

Module-1: Chemical Bonding

~~Ionic Bond: Radius Ratio rule, Born-Landé equation,  
Born-Haber cycle.~~

~~Metallic Bond: Valence bond and Pauli theories, defects in solids  
Werner's theory, Bonding in Transition metal complexes,  
Ligands, coordination complexes, ligand field,  
Crystal field theory, octahedral, tetrahedral, & square planar complexes, CFSE, John Teller Theorem,  
electronic spectra, magnetism, & isomerization  
in Coordination compounds.~~

# Werner's Theory of Coordination Compounds

The systematic study of coordination compounds was started by Alfred Werner whose pioneering work opened an entirely new field of investigation in inorganic chemistry. He prepared and characterized a large number of coordination compounds and studied their physical, chemical & isomeric behaviour by simple experimental techniques. On the basis of these studies, Werner, in 1898, propounded his theory of coordination compounds.

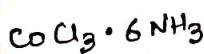
Series of coloured compounds obtained by the interaction of aqueous  $\text{CoCl}_3$  &  $\text{NH}_3$

compound

colour

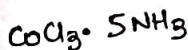
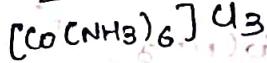
Name according to colour

coordinate formula



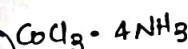
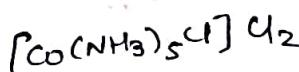
Yellow

Utao complex



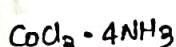
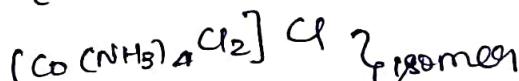
Purple

Purpurine complex



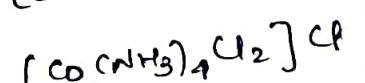
Green

Praseo complex



Violet

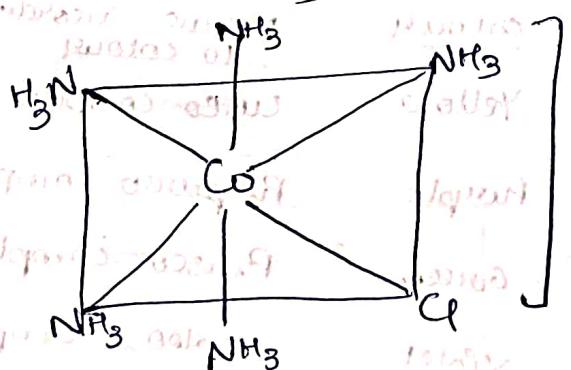
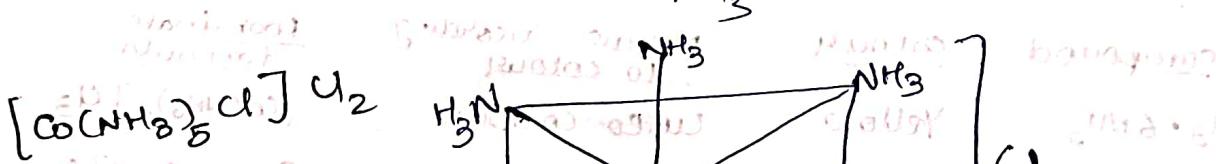
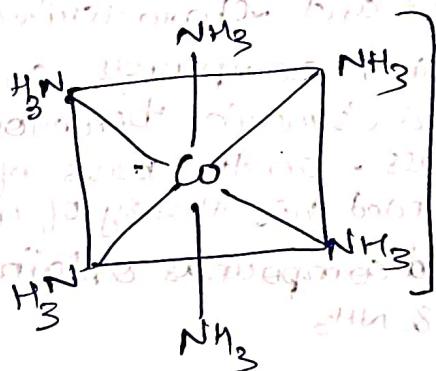
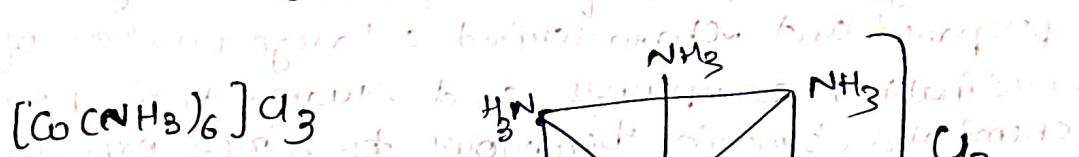
Violeo complex

