

**METAL- LIGAND BONDING**

**IN**

**TRANSITION METAL COMPLEXES**

**BY**

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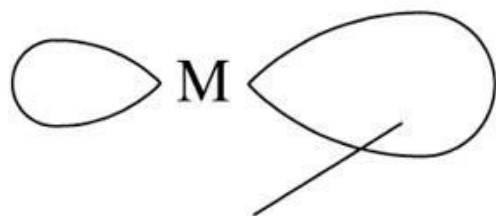
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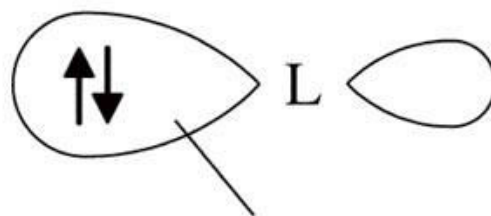
# VALENCE BOND THEORY – Linus Pauling (1931)

- Bonding occurs between metal and ligands.
- Vacant valence orbitals (s, p, d) of the metal atom hybridize to give rise to same number of hybrid orbitals.
- The hybrid orbitals are directed towards the ligands acc. to the geometry of the complex.
- Filled ligand orbital having a pair of electrons overlap with a vacant hybrid orbital of the metal

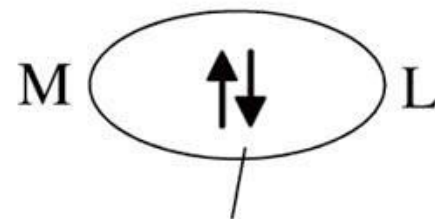
- Vacant hybrid orbitals of the metal atom/ion overlaps with the filled orbital of the ligand.
- Co-ordinate covalent bond is formed.
- The bonding is considered to be purely covalent.



Empty metal  
ion hybrid  
atomic orbital



Lone pair on the  
ligand in a hybrid  
atomic orbital



Coordinate  
covalent  
bond

- Total number of orbitals of the metal atom/ ion which undergo hybridization is equal to the co-ordination number of the central metal atom/ion.
- The d - orbitals involved in hybridization can be either inner (n-1)d orbitals ( $d^2sp^3$ ) or the outer n-d orbitals ( $sp^3d^2$ ) in case of octahedral complexes.
- Tetrahedral complexes have  $sp^3$  hybridization.
- Square planar complexes have  $dsp^2$  hybridization.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$sp^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$ , $[\text{NiCl}_4]^{2-}$
4	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$ ( $d_{x^2-y^2}$ orbital is involved)	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$
6	$d^2sp^3$ ( $d_z^2$ and $d_{x^2-y^2}$ orbitals of inner shell are involved)	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{2-}$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Inner orbital complexes)
6	$sp^3d^2$ ( $d_z^2$ and $d_{x^2-y^2}$ orbitals of the outer shell are involved)	Octahedral	$[\text{FeF}_6]^{4-}$ , $[\text{CoF}_6]^{4-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (Outer orbital complexes)

## LIMITATIONS OF VALENCE BOND THEORY

- Only provides qualitative explanation.
- Does not explain the colour and electronic spectra of complexes.
- Fails to explain why a metal ion in a particular oxidation state form low spin & high spin complexes.
- E.g. :  $\text{Co}^{3+}$  form complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$  , the former is **low spin** and the latter is **high spin**.

- Does not predict the relative stability of the complexes.
- Fails to explain why some complexes are labile and others inert.
- Labile complexes are those in which one or more ligands are easily displaced by some other ligand.
- Inert complexes are those in which displacement of ligand from the complexes is very slow / difficult.
- Does not take into account the splitting of d- orbitals.



- Does not explain the variation of magnetic moment with temperature.
- Fails to explain the difference between measured & calculated magnetic moment.
- Does not predict whether the complexes having coordination number **4** will have tetrahedral or square planar geometry
- VBT considers  $\text{Ni}(\text{acac})_2$  to have tetrahedral geometry , actually it has octahedral geometry.

# CRYSTAL FIELD THEORY

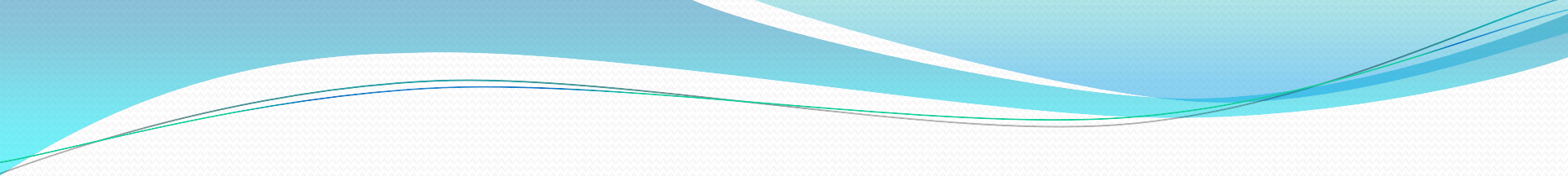
- Given by **H. Bethe** and **V. Bleck**.
- Main difference from VBT is that in CFT , bond between metal and ligands is considered to be **purely electrostatic**.
- If the ligands are **-vely** charged (  $\text{CN}^-$ ,  $\text{Br}^-$  etc.), the interaction between metal and ligand is called **ion-ion interactions**.
- If the ligands are neutral (like  $\text{CO}$ ,  $\text{NH}_3$  ,  $\text{H}_2\text{O}$ ) , the interaction between metal and ligand is called **ion-dipole interactions**.

# ASSUMPTIONS OF CRYSTAL FIELD THEORY

- Central metal atom / ion is surrounded by a number of ligands.
- Ligands are considered as **point charges**.
- Point charges are electric charges that exist as single point. They do not have volume or area.
- If the ligands have **-ve charge**, the **interaction** between the central metal atom/ion and the ligands is **100% ionic**.
- If the ligands are **neutral**, the negative end of the dipole of the ligand is oriented towards the central metal atom/ion, resulting in **electrostatic interaction**.

- For a **isolated metal atom / ion** , all the five d- orbitals have the **same energy**. (Degenerate Orbitals)
- As ligands approach the central metal atom/ion, the electrons in the metal orbitals will experience **repulsion** due to lone pair of electrons of the ligand.
- Due to **different shapes and orientation** of the d - orbitals, the **repulsions** experienced by the d – orbitals will be **different**.
- Orbitals **lying in the direction of the ligands** will experience **greater repulsion** & their **energies** will **increase** more.

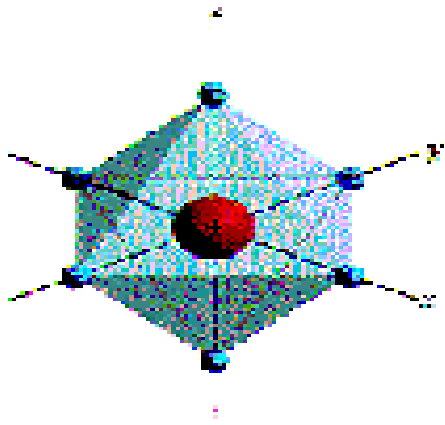
- Orbitals lying **away from the direction of approach of the ligands** will experience **lesser repulsion** & their energies will be **raised to a lesser extent**.
- So, the d- orbitals of the central metal atom/ion are split up due to **electric field of the ligands**.
- The splitting of five d- orbitals of central atom/ion into two sets of orbitals having different energies in the presence of electric field of the ligands is called **Crystal Field Splitting**.

- 
- The **variation in the number of ligands** around the central metal atom/ion will affect the **relative energies of d-orbitals differently**.
  - Crystal field splitting of the d-orbitals will be **different for different co-ordination numbers and geometries**.
  - Magnetic properties, colour of the compounds , electronic spectra and preference for a particular geometry can be explained by CFT.

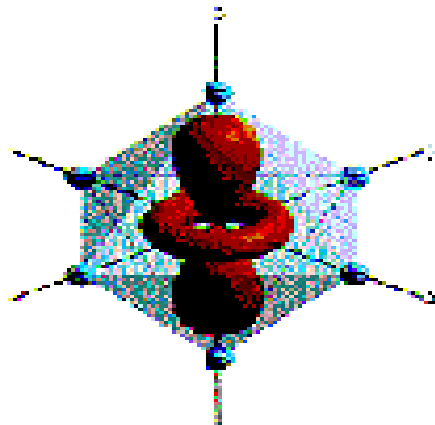
# CFT IN OCTAHEDRAL COMPLEXES

- ❖ Coordination number in octahedral complexes is **6**.
- ❖ Metal atom/ion is at the centre of the octahedron and the ligands are at the six corners.
- ❖ In octahedral complexes  $\text{MX}_6$ , all the five d- orbitals will not have the **same energy**.
- ❖ The  $d_z^2$  &  $d_{x^2-y^2}$  orbitals point **directly** towards the six point charges i.e. ligands.
- ❖ These orbitals interact **directly and strongly** with the point charges.

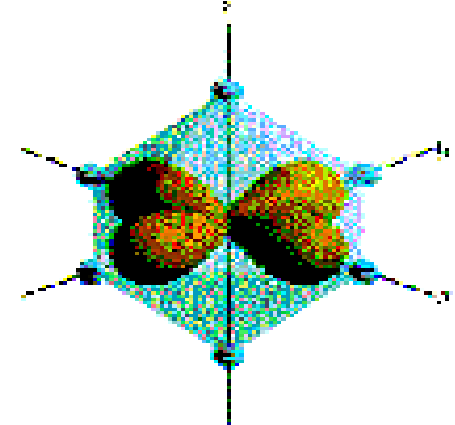
# ORIENTATION OF DIFFERENT d- ORBITALS WITH LIGANDS



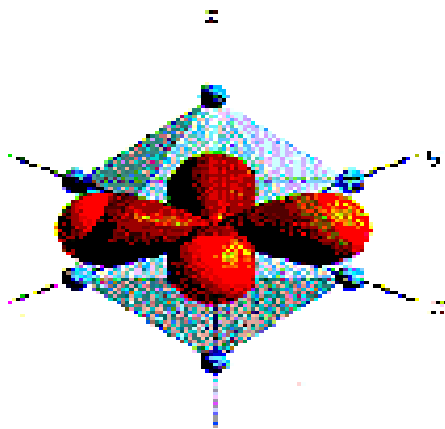
Ligands as point charges



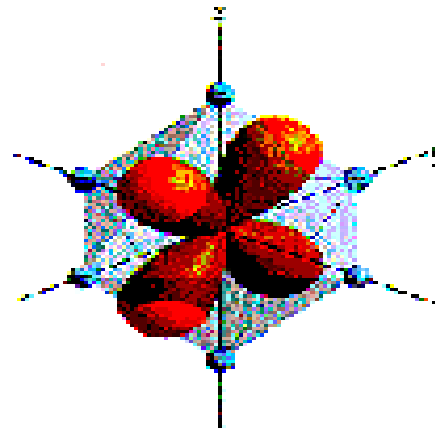
$dz^2$



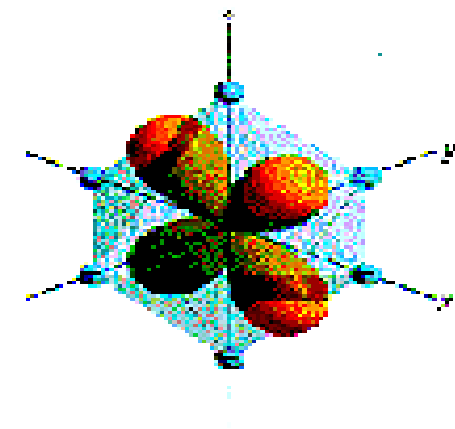
$dx^2-y^2$



$dxy$



$dyz$



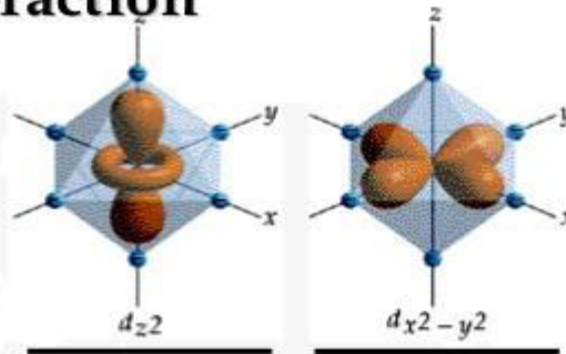
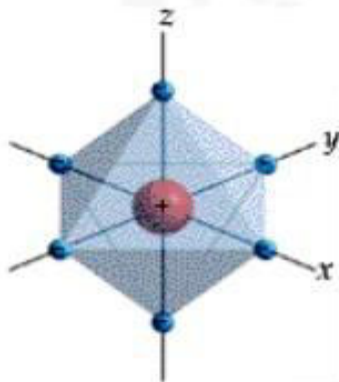
$dxz$



