp}$

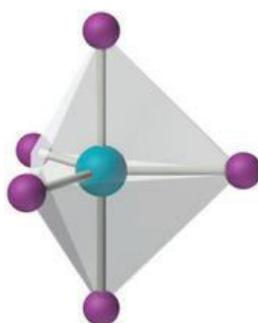
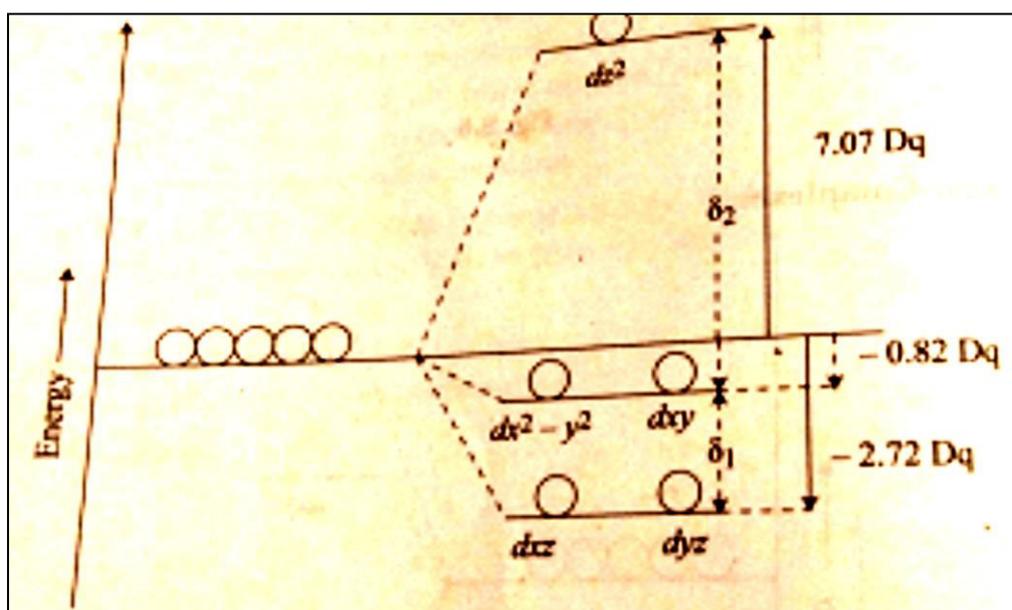


#### 4. Coordination number 5; [ML<sub>5</sub>]

(geometry can be trigonal bipyramidal or square pyramid .)

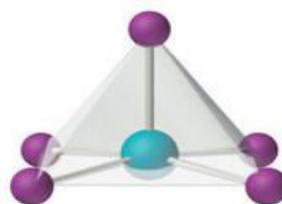
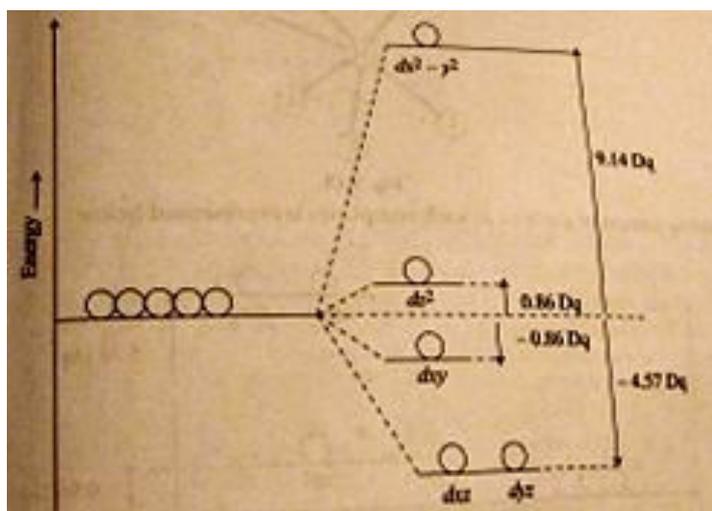
## TRIGONAL BIPYRAMIDAL

- In these complexes  $d_{z^2}$  orbital faces the two ligands directly and hence will experience maximum repulsion and thus has the highest energy
- Three equatorial ligands in xy plane,  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals do not face ligands directly but are equidistance with each other.
- Orbitals  $d_{xz}$  and  $d_{yz}$  will be the lowest energy, hence most stabilized
- The order of energy is  $d_{xz} = d_{yz} < d_{x^2-y^2} = d_{xy} < d_{z^2}$
- It is observed that that  $\delta_1 < \delta_2$ ,  $\delta_1$  can never exceed pairing energy (P) of a metal ion.  $\delta_2$  may be lesser or greater than pairing energy P.
- Hence TBP complexes of  $d^1$ ,  $d^2$ ,  $d^3$  and  $d^4$  ions always be high spin complexes and those of  $d^5$ ,  $d^6$ ,  $d^7$  and  $d^8$  ions may be either high spin or low spin complexes