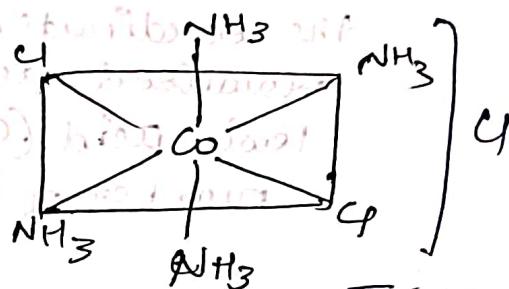
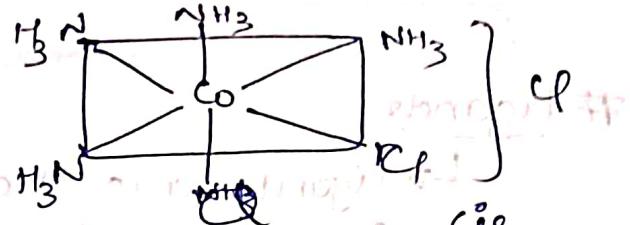
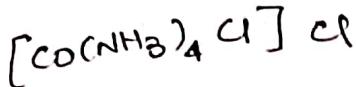


The main postulates of Werner's Theory are :-

- In a coordination complex, a metal ion is engaged in two types of linkages or valence.
- (i) Primary or ionisable linkage which can be satisfied by negative ions & equal the oxidation state of the metal
- (ii) Secondary or non-ionisable linkage which can be satisfied by neutral or negative ions/groups. The secondary linkages equal to the coordination number of central metal atom/ion.

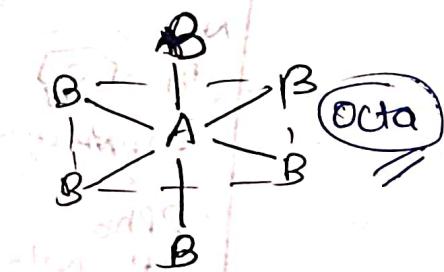
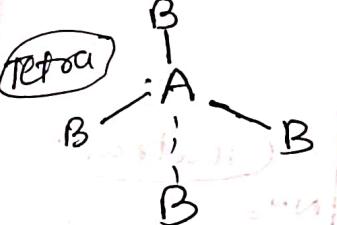
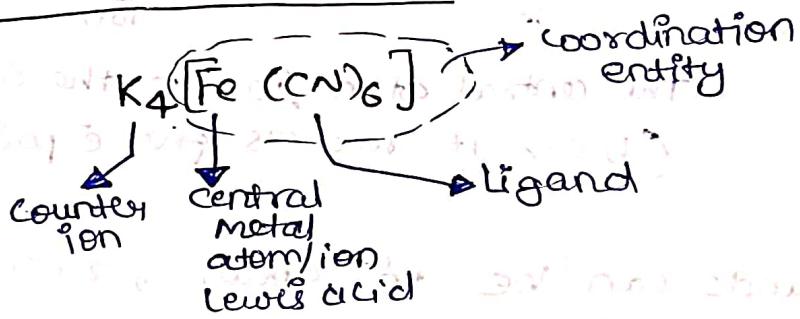
- The ions/groups bound by the secondary linkages have characteristics spatial arrangements corresponding to different co-ordination numbers in the modern terminology, such spatial arrangements are called Coordination Polyhedra.



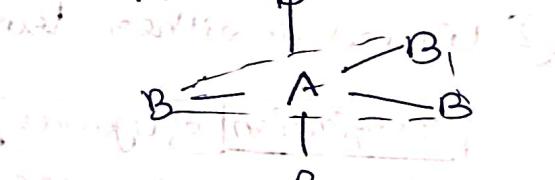
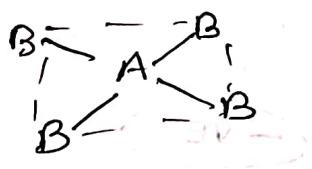


square planar & tetrahedral are same

### Some imp. terms of C.C.



square planar



## # Ligands

Ligands are the ions or molecules bound to the central atom/ion in the coordination entity. This is better visualised as the combination of a Lewis acid (central atom/ion) with a number of Lewis bases (ligands).