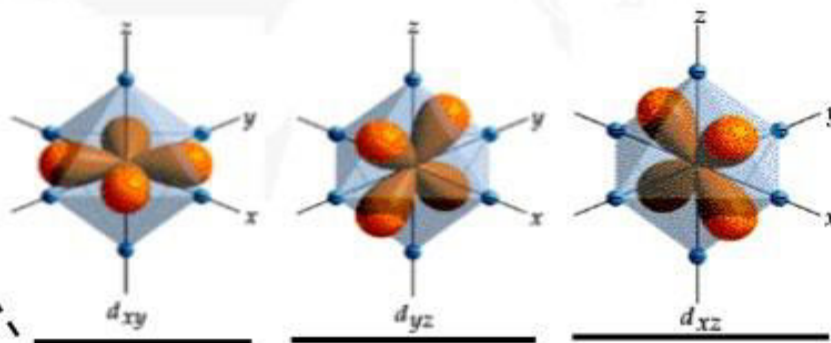
- So,  $d_z^2$  &  $d_{x^2-y^2}$  orbitals experience **strong repulsive interaction**, as a result their **energies get increased**.
- The other 3 d- orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ) are **not much affected** as compared to the  $d_z^2$  &  $d_{x^2-y^2}$  orbitals.
- In these 3 d- orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ), the orbitals are **oriented in between the axes**.
- The energies of these 3 d- orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ) are **lowered**.
- The set of  $d_z^2$  &  $d_{x^2-y^2}$  orbitals is designated as  **$e_g$  orbitals**.
- The set of  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals is designated as  **$t_{2g}$  orbitals**.

# d-Orbitals and Ligand Interaction (Octahedral Field)

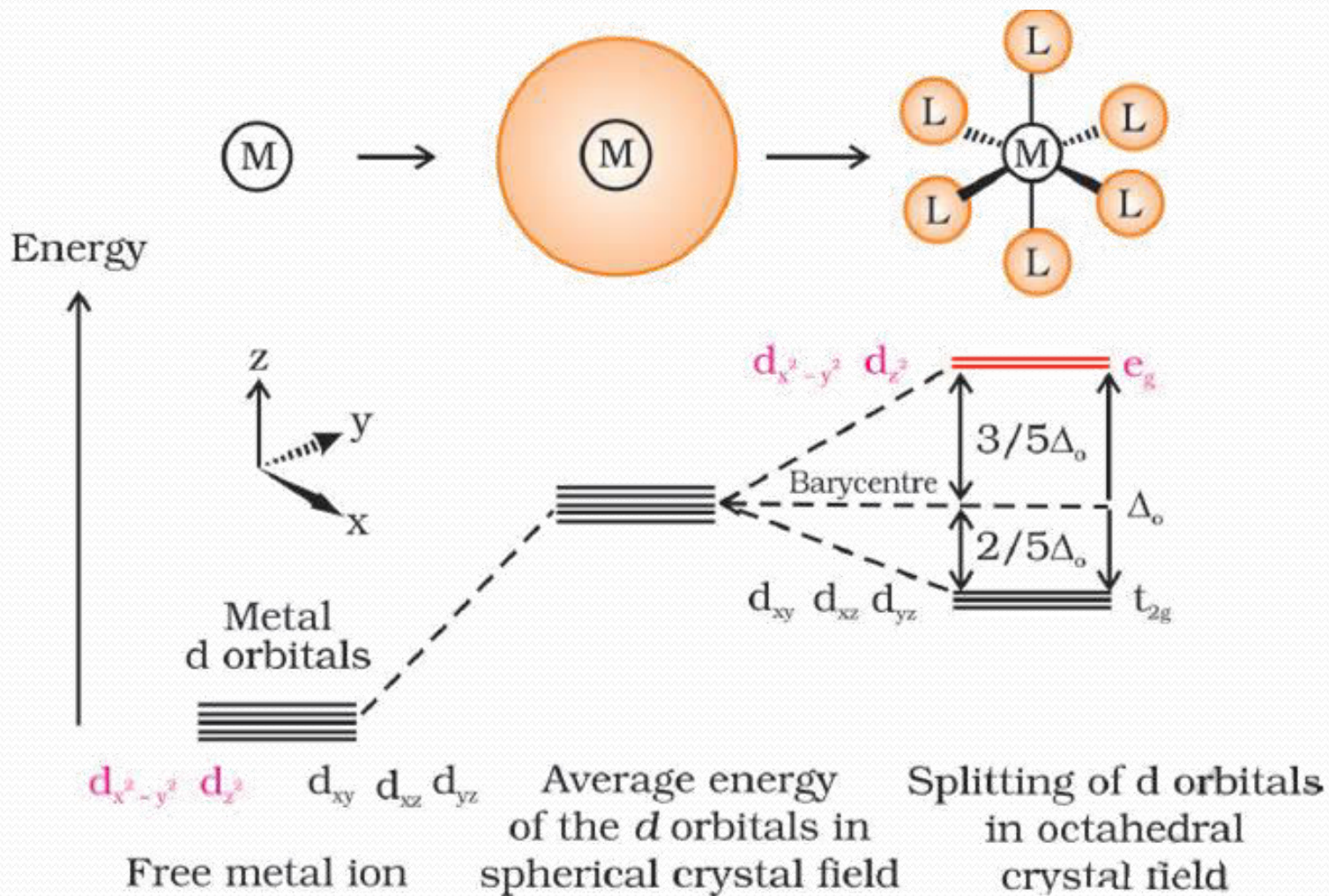
Ligands  
approach  
metal



d-orbitals pointing directly at axis are  
affected most by electrostatic interaction



d-orbitals not pointing directly at axis are least  
affected (stabilized) by electrostatic interaction



*d orbital splitting in an octahedral crystal field*

- ❖ In octahedral complexes, the five d- orbitals are split into **two sets**:
  - One set of two orbitals of higher energy ( **$e_g$  orbitals**)
  - Second set of three orbitals of lower energy ( **$t_{2g}$  orbitals**)
- ❖ The energy difference between the two sets of orbitals is called the **crystal field splitting/stabilization energy(CFSE)**.
- ❖ **Crystal field splitting energy** is represented as  **$\Delta_o$** , where the subscript ( **$_o$** ) refers to octahedral.
- ❖ The value of  **$\Delta_o$**  varies for different complexes.
- ❖ CF Splitting is also measured by another parameter  **$D_q$**

❖ The two are related as :

$$\Delta_o = 10Dq$$

❖ Crystal field splitting occurs in such a way that the average energies of d- orbitals do not change. (**Barycentre Rule**).

❖ “**The centre of gravity**” of the orbitals remain constant.

❖ The decrease in energy of the set of orbitals that lie lower must be equal to the energy by which the other set of orbitals is raised higher.

❖ In terms of total energy  $10Dq$  ,  
the energy of each of the  $e_g$  orbital is increased/raised by  $6 Dq$

and

the energy of each of the  $t_{2g}$  orbital is decreased by  $4 Dq$

❖ In terms of  $\Delta_o$  ,  
the energy of each of the  $e_g$  orbital is  
increased/raised by  $3/5 \Delta_o$  or  $0.6 \Delta_o$

and

the energy of each of the  $t_{2g}$  orbital is decreased by  $2/5 \Delta_o$   
or  $0.4 \Delta_o$

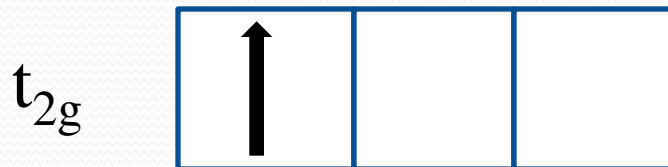
## CRYSTAL FIELD STABILIZATION ENERGY (CFSE)

- ❖ The difference in the amount of energy on filling of electrons in the split d- orbitals , is known as **CFSE**.
- ❖ In octahedral complexes,
  - For a electron entering the  **$t_{2g}$  orbital** , the crystal field stabilization is  $-4 Dq$  or  $-0.4 \Delta_o$
  - For a electron entering the  **$e_g$  orbital** , the crystal field stabilization is  $+6 Dq$  or  $+0.6 \Delta_o$

# CFSE for various Octahedral Compounds

## d<sup>1</sup> to d<sup>3</sup> system

- For a d<sup>1</sup> system ( like Ti<sup>3+</sup> ), the electron can be present in any of the low energy **t<sub>2g</sub> orbital** . The electronic configuration will be written as **t<sub>2g</sub><sup>1</sup>** .



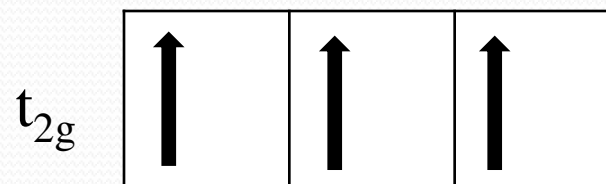
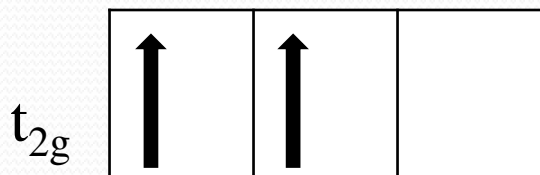
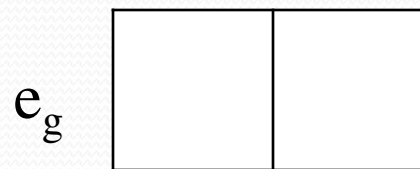
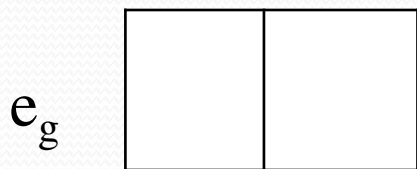
$$\text{CFSE} = 1( - 4D_q ) = -4D_q$$



- For **d<sup>2</sup>** system ( like V<sup>3+</sup> ) and **d<sup>3</sup>** system ( like Cr<sup>3+</sup> ), the electrons are filled in the lower energy **t<sub>2g</sub> orbitals** according to Hund's rule of maximum multiplicity .

- d<sup>2</sup> system**

- d<sup>3</sup> system**



$$\text{CFSE} = 2(-4D_q) = -8D_q$$



$$\text{CFSE} = 3(-4D_q) = -12D_q$$



## d<sup>4</sup> to d<sup>7</sup> system

For the above systems, there are **2 ways of filling** of d-orbitals.

**CASE 1** : All the electrons can enter the **low energy t<sub>2g</sub> orbitals**, resulting in **pairing of electrons**.

**CASE 2** : Three electrons occupy the **low energy t<sub>2g</sub> orbital** and the fourth electron occupies the higher energy **e<sub>g</sub> orbital**.