## SQUARE PYRAMID

- Four ligands will approach towards  $d_{x^2-y^2}$  orbital and one ligand towards  $d_{z^2}$  orbital.
- Since  $d_{x^2-y^2}$  orbital is face to face with the four ligands lying in the xy plane it will experience maximum repulsion and will have highest energy and thus most destabilized. Presence one ligand near  $d_{z^2}$  orbital will have less repulsion and hence destabilisation is less.
- The stabilisation of  $d_{xy}$  orbital is less as four ligand are in the xy plane.
- The most stable orbitals are  $d_{xz}$  and  $d_{yz}$  as these orbitals have nodal plane in xy plane and thus no repulsion with the approaching ligands
- The order of energy is:  $d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$



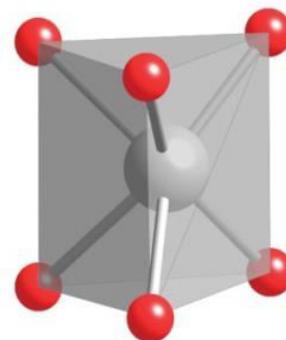
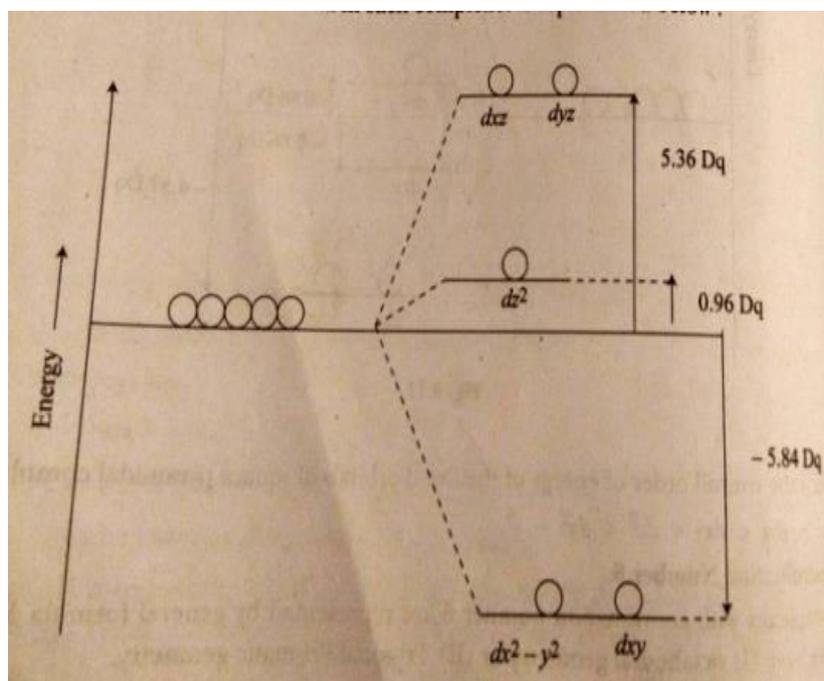
### 5. Coordination number 6; [ML<sub>6</sub>]

Geometry can be octahedral or trigonal prismatic

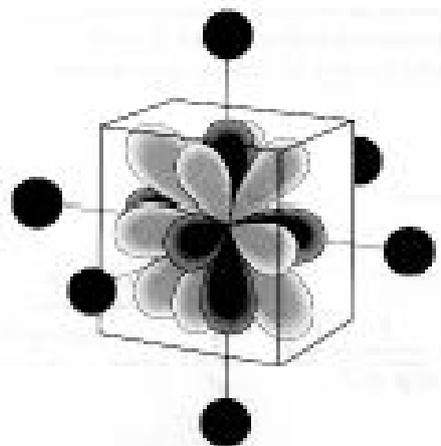
## TRIGONAL PRISMATIC

- Trigonal prismatic geometry describe as ligands are arranged around a central atom defining the vertices of a triangular prism