The atom in the Lewis base that forms the bond to the Lewis Acid (Central atom/ion) is called donor atom (bcz it donates the pair of electrons required for bond formation)

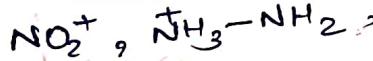
The central atom/ion is the acceptor atom/ion (bcz it receives the e pairs from ligands)

- Ligands can be  $\text{1e}^-$  donor,  $\text{2e}^-$  donor (LP donor)
- Ligand is either Lewis base or not

### Classification of Ligands

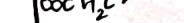
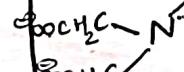
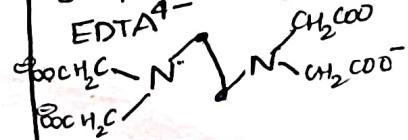
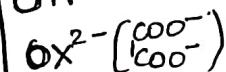
① Based on charge

+ve

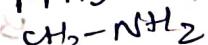
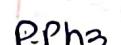
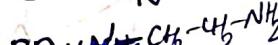


NO<sup>+</sup>

-ve



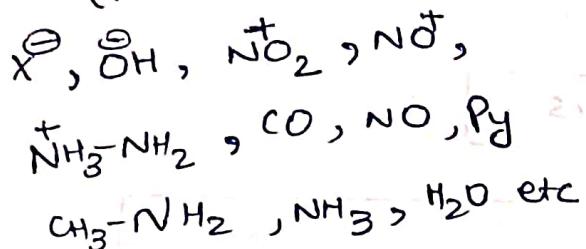
Neutral



## ② Based on donation (dentricity)

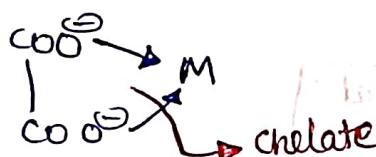
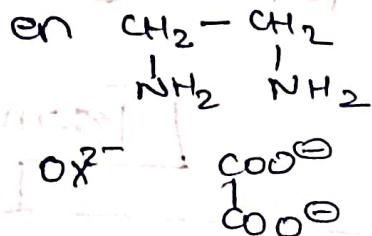
### Monodentate

(1 atom donor)



### Bidentate

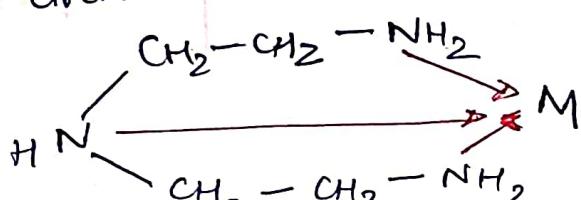
(2 donor atom)



### T Tridentate

(3 donor atom)

dien

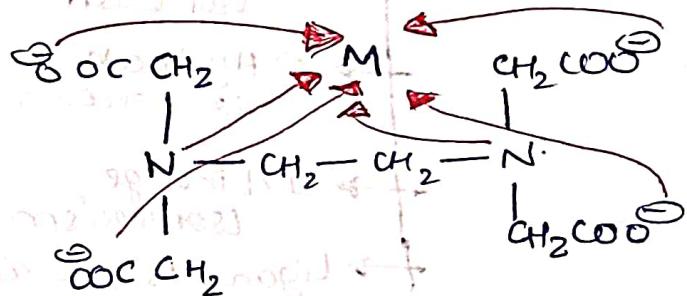


2-chelate form

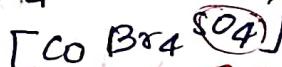
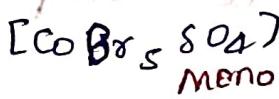
### Polydentate

Hexadentate

(6 donor atom)