The actual possibility is decided on the basis of the **crystal field splitting energy ( $\Delta_o$ )** for octahedral compounds

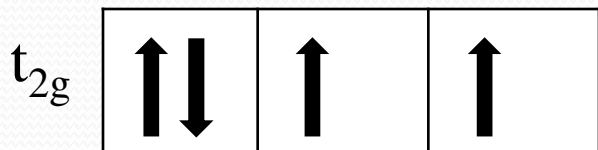
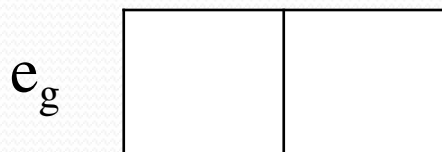
and

the **pairing energy (P)** (i.e. the energy required to pair the electrons)

# d<sup>4</sup> SYSTEM (e.g. Mn<sup>2+</sup>)

## CASE : 1

- $\Delta_o > P$
- Strong field complexes
- Low spin complexes

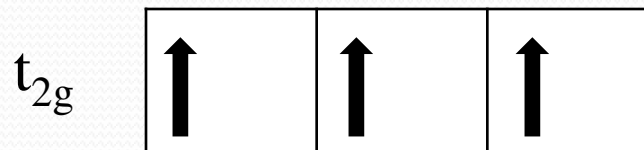
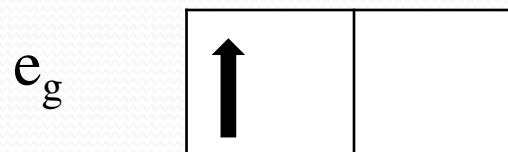


$$\text{CFSE} = 4(-4D_q) = -16D_q + P$$



## CASE : 2

- $\Delta_o < P$
- Weak field complexes
- High spin complexes



$$\text{CFSE} = 3(-4D_q) + 1(6D_q) = -6D_q$$



If the **pairing energy (P)** is taken into account , then the CFSE can be written as :

➤ **Case 1**:  $CFSE = - 16D_q + P$

➤ **Case 2**:  $CFSE = - 6D_q$

➤ **GENERALIZATION:**

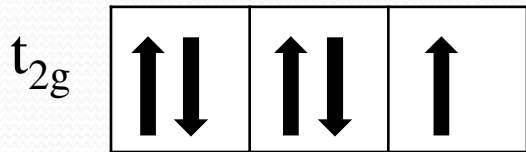
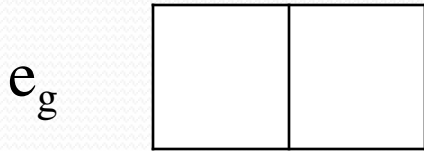
➤  $\Delta_o > P$  (Strong field)      **Low Spin Complex**

➤  $\Delta_o < P$  (Weak Field)      **High Spin Complex**

# d<sup>5</sup> SYSTEM (e.g. Fe<sup>3+</sup>)

## CASE : 1

- $\Delta_o > P$
- Strong field complexes
- Low spin complexes

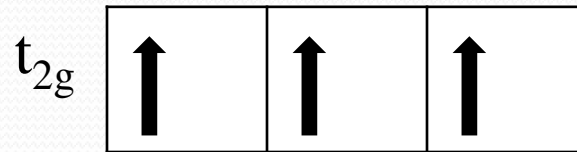
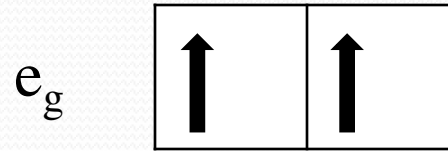


$$\text{CFSE} = 5(-4D_q) = -20D_q + 2P$$



## CASE : 2

- $\Delta_o < P$
- Weak field complexes
- High spin complexes



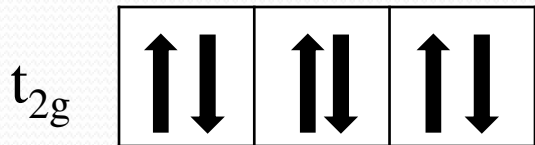
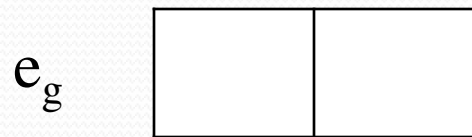
$$\text{CFSE} = 3(-4D_q) + 2(6D_q) = 0D_q$$



## d<sup>6</sup> SYSTEM (e.g. Co<sup>3+</sup>)

### CASE : 1

- $\Delta_o > P$
- Strong field complexes
- Low spin complexes

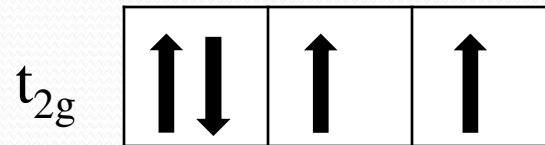
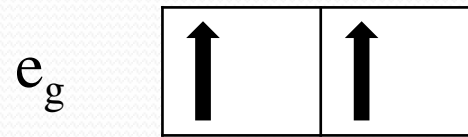


$$\text{CFSE} = 6(-4D_q) = -24D_q + 2P$$



### CASE : 2

- $\Delta_o < P$
- Weak field complexes
- High spin complexes



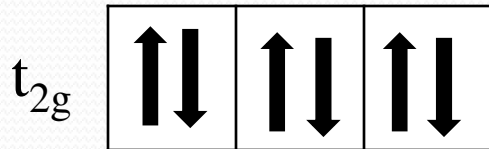
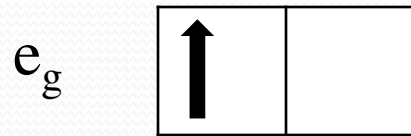
$$\text{CFSE} = 4(-4D_q) + 2(6D_q) = -4D_q$$



## d<sup>7</sup> SYSTEM (e.g. Co<sup>2+</sup>)

### CASE : 1

- $\Delta_o > P$
- Strong field complexes
- Low spin complexes

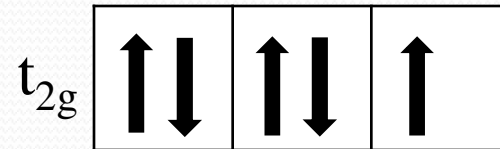
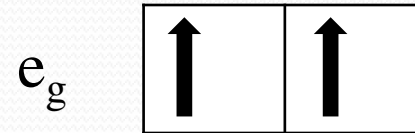


$$\text{CFSE} = 6(-4D_q) + 1(6D_q) = -18D_q + 2P$$



### CASE : 2

- $\Delta_o < P$
- Weak field complexes
- High spin complexes

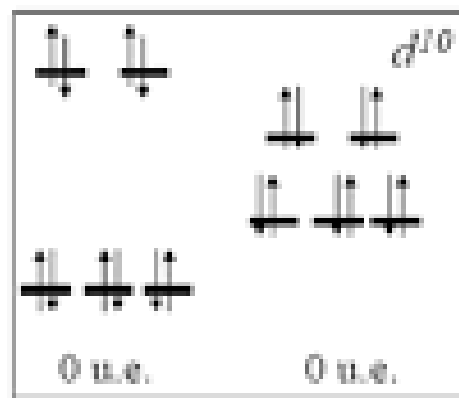
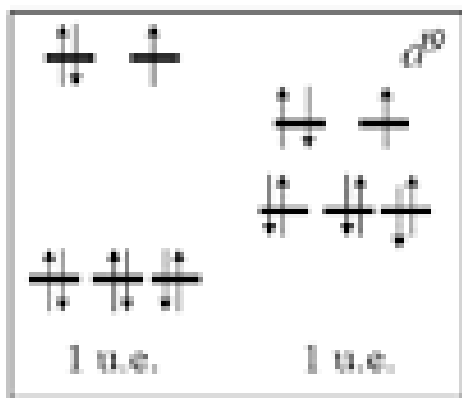
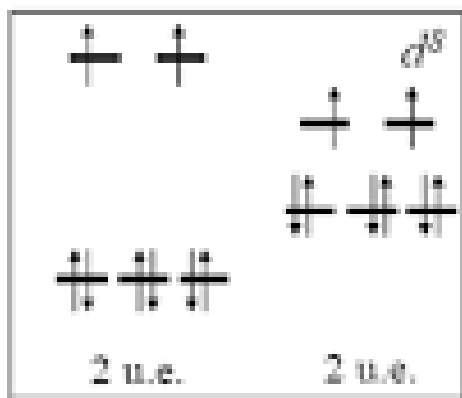


$$\text{CFSE} = 5(-4D_q) + 2(6D_q) = -8D_q$$



## d<sup>8</sup> to d<sup>10</sup> system

- ✓ In these systems there are **no strong field or weak field complexes**.
- ✓ Both type of complexes lead to the same configurations.





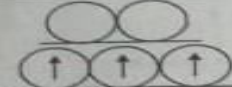
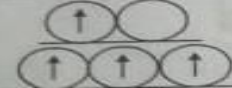

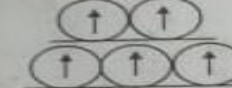
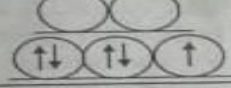

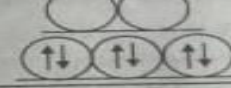
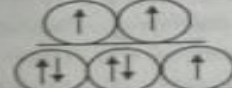
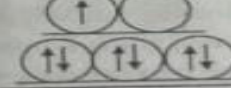
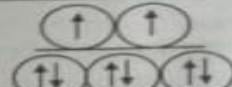
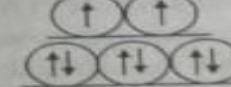
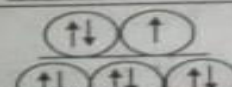
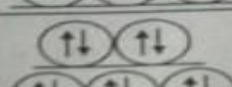
$$\text{For } d^8, \text{CFSE} = (6 \times 0.4) - (2 \times 0.6) = 1.2 \Delta_o$$

$$\text{For } d^8, \text{CFSE} = (6 \times 0.4) - (3 \times 0.6) = 0.6 \Delta_o$$

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



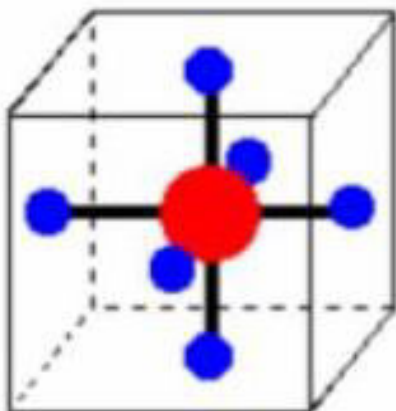
Table 2. Crystal field stabilization energies for metal ions having different numbers of *d*-electrons in octahedral complexes.

Number of <i>d</i> electrons	Weak field	CFSE	Strong field*	CFSE
$d^1$		$-4Dq$ or $-0.4\Delta_o$		
$d^2$		$-8Dq$ or $-0.8\Delta_o$		
$d^3$		$-12Dq$ or $-1.2\Delta_o$		
$d^4$		$-6Dq$ or $-0.6\Delta_o$		$-16Dq + P$ or $-1.6\Delta_o + P$
$d^5$		0		$-20Dq + 2P$ or $-2.0\Delta_o + 2P$
$d^6$		$-4Dq$ or $-0.4\Delta_o$		$-24Dq + 2P$ or $-2.4\Delta_o + 2P$
$d^7$		$-8Dq$ or $-0.8\Delta_o$		$-18Dq + P$ or $-1.8\Delta_o + P$
$d^8$		$-12Dq$ or $-1.2\Delta_o$		$-12Dq$ or $-1.2\Delta_o$
$d^9$		$-6Dq$ or $-0.6\Delta_o$		
$d^{10}$		0		

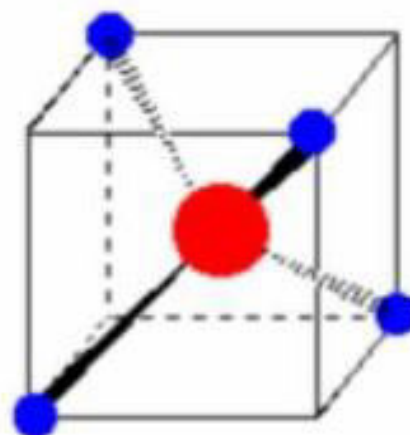
\*The systems  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^4$ ,  $d^5$  and  $d^{10}$  have same configuration in weak field and strong field and, therefore have same CFSE values.