- b. Triangular vertices are in  $xz$  and  $yz$  plane, which are also near to  $d_{z^2}$
- c. Thus  $d_{xz}$  and  $d_{yz}$  orbitals experience maximum repulsion because ligands are very near to these orbitals, hence  $d_{xz}$  and  $d_{yz}$  are most destabilized and situated at highest energy.
- d.  $d_{z^2}$  orbital also destabilized to a small extent as ligands are near to  $z$ -axis
- e. The most stable orbitals are  $d_{xy}$  and  $d_{x^2-y^2}$  as ligands are not near to these orbitals
- f. The order of energy is:  $d_{xy} = d_{x^2-y^2} < d_{z^2} < d_{xz} = d_{yz}$

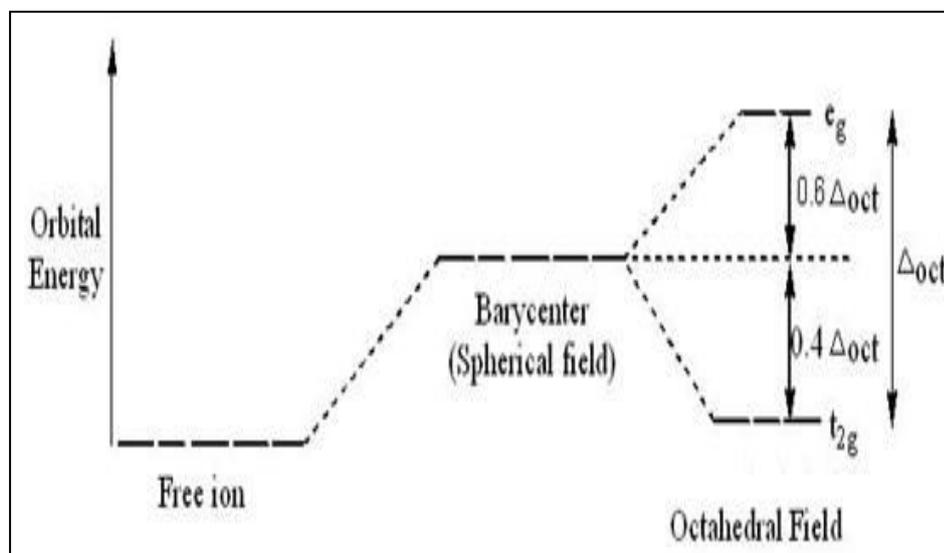


## OCTAHEDRAL COMPLEXES :



- In an octahedral complex, the metal is the centre and the ligands at the six corners of octahedron along x, y and z axes.
- e<sub>g</sub>** orbitals (**d<sub>z<sup>2</sup></sub>** and **d<sub>x<sup>2</sup>-y<sup>2</sup></sub>**) are directed along the axes x, y and z where as **t<sub>2g</sub>** orbitals (**d<sub>xy</sub>**, **d<sub>yz</sub>** and **d<sub>xz</sub>**) are directed in between the axes.
- Hence **d<sub>z<sup>2</sup></sub>** and **d<sub>x<sup>2</sup>-y<sup>2</sup></sub>** orbitals with their lobes pointing directly at the ligands along the axes, will be electrostatically less comfortable (more repulsion) than **d<sub>xy</sub>**, **d<sub>yz</sub>** and **d<sub>xz</sub>** orbitals with lobes pointing into the empty space between the ligands.
- Hence the energy of **e<sub>g</sub>** orbitals will be raised to a greater extent than that of the **t<sub>2g</sub>** orbitals.
- The **d-orbital** are thus, no longer degenerate with respect to energy and are split into two levels, the upper set of **e<sub>g</sub>** orbitals and the lower set of **t<sub>2g</sub>** orbitals.
- The difference in energy between the two sets of **d-orbitals** is denoted by  $\Delta_0$  and is measured in terms of a parameter called **Dq**. this quantity may be small or large but in any event it is arbitrarily taken as **10 Dq**.
- The approach of six ligands towards the central metal can be considered as a two-step process.

- I. In the first step, the ligands just approach the metal and produce a hypothetical spherical field which repels all the *d-orbitals* to the same extent.
- II. In the second step, the octahedral field brings out the splitting of d orbitals.



- h. The ‘barycentre’ or centre of gravity of the orbitals remains the same during the second step. That means, the energy of all the orbitals may be raised by the repulsion of the advancing ligands in step one but the arrangement of ligands from hypothetical spherical field to an octahedral field, will not alter the average energy of the set of *d-orbitals*.
- i. In other words, if the energy of the  $t_{2g}$  orbitals is  $4Dq$  less, then to maintain barycentre constant the  $e_g$  orbitals should be  $6Dq$  higher in energy than the hypothetical orbitals.

## SUMMARY:

- Limitation of valence bond theory
- Crystal field theory
- Crystal field splitting in various complexes from coordination no.2to 6