### Flexidentate



### Ambidentate

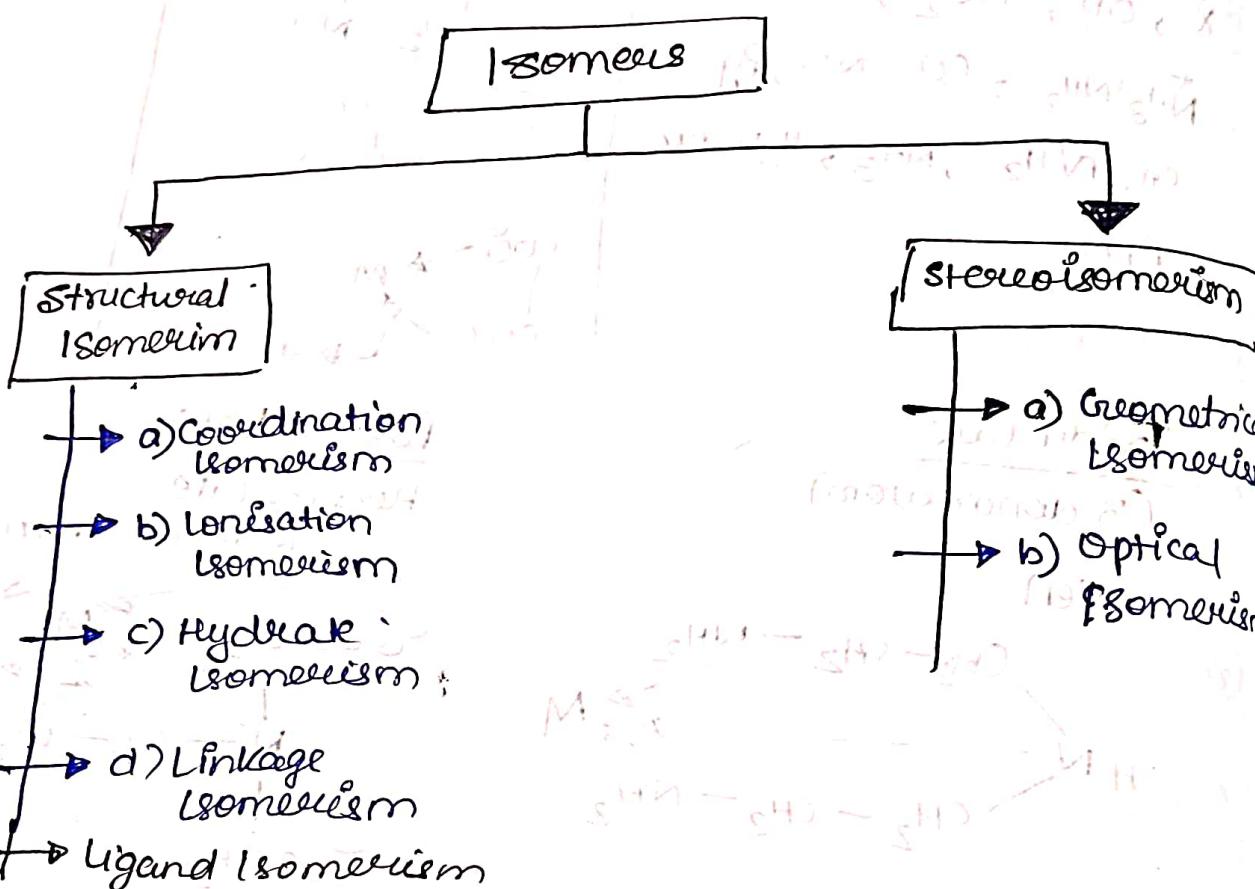
(2 donor atoms)

but only one can  
donate at a time



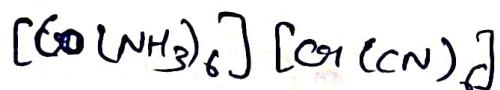
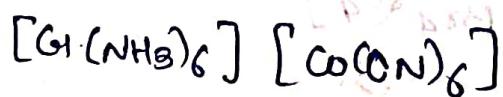
## # Isomerism

↳ Two or more different compounds having same formula are called Isomers.

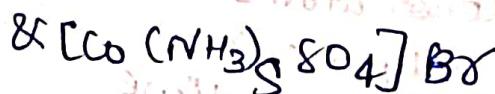
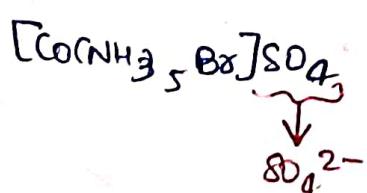