# TETRAHEDRAL COMPLEXES

**d-Orbital splitting for tetrahedral coordination.** A cube, an octahedron, and a tetrahedron are related geometrically. Octahedral coordination results when ligands are placed in the centers of cube faces. Tetrahedral coordination results when ligands are placed on alternate corners of a cube.



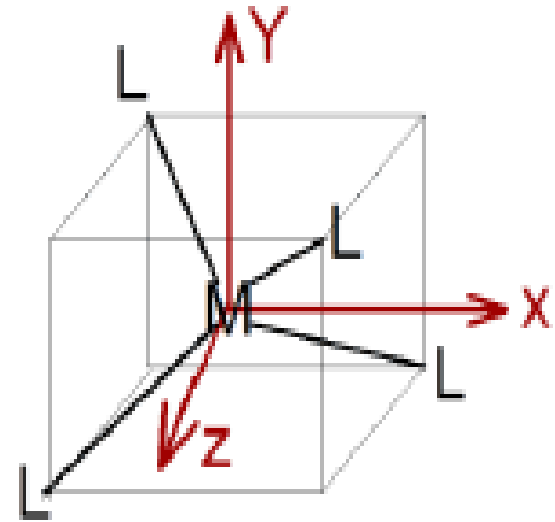
Octahedral complex in a cube.  
Ligands are on the centers of  
the cube faces.



Tetrahedral complex in a cube.  
Ligands are on alternate corners  
of the cube.

# CFS in Tetrahedral Complexes

- ❑ Coordination Number for tetrahedral complexes is **4**.
- ❑ The metal is at the centre and the ligands are placed at **four corners of the cube**.
- ❑ The X, Y and Z axes **point to the centre of the faces** of the tetrahedron.



tetrahedral geometry  
having central metal M &  
four ligands at the  
corners

❑ The orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  lie **between** the X, Y, Z axes

whereas the  $d_z^2$  &  $d_{x^2-y^2}$  orbitals **lie along** the X, Y, Z axes.

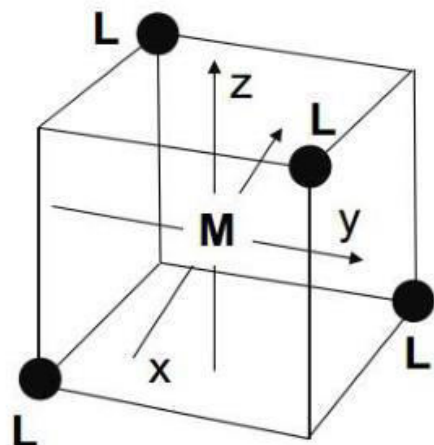
❑ Basically, **none** of the d orbitals are **lying directly** towards the ligands.

❑ The CFS energy in tetrahedral complexes **will be less than** that of octahedral complexes, as they **experience less repulsion**.

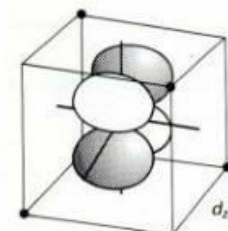
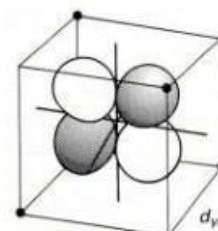
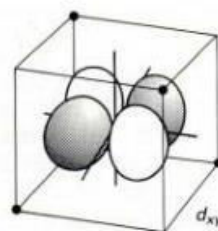
❑ The  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals **lie close to the direction of the approaching ligands**, so their energies are raised / increased.

# Ligand Field Theory – Tetrahedral

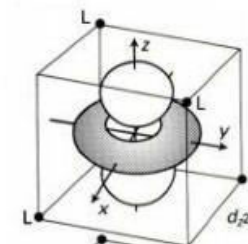
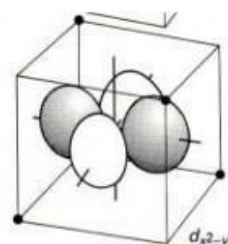
opposite splitting of  
octahedral field



barycenter  
(spherical field)



$t_2$  orbitals point more directly at ligands and are destabilized.



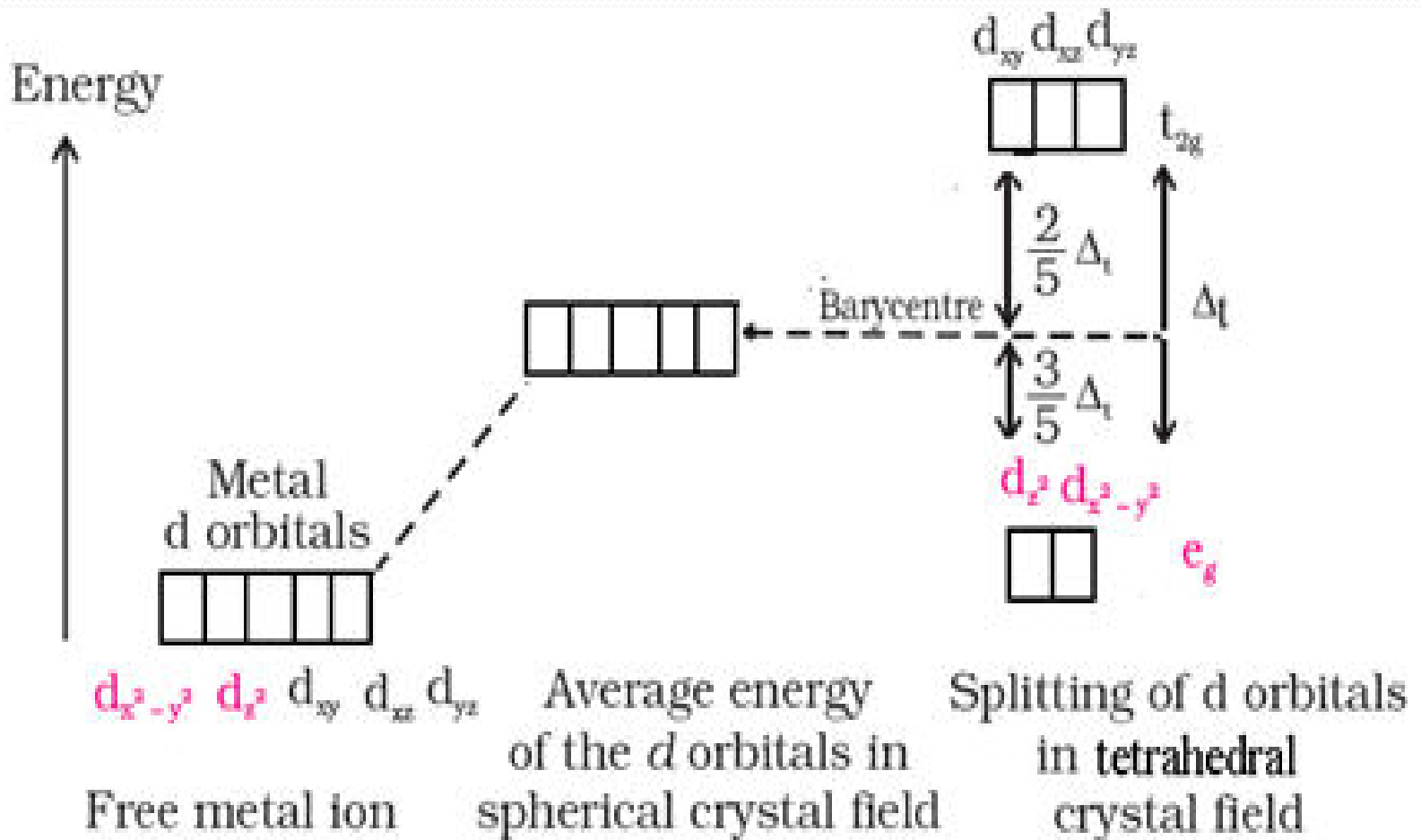
$e$  orbitals point less directly at ligands and are stabilized.

- ❑ The  $d_z^2$  &  $d_{x^2-y^2}$  orbitals **lie in between** the ligands , experience **less repulsion** than the other three d- orbitals.
- ❑ So, the energy of  $d_z^2$  &  $d_{x^2-y^2}$  orbitals is **lowered/ decreased** as compared to other d- orbitals.

## GENERALIZATION :

- The  $d_{xy}$  ,  $d_{yz}$  ,  $d_{xz}$  orbitals experience **more repulsion** and their **energies are raised**, designated as **'t<sub>2</sub>' orbitals**
- The  $d_z^2$  &  $d_{x^2-y^2}$  orbitals experience **less repulsion** and their energies are **lowered**, designated as **'e' orbitals**

## DIAGRAMMATIC REPRESENTATION OF CRYSTAL FIELD SPLITTING IN TETRAHEDRAL FIELD





- ❑ Magnitude of CFS in tetrahedral complexes is given as  $\Delta_t$
- ❑ Measured in terms of  $Dq$  and

$$\Delta_t = 10Dq$$

- ❑ The CF splitting in tetrahedral complexes is **quite less** than that in octahedral complexes.
- ❑ CF splitting in tetrahedral complexes is

$$\Delta_t = \frac{4}{9} \Delta_o$$



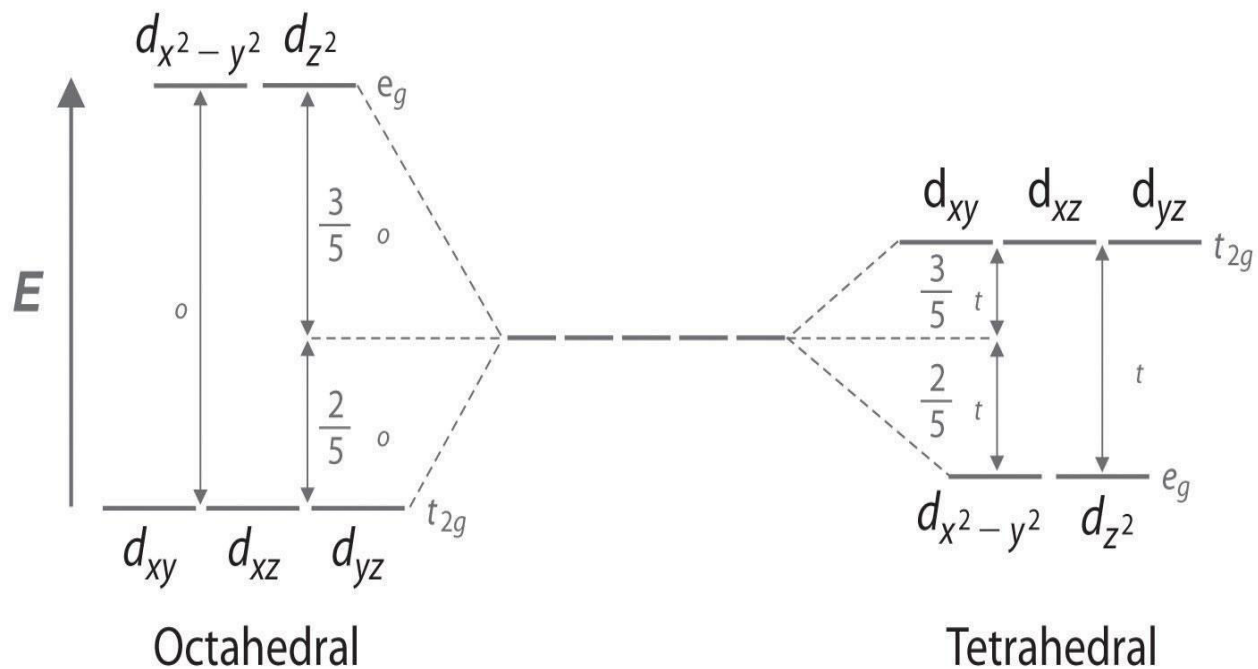
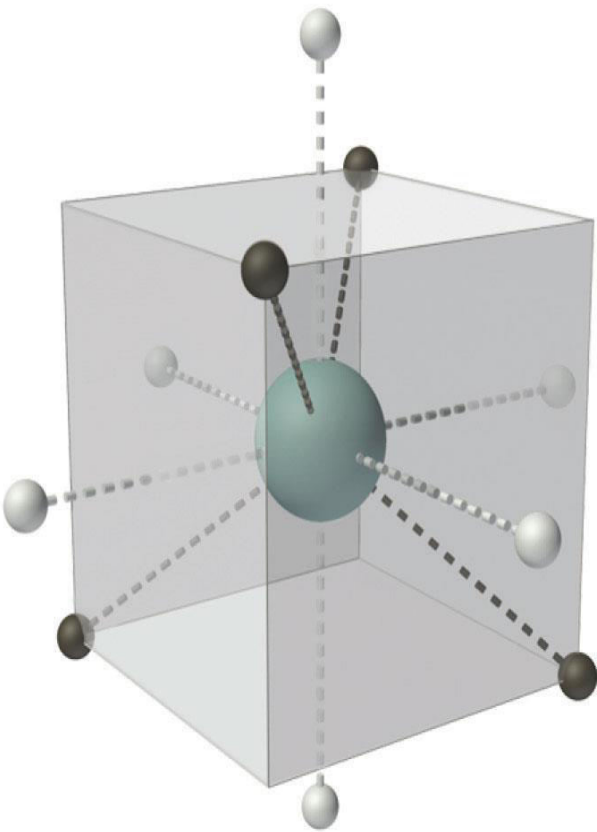
Why crystal field splitting in tetrahedral complexes have low value as compared to octahedral complexes ?

- ❖ **Lesser number** of ligands result in **less CF splitting**
- ❖ No d-orbitals **lies/points directly towards** the ligands
- ❖ So, the CF splitting in tetrahedral complexes is about  $\frac{2}{3}$  of that of octahedral complexes.

## POINTS TO REMEMBER

- ❖ Magnitude of CFS in tetrahedral complexes is **less than the pairing energy**
- ❖ Pairing of electrons is **not energetically favourable**.
- ❖ Pairing **will not occur** till all the d-orbitals are **half filled**, irrespective of whether they have lower or higher energy.
- ❖ So, only **high spin complexes** are found in tetrahedral compounds.
- ❖ Also, the subscript 'g' is **not used** in tetrahedral complexes because tetrahedral geometry does **not have centre of symmetry**

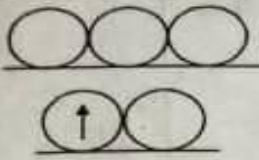
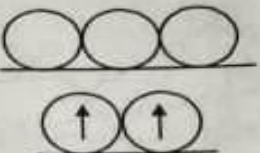
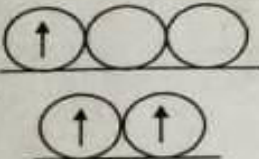
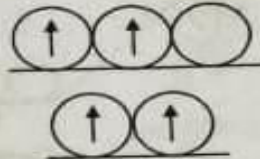
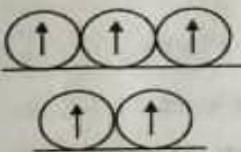
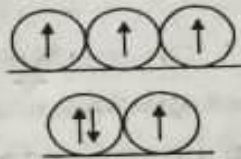
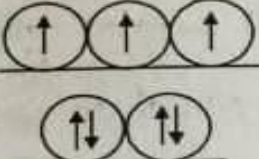
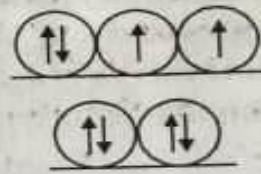
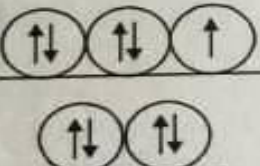
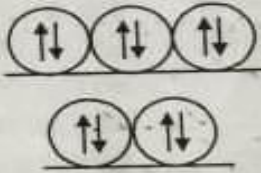
# COMPARISON B/W CFS OF OCTAHEDRAL & TETRAHEDRAL COMPLEXES



(a) (b)

- Black circles in the cube denote ligands in a tetrahedral field.
- Grey circles denote ligands in an octahedral field.

# CFSE FOR TETRAHEDRAL COMPLEXES

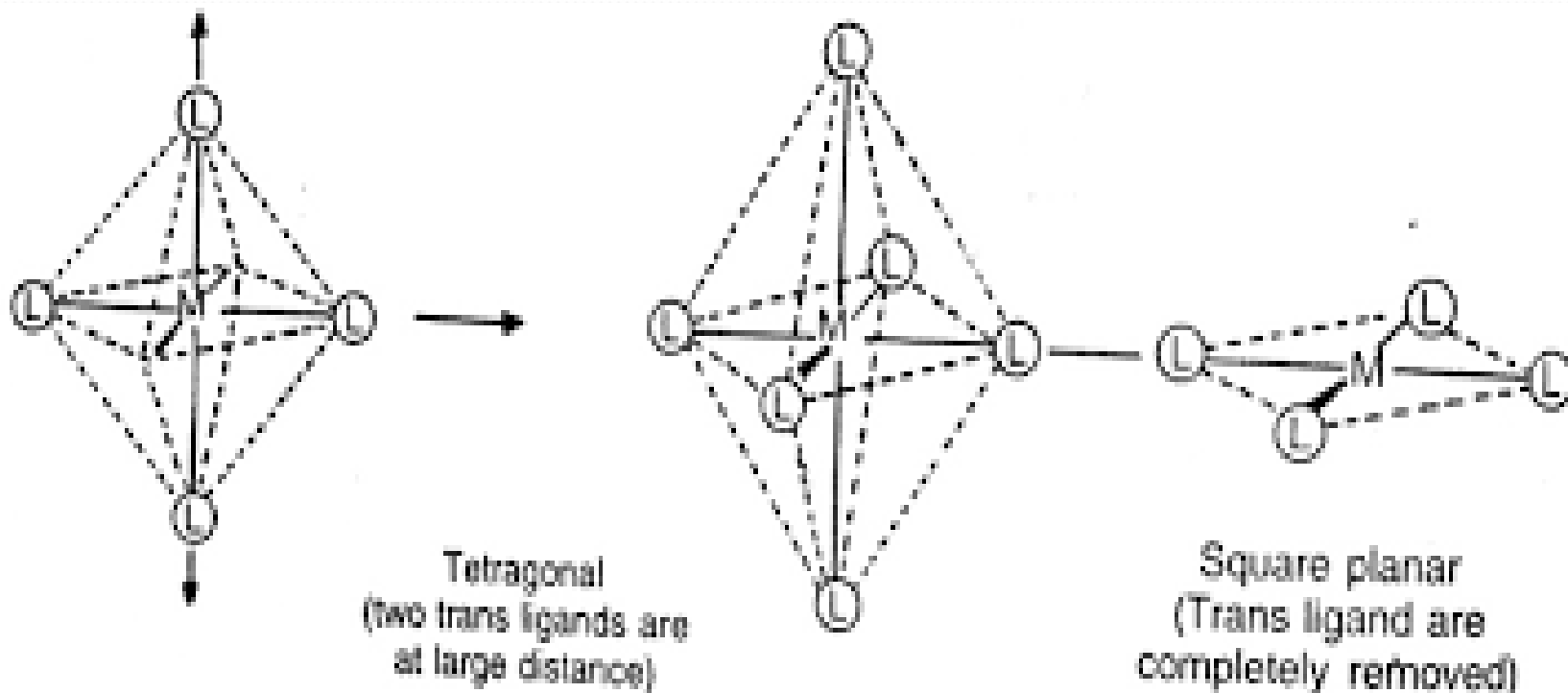
$d^1$  $CFSE = -6Dq$	$d^2$  $CFSE = -12Dq$
$d^3$  $CFSE = -8Dq$	$d^4$  $CFSE = -4Dq$
$d^5$  $CFSE = 0$	$d^6$  $CFSE = -6Dq$
$d^7$  $CFSE = -12Dq$	$d^8$  $CFSE = -8Dq$
$d^9$  $CFSE = -4Dq$	$d^{10}$  $CFSE = 0$

\*For simplicity, the pairing energies are not given.

# CRYSTAL FIELD SPLITTING IN SQUARE PLANAR COMPLEXES

- CF splitting in Square planar complexes can be understood easily from the **splitting of octahedral complexes**.
- In order to understand how square planar complexes are formed, the **two trans ligand** (above and below the plane) are withdrawn from the octahedral complexes.
- This process is called **elongation**.
- **Elongation** of octahedral complexes leads to another geometry known as **Tetragonal or tetragonally distorted octahedron**.

- In other words, in going from octahedral to square planar geometry, we come across another geometry/complexes known as **Tetragonal or tetragonally distorted octahedron**.



- In going from octahedral to square planar geometry **two processes** are involved:
- **Elongation or Flattening (of the trans ligand )**
- **Removal of the trans ligand completely**

### FIRST PROCESS (ELONGATION)

- The **two ligands** lying on the **Z – axis** (above and below the plane) **are moved away**.
- The ligands lying on the **XY axes** move **closer** to the central metal atom/ion.

- As the electrons on the Z axis move away, the **repulsion** experienced by  $d_z^2$  orbital from the ligands **decrease**.
- The **energy** of the  $d_z^2$  orbital is **lowered / decreased**.
- The ligands lying on the **XY plane move closer** to the central metal atom/ion , as the electrons on the Z axis move away.
- The d- orbital lying in the XY plane i.e.  $d_{x^2-y^2}$  orbital experience **more repulsion**.
- The **energy** of the  $d_{x^2-y^2}$  orbital is **raised / increased**.



- Similarly, the energy of  **$d_{xy}$**  orbital is **raised / increased**.
- The energies of the  **$d_{yz}$ ,  $d_{xz}$**  orbitals is **lowered /decreased** as **repulsion along Z axis decreases**.
- The state / geometry which arise due to this elongation process is called **Tetragonal or tetragonally distorted octahedron**.
- The amount by which energy of the orbitals is increased or decreased varies.

## FLATTENING

- Tetragonally distorted structure can also be obtained by bringing the two trans ligands **close** to the metal atom / ion.
- This is called **Flattening of the octahedron**.
- In this, the **two M-L bonds** (lying on the Z axis) **are shortened**.
- The **four M-L bonds** (lying in the plane of the central metal atom / ion) **are lengthened**.
- The splitting of d-orbitals will be **reverse** of that of elongation.