### ① Structural

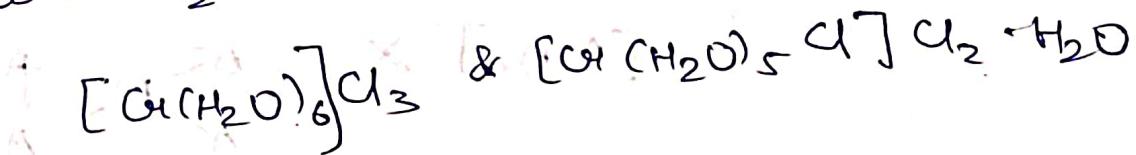
a) Coordination Isomerism : when cation & anion both are complex,



b) Ionization Isomerism compound which give different ion in soln

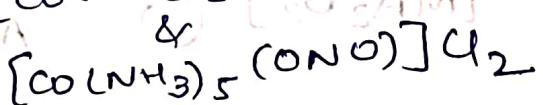
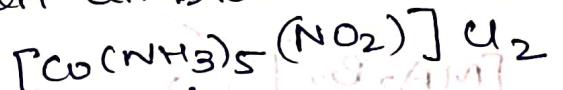


c) Hydrate Isomerism  
when  $\text{H}_2\text{O}$  acts as ligand & water of crystallization



d) Linkage Isomerism

↳ when ambidentate ligand is present.



\* Ligand Isomerism

e.g. 1,2-diaminopropane

1,3-diaminopropane

or  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$  & para toluidine ( $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ )

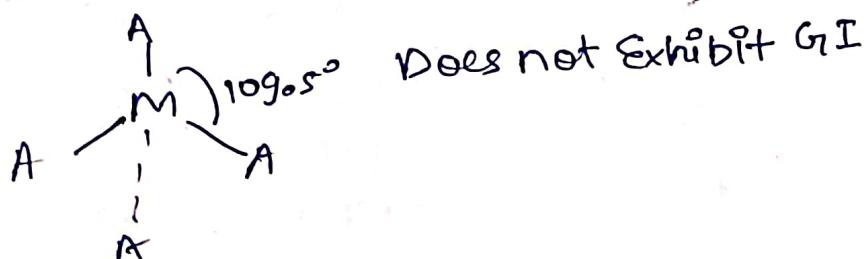
## ② Stereoisomerism

a) Geometrical Isomerism

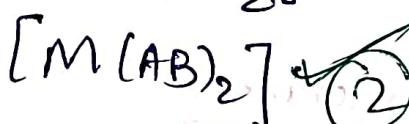
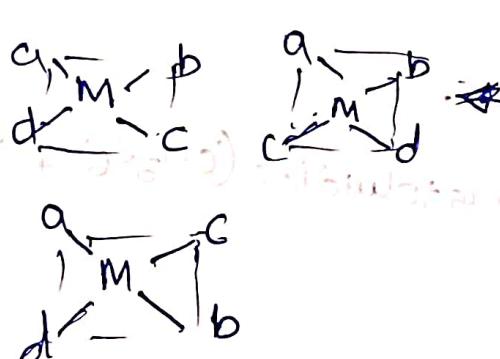
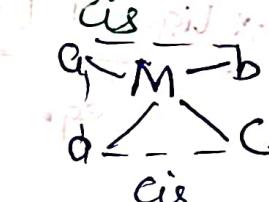
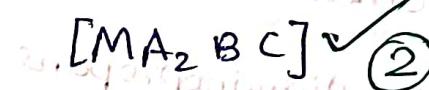
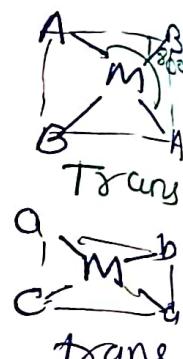
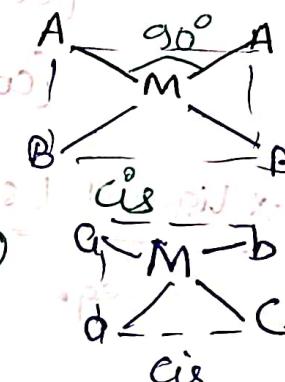
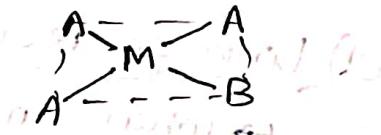
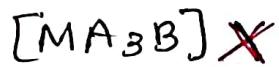
↳ GI differ in the spatial arrangement of atoms within the same structural framework.  
It is also called cis-trans isomerism.