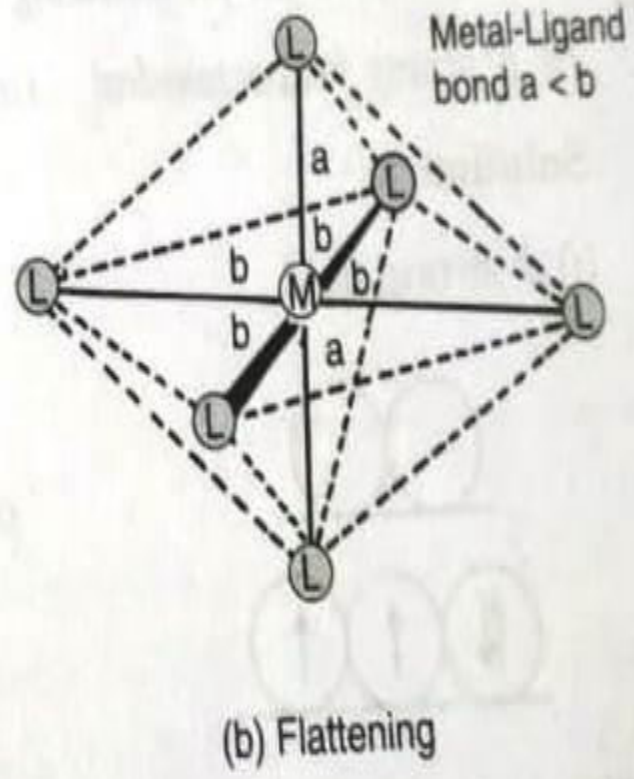
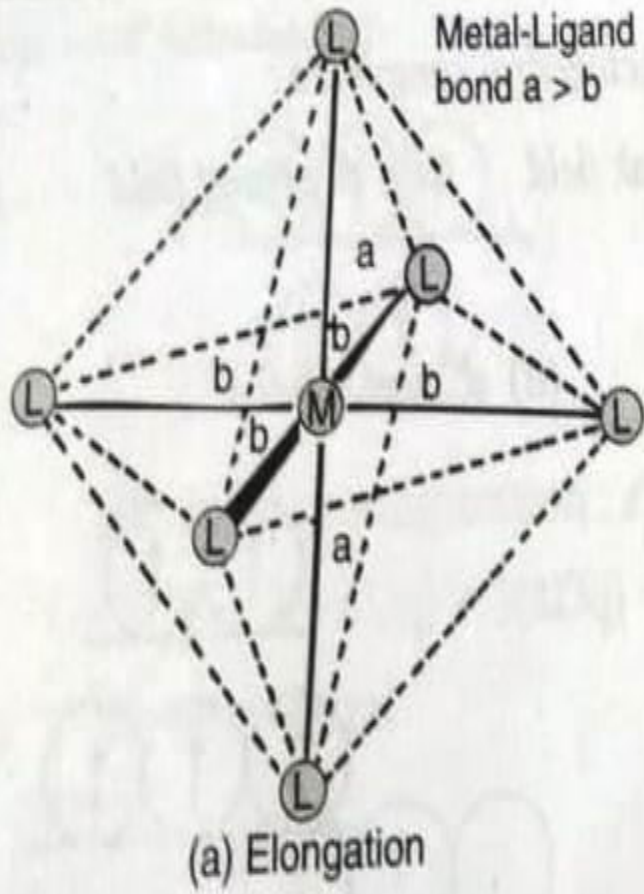
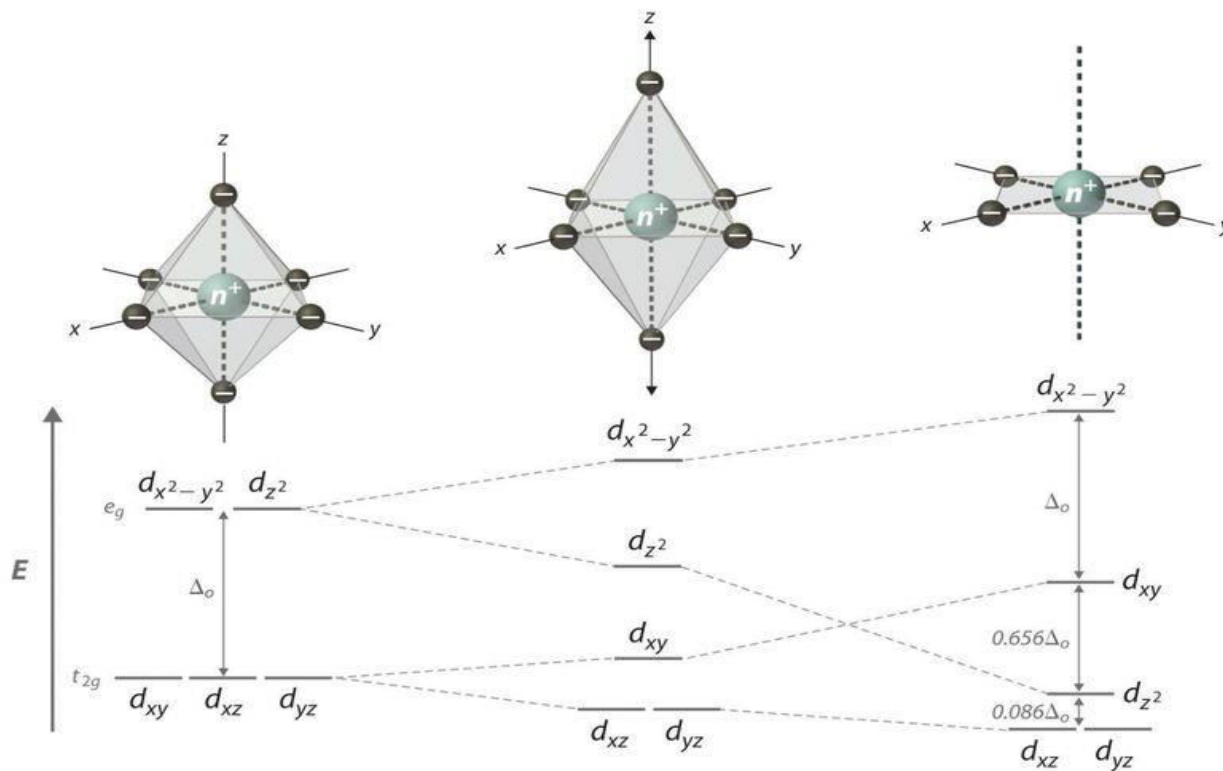


Fig. 12. Tetragonally distorted octahedron (a) elongation (b) flattening.

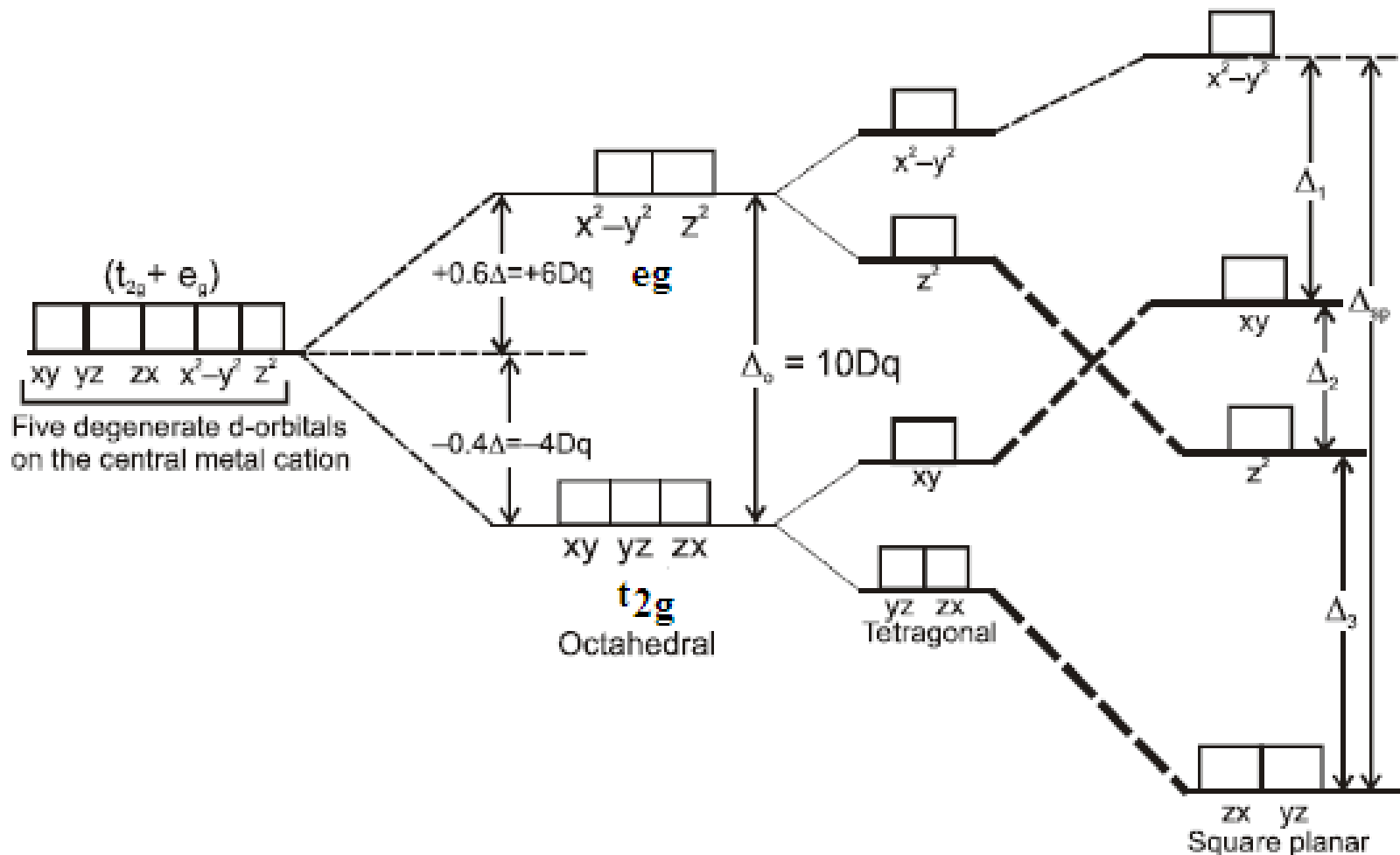
## Tetragonal z out distortion extended : The Square Planar Case



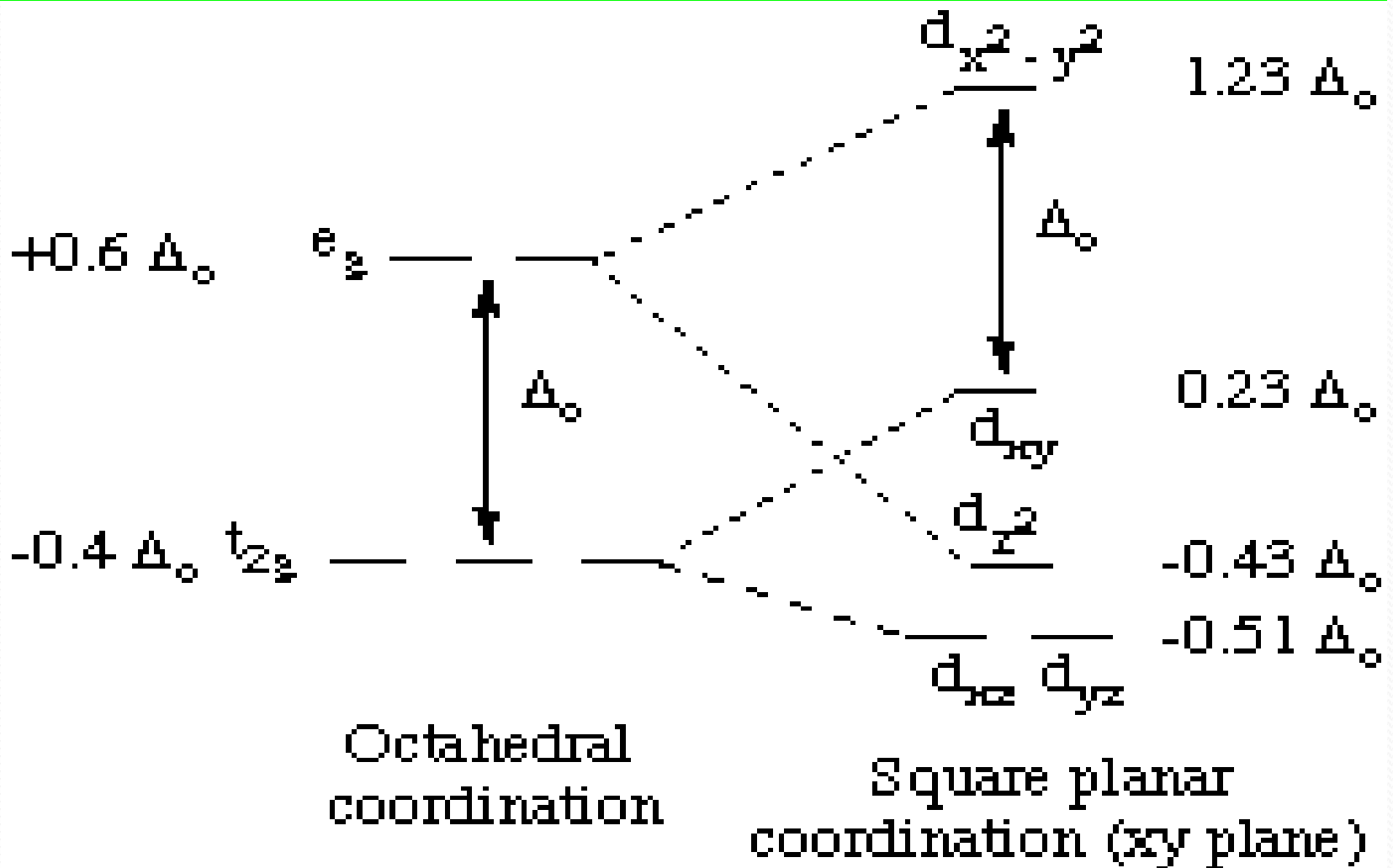
## SECOND PROCESS : REMOVAL OF TRANS LIGAND

- **Removal of the trans ligands completely, result in square planar geometry.**
- **Complete removal results in more repulsion** between the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals and the ligands.
- So, the energy of these  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals again **increase**.
- The energies of the  $d_z^2$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals again **decrease** as **repulsion** experienced by them **decreases** .

# CF SPLITTING IN TETRAGONAL & SQUARE PLANAR COMPLEXES



# CF SPLITTING IN SQUARE PLANAR COMPLEXES



# MAGNETIC PROPERTIES OF COMPLEXES

- ❑ Magnetic property of a compound depends on whether a complex is
  - Paramagnetic (Unpaired electrons) **or**
  - Diamagnetic (Paired electrons).
  
- ❑ The number of unpaired electrons in a complex can be determined if we know whether the complex is **high spin or low spin** in nature.
  
- ❑ This depends on the magnitude of  $\Delta_o$  and the pairing energy (**P**)



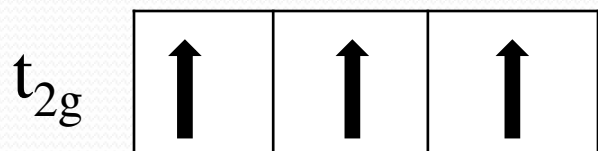
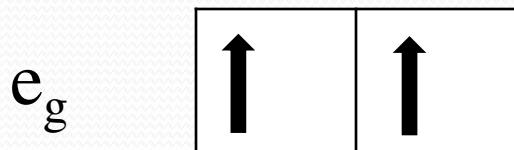
- ❑ The electrons **will not undergo pairing** if  $P > \Delta_o$ , resulting in **high spin complexes**.
- ❑ The electrons **will undergo pairing** if  $P < \Delta_o$ , resulting in **low spin complexes**.
- ❑ So, **high spin complexes** are formed due to compound formation of transition metals with **weak field ligand**

**and**

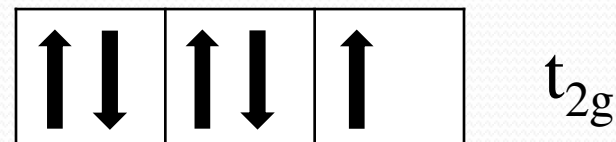
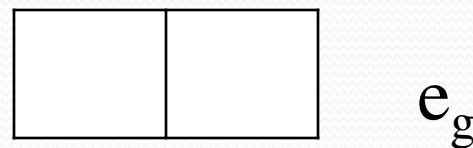
**low spin complexes** are formed due to compound formation of transition metals with **strong field ligand**.

□ Consider the case of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$

- In both the complexes, the central metal ion **Fe** is in **+3 O.S.** and has **five d – electrons**.
- $\text{H}_2\text{O}$  is a **weak field ligand** as compared to  $\text{CN}^-$ .
- So, in case of  $\text{H}_2\text{O}$ ,  $P > \Delta_o$ , resulting in unpaired electrons and the complex formed is **high spin** in nature.
- Whereas in case of  $\text{CN}^-$ ,  $P < \Delta_o$ , results in pairing of electrons and the complex formed is **low spin** in nature.



- **Difference b/w  $e_g$  &  $t_{2g}$  is less**
- **$P > \Delta_o$**
- **High spin complex**



- **Difference b/w  $e_g$  &  $t_{2g}$  is more**
- **$P < \Delta_o$**
- **Low spin complex**

## FACTORS AFFECTING THE CRYSTAL FIELD PARAMETERS

The extent of magnitude of crystal field splitting depends on the following factors

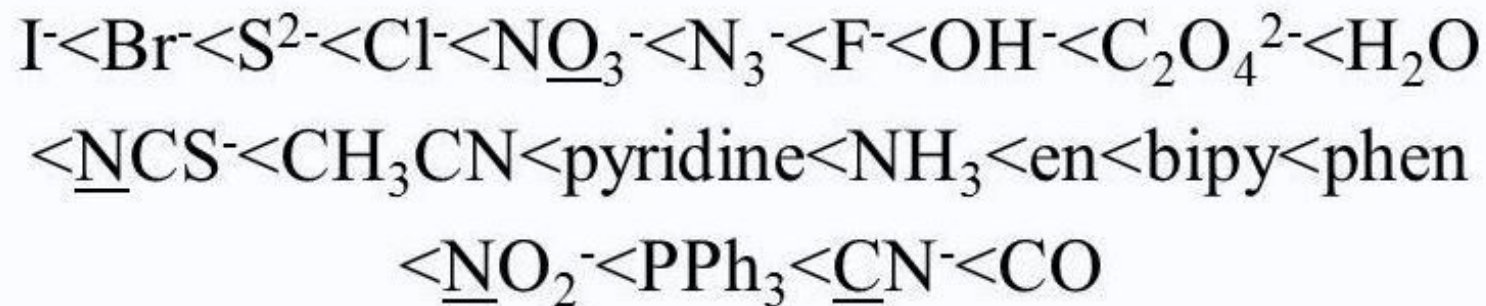
- Nature of ligands
- Oxidation state of metal ion
- Type of d – orbitals i.e. which transition series is involved.
- Geometry of the complex

# NATURE OF LIGANDS

- Crystal field splitting primarily depends on the **nature of ligands** surrounding the central metal atom /ion.
- **More easy the approach** of the ligand to the central metal atom /ion , **more** will be the CF splitting.
- **Weak field ligands** result in **small amount** of CF splitting.
- **Strong field ligands** result in **large amount** of CF splitting.
- Ligands can be **arranged in a series on the basis of increasing magnitude** of CF splitting

This series is called the **spectrochemical series**.

Weak Field ligands



Strong Field ligands

Increasing Crystal Field



**Variation in CF Splitting** is caused by a number of factors:

- **Smaller** the size of the ligand, **closer** is the approach to the central metal ion, **more** is the CF splitting.
- For e.g. in halogens, **F<sup>-</sup>** has **smallest** size and causes **greater** CF splitting than other halogens.
- Ligands having **easily polarizable electron pair** will be more drawn towards the central metal ion.
- Ligands like **CO, CN<sup>-</sup> and NO<sup>-</sup>** cause **greater** CF splitting because they have **greater** tendency to form **multiple bonds ( $\pi$  bonds)**.

## OXIDATION STATE OF METAL ION

- Higher the oxidation state of the metal ion, more is the CF splitting.

Metal ion	Oxidation state	$\Delta_0$ (cm <sup>-1</sup> )	Metal ion	Oxidation state	$\Delta$ (cm <sup>-1</sup> )
V <sup>2+</sup>	II	11,800	V <sup>3+</sup>	III	18,000
Cr <sup>2+</sup>	II	14,000	Cr <sup>3+</sup>	III	17,400
Mn <sup>2+</sup>	II	7,500	Mn <sup>3+</sup>	III	21,000
Fe <sup>2+</sup>	II	10,400	Fe <sup>3+</sup>	III	14,000
Co <sup>2+</sup>	II	9,400	Co <sup>3+</sup>	III	18,600

**CF splitting for hexaaquo complexes of M<sup>2+</sup> and M<sup>3+</sup> ions of first transition series**



For complexes having **different ligands**, the CF splitting value in complexes having **lower O.S.** is less

Complex	Oxidation state	Electronic configuration	$\Delta_o$ (cm <sup>-1</sup> )
[Fe (CN) <sub>6</sub> ] <sup>4-</sup>	II	3d <sup>6</sup>	32,200
[Fe (CN) <sub>6</sub> ] <sup>3-</sup>	III	3d <sup>5</sup>	35,000
[Co (NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	II	3d <sup>7</sup>	10,200
[Co (NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	III	3d <sup>6</sup>	22,870
[Co F <sub>6</sub> ] <sup>3-</sup>	III	3d <sup>6</sup>	13,100
[Co F <sub>6</sub> ] <sup>2-</sup>	IV	3d <sup>5</sup>	20,300

## TYPE OF d - ORBITALS

- ❑ The extent of CF splitting in the **same** transition series **does not vary greatly**.
- ❑ On going from **3d to 4d** series and from **4d to 5d** series, approximately **30 to 50% increase** in CF splitting is observed.

Complex ion	Electronic configuration	$\Delta_0$ (cm <sup>-1</sup> )
$[\text{Co}(\text{NH}_3)_6]^{3+}$	$3d^6$	23000
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	$4d^6$	34000
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	$5d^6$	41000

- This **increase in CF splitting** in going from one transition series to other can be explained:
  - **Size of the d - orbitals increase** in going from **3d to 4d** and **4d to 5d** orbitals in the transition series.
  - With **increase in size** ,the orbitals **extend further in space**.
  - **More** the extension, **greater the interaction** with the ligands.
  - Resulting in **more CF splitting** in going from one transition series to other.

## GEOMETRY OF THE COMPLEX

- ❑ CF splitting in tetrahedral complexes is **less** than that of octahedral complexes.
- ❑ This is because in tetrahedral complexes **no ligand lies directly along any axis.**
- ❑ There are **only four ligands** surrounding the central metal ion in tetrahedral complexes.
- ❑ The CF splitting in octahedral complexes has been found to be **slightly more than double** as for tetrahedral complexes having the same metal ion and the same ligand.

□ Relation Between  $\Delta_o$  and  $\Delta_t$  can be given as :

$$\Delta_t = \frac{4}{9} \Delta_o$$

□ So,  $P > \Delta_o$  for tetrahedral complexes and they form high spin complexes

Complex	Oxidation state of metal	Geometry	$\Delta$ (cm <sup>-1</sup> )
$[\text{Co}(\text{NH}_3)_4]^{2+}$	II	Tetrahedral	59,00
$[\text{Co}(\text{NH}_3)_6]^{2+}$	II	Octahedral	10,200
$\text{VCl}_4$	IV	Tetrahedral	7,900
$[\text{VCl}_6]^{2-}$	IV	Octahedral	15,400

## COLOUR OF TRANSITION METAL COMPLEXES

- Most of the transition metal compounds are **coloured**.
- Transition metals **absorbs** certain wavelengths of light in the visible region, the color of the substance is determined by the wavelengths of visible light that is **reflected / transmitted back**.
- Transition metals exhibits the color **complementary** to the colours absorbed.
- The colour of transition metal complexes depend on the **energy** required to **excite electrons between  $t_{2g}$  &  $e_g$**  orbital.