Case - ①  $\text{Ln CN} = 4$

a) Tetrahedral geometry ( $\text{MA}_4$ )



b) In square planar geometry



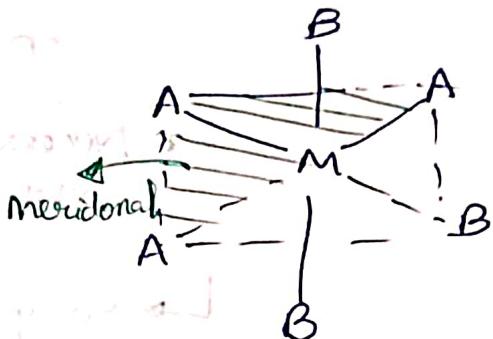
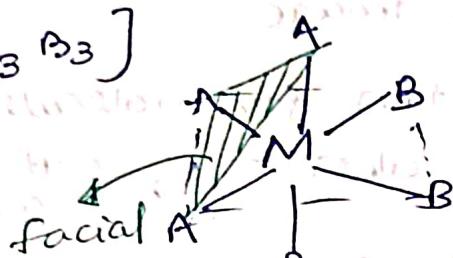
case-2

In  $C \cdot N = 6$

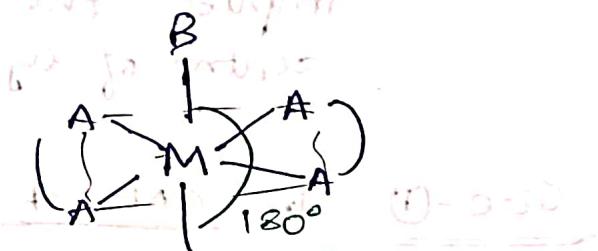
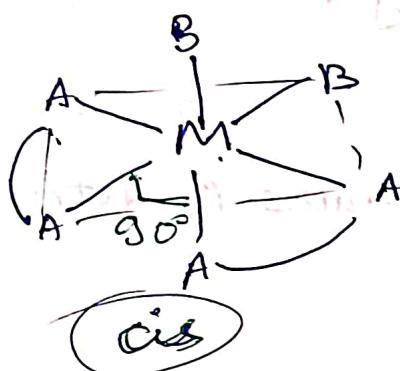
Octahedral

$Ma_6, ma_5b \rightarrow 1$  Geometric form

$[Ma_3 B_3]$



$[M(AA)_2 B_2]$



Complexes

No. of GI

$[MA_4 B_2] \rightarrow 2$

$[MA_4 BC] \rightarrow 2$

\*  $[MA_3 B_3] \rightarrow 2$  C2H of sub.

$[MA_3 B_2 C] \rightarrow 3$  (for solid)

$[MA_3 B CD] \rightarrow 4$

$[MA_2 B_2 C_2] \rightarrow 5$

$[MA_2 B_2 CD] \rightarrow 6$

$[MA_2 B CD E] \rightarrow 9$

$[MABCDEF] \rightarrow 15$

$[M(CAA)_2 B_2] \rightarrow 2$

$[M(AA)_2 BC] \rightarrow 2$

$[M(AB)_3] \rightarrow 2$

$M(AA)_3$

does not exhibit GI

## b) Optical Isomerism

- ↳ A chiral complex is optically active if its structure cannot be superimposed on its mirror image.
- ↳ Necessary condition for molecule to exhibit OI is absence of rotation-reflection axis ( $S_n$ )
- ↳ Easy judgement for optical activity implies the absence of plane or centre of symmetry.

Case - ①

$$\text{In, } \underline{\text{CN}} = 4$$

OI does not exhibits in Tetrahedral & Square planar.

Tetra X

Sq. Planar X

Sq. Planar complexes  $\rightarrow$  generally optically inactive due to POS ✓

b'coz of presence of asymmetric ligand

↳ optical isomerism may appear.

D L

D L

D L

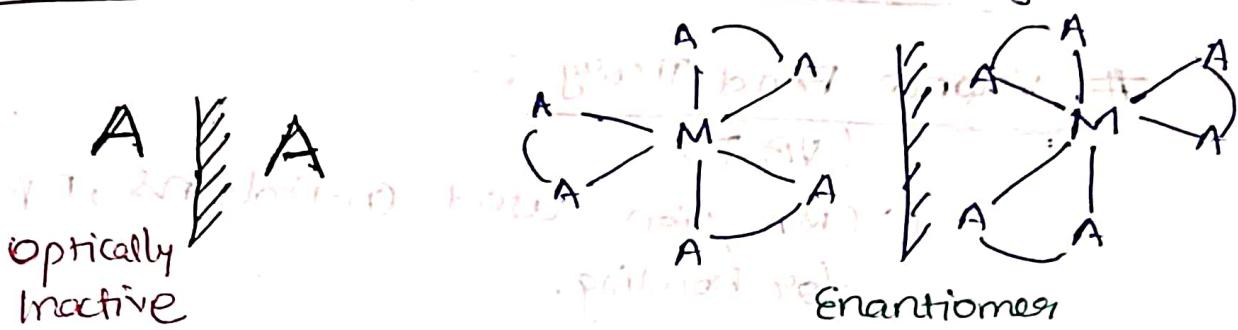
D L

[DDL] [SLSM]

[DLD] [SLSM]

[DLD] [DLDS]

\* Enantiomer → Non-superimposable mirror images.



P || Q → optically active

\* Diastereomers → Stereoisomers which do not possess mirror image relation.

\* Asymmetric molecule : A molecule without any symmetry.

$M(AA)_3$  exhibits OI  
Not GI OI  
GI X

Case - ②  $[M_n(CN = G)]$  binds to  $n$  ligands.

complexes      GI      Enantiomer Pair

$[MA_4B_2]$	$\rightarrow 2$	$-90^\circ$	$0$	$\begin{array}{c} \text{top} \\ \text{bottom} \end{array}$	$2$
$[MA_4BC]$	$\rightarrow 2$	$-90^\circ$	$0$	$\begin{array}{c} \text{top} \\ \text{bottom} \end{array}$	$2$
$[MA_3B_3]$	$\rightarrow 2$	$-90^\circ$	$0$	$\begin{array}{c} \text{top} \\ \text{bottom} \end{array}$	$3$
$[MA_3B_2C]$	$\rightarrow 3$	$-$	$0$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$3$
$[MA_3B_2CD]$	$\rightarrow 4$	$-$	$1$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$6$
$[MA_2B_2C_2]$	$\rightarrow 5$	$-120^\circ$	$1$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$8$
$[MA_2B_2CD]$	$\rightarrow 6$	$-120^\circ$	$2$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$15$
$[MA_2B_2CDG]$	$\rightarrow 9$	$-$	$6$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$30$
$[MABCDEF]$	$\rightarrow 15$	$-$	$15$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$3$
$[M(AA)_2B_2]$	$\rightarrow 2$	$-$	$1$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$3$
$[M(AA)_2BC]$	$\rightarrow 2$	$b$	$1$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$4$
$[M(AB)_3]^P$	$\rightarrow 2$	$-$	$2$	$\begin{array}{c} \text{top} \\ \text{middle} \\ \text{bottom} \end{array}$	$1$

## Bonding Theories

### # Valence Bond Theory :-

(VBT)

- ① CMA / ion used  $cn-1d, ns, np$  or  $ns, np,$  for bonding.
- ② Ligand will donate LP to the vacant orbital of CMA / ion
- ③ Pairing occurs when strong field ligands like  $\text{NH}_3, \text{CN}^-, \text{CO}$  etc are present

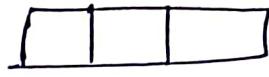
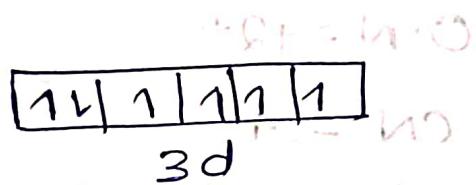
Some hybridisation schemes for complex comp.

C N	Geometry	Hybridisation	Orbitals involved
2	Linear	$sp$	$(s, p_z)$
3	Trigonal Planar	$sp^2$	$(s, p_x, p_y)$
4	Tetrahedral	$sp^3$	$sp^3 (s, p_x, p_y, p_z)$
	Square planar	$dsp^2$	$(d_{z^2}, s, p_x, p_y)$
5	Trigonal bipyramidal	$dsp^3$	$dsp^3 (d_{z^2}, s, p_x, p_y, p_z)$
	Square pyramid	$dsp^3$	$dsp^3 (d_{x^2-y^2}, s, p_x, p_y, p_z)$
6	Octahedral	$d^2sp^3$ $sp^3d^2$	$d_{z^2}, d_{x^2-y^2}, s, p_x, p_y, p_z$
7	Trigonal Prism	$d^2sp^3$	$d_{yz}, d_{xz}, s, p_x, p_y, p_z$

e.g.