- Depending on the energy difference **between  $t_{2g}$  &  $e_g$** , **wavelength** of suitable frequency is **absorbed** by the compound.
- The amount of energy required / absorbed for excitation of electrons can be calculated from the relation:

$$E = h\nu = \frac{hc}{\lambda}$$

- Let's consider the case of  **$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$**  which is **purple** in colour.
- Ti has **+3 O.S. and  $d^1$**  configuration.

The absorption spectra of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  shows that absorption of radiation occurs at  $5000 \text{ \AA}$  or  $20,000 \text{ cm}^{-1}$

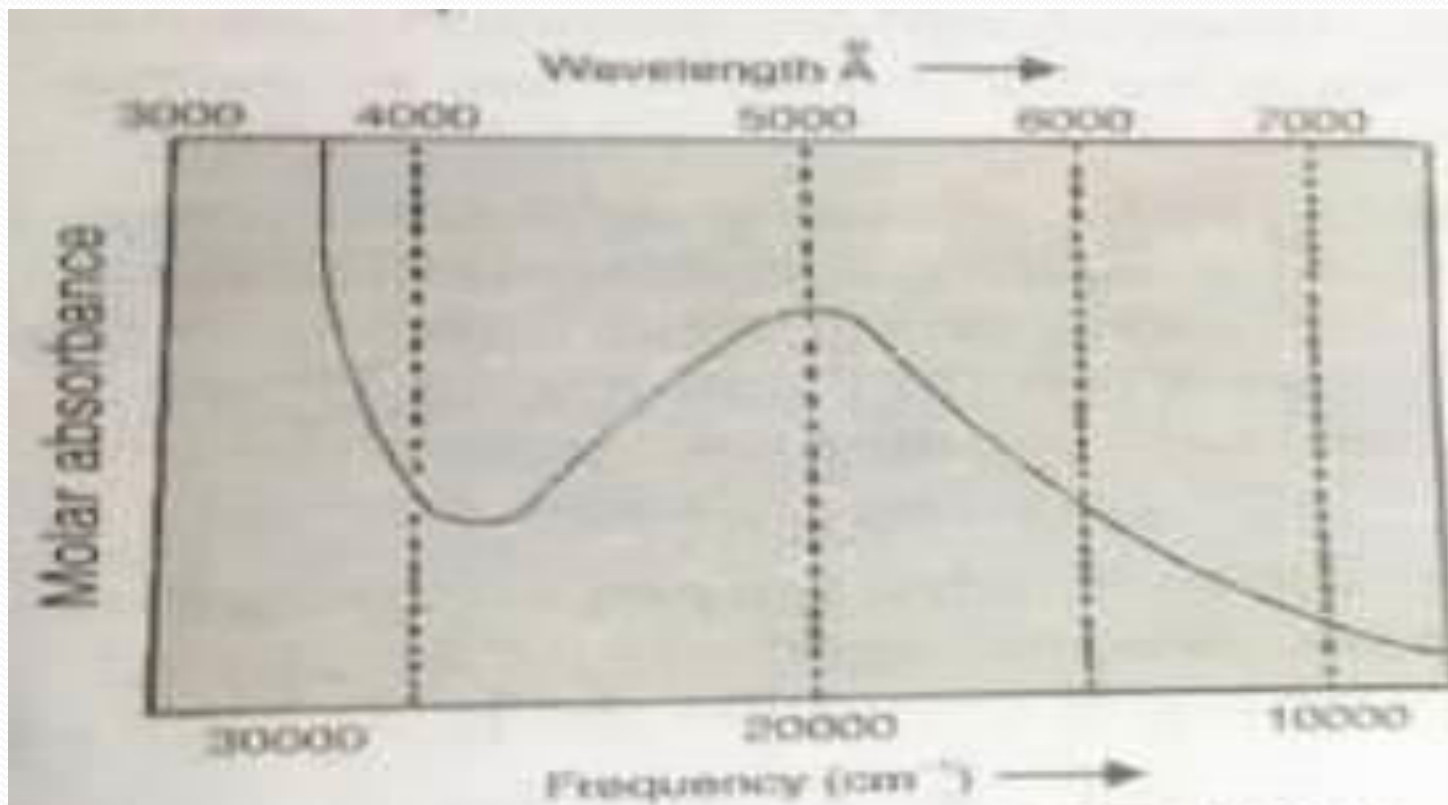


Fig. 16. Absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .



- The **energy** corresponding to the wavelength of light radiation absorbed can be calculated from the relation;

$$E = N_o h\nu = N_o \frac{hc}{\lambda}$$

where  $N_o$  = Avogadro's constant ( $6.023 \times 10^{23}$ )

$h$  = Planck's constant ( $6.626 \times 10^{-34}$  Js)

$c$  = velocity of light ( $3.0 \times 10^8$  m/s)

and  $\lambda$  = wavelength of radiation absorbed

- For Titanium metal ion the wavelength of radiation absorbed is

$$\lambda = 5000 \text{ \AA} = 5000 \times 10^{-8} \text{ m}$$

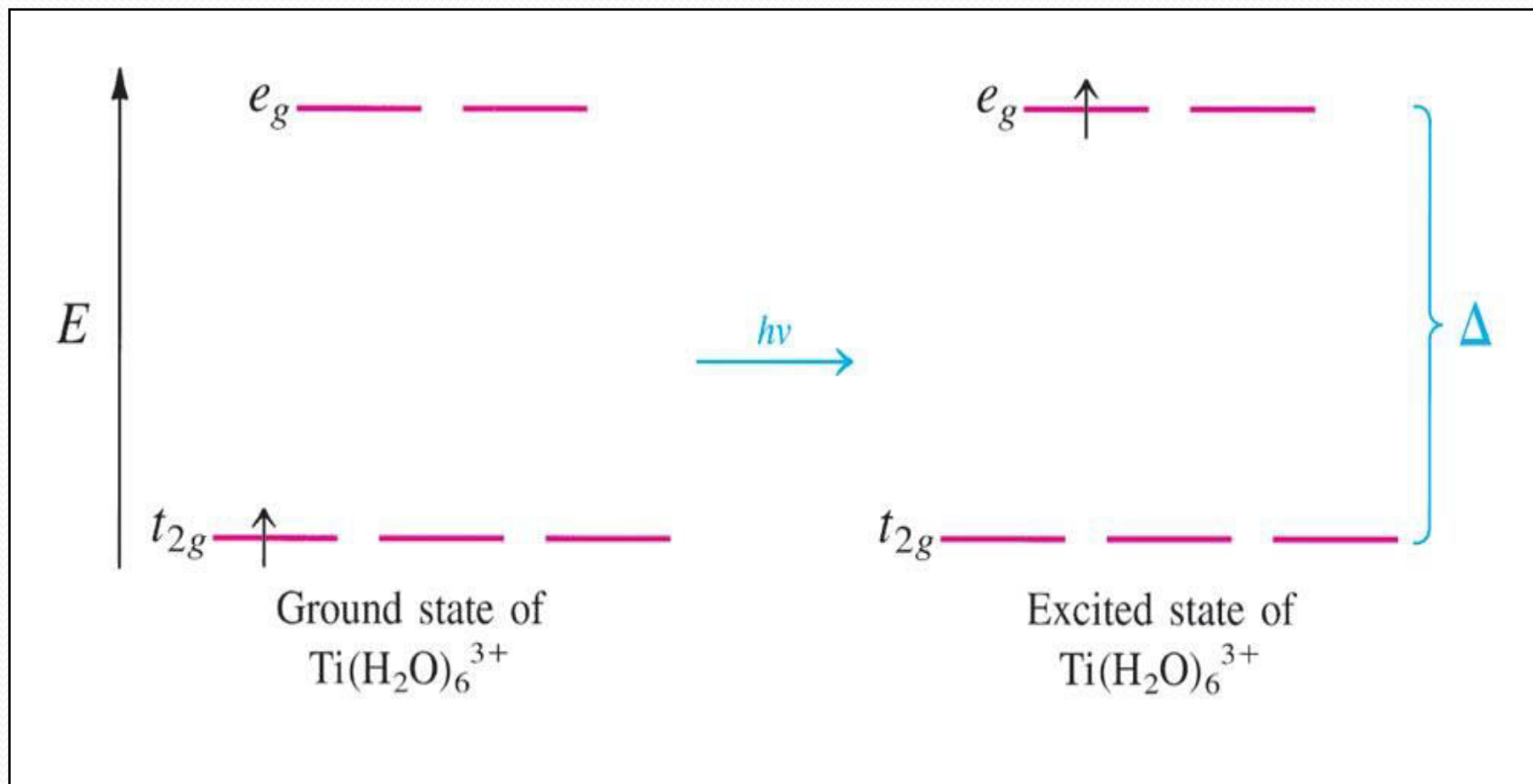
- On substituting these values in the relation,

$$E = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{34} \text{ Js} \times 3.0 \times 10^8 \text{ m/s}}{5000 \times 10^8 \text{ m}}$$

$$E = 239 \text{ KJ/ mol}$$

- This is the **energy difference** between the two sets of d-orbital of octahedral  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex.
- This is also the energy requirement for **excitation of a single electron** from lower energy to higher energy level.
- In other words, absorption of radiation **corresponding to this energy is absorbed** and the rest is transmitted back.

## Absorption of Visible Light by the Complex Ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$



- The **wavelength** corresponding to the **absorbed energy** belongs to **green and yellow lights** of the visible light.
- The **blue and red portion** of the visible light is **transmitted/ reflected**, resulting in purple colour of the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex.
- Colour of transition metal complexes **depend** on the following factors:
  - a) Transition metal forming the complex
  - b) Ligands and their nature

- The ligands **coordinated** to a given metal ion determine the **size of the  $d$ -orbital splitting**, thus the colour changes as the ligands are changed.
- A change in splitting means a change in the wavelength of light needed to transfer electrons between the  $t_{2g}$  and  $e_g$  orbitals.
- Take the example of **Cobalt in +3 O.S.** combining with three different ligands  **$H_2O$ ,  $NH_3$  and  $CN^-$**  forming octahedral complexes.
- According to spectrochemical series, the **strength** of the ligands increase in the order



- So, CF splitting will be in the order



and the energy required to excite the electron will follow the order



	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Co}(\text{CN})_6]^{3-}$
$\Delta_o$ value	small	intermediate	large
Excitation energy ( $\Delta E$ )	small	intermediate	large
Absorption wavelength ( $\lambda$ )	large	intermediate	small
Colour absorbed	orange	blue	violet
Colour transmitted	blue	orange	yellow

## COLOUR OF $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

- Hydrated  $\text{CuSO}_4$  is a  **$d^9$**  system as Cu exists in +2 O.S. ( $\text{Cu}^{2+}$ )
- The spectrum of  $d^9$  system is the **same as  $d^1$  system**, but in case of  **$d^9$  system** it is considered as **hole formulism**.
- It means that Cu(II) has a spherically symmetrical  **$d^{10}$  system** with a missing electron or hole.
- When visible light falls on  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , **the hole behaves in the same way as electron** and absorbs radiation corresponding to  $5750 - 5900 \text{ \AA}$  (Red region).
- Hydrated  $\text{CuSO}_4$  transmits blue colour.

- Cuprous compounds ( $\text{Cu}^{1+}$ ) e.g.  $\text{Cu}_2\text{SO}_4$  is a  **$d^{10}$  system**, so **no d – d transitions are possible**.
- So,  $\text{Cu}_2\text{SO}_4$  is colourless.
- Anhydrous  $\text{CuSO}_4$  is white /colourless.
- It is a  **$d^9$  system**, so it should be coloured.
- In anhydrous state there is **no crystal field of ligand and splitting of d –orbitals does not occur**.
- Excitation of electrons is **not possible**, resulting in white /colourless complex.