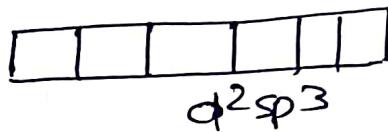
Diamagnetic Octahedral complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$

$\text{Co}^{3+}$   
 $d^6$

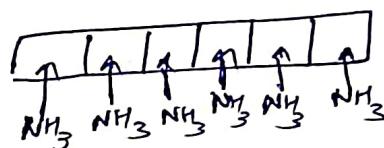
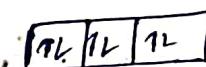


$\text{E} \leftarrow \text{S} \leftarrow \text{B} \leftarrow \text{O} \leftarrow \text{N} \leftarrow \text{C}$

$d^2sp^3$



$[\text{Co}(\text{NH}_3)_6]^{3+}$



inner orbital

or low spin

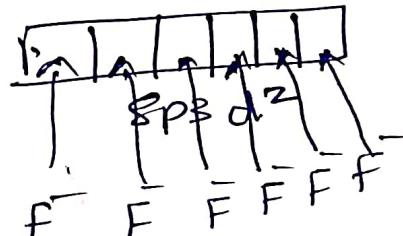
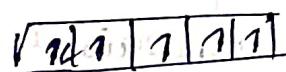
$\text{E} \leftarrow \text{S} \leftarrow \text{B} \leftarrow \text{O} \leftarrow \text{N} \leftarrow \text{C}$

$[\text{CoF}_6]^{3-}$

outer orbital or high spin complex

$(sp^3d^2)$

$\text{Co}^{3+}$



$\text{Co}^{3+} + 6\text{F}^- \rightarrow [\text{CoF}_6]^{3-}$

$\Rightarrow \text{Pt}^{+2}, \text{Pb}^{+2} \rightarrow \text{CN}=4$

2d equals

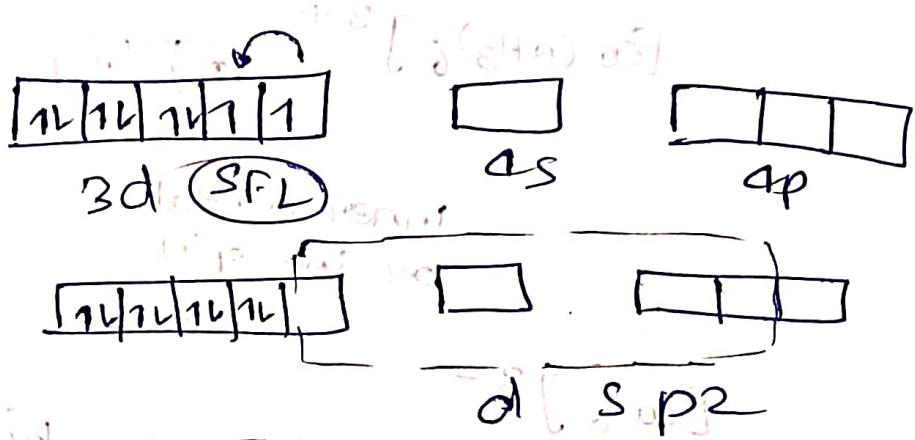


$$\text{O.N} = +2^-$$

$$\text{CN} = 4$$

$$\text{EC. } \text{Ni}^{\circ} \Rightarrow [\text{Ar}] 4s^2 3d^8$$

$$\text{Ni}^{\circ} \Rightarrow [\text{Ar}] 3d^8$$



Sq. planar

unpaired e<sup>-</sup>s = 0

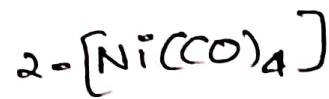
$$n=0$$

M.M = 0 Diamagnetic

$$\text{EAN} = \text{AN} - \text{D.N} + 2 \times \text{CN}$$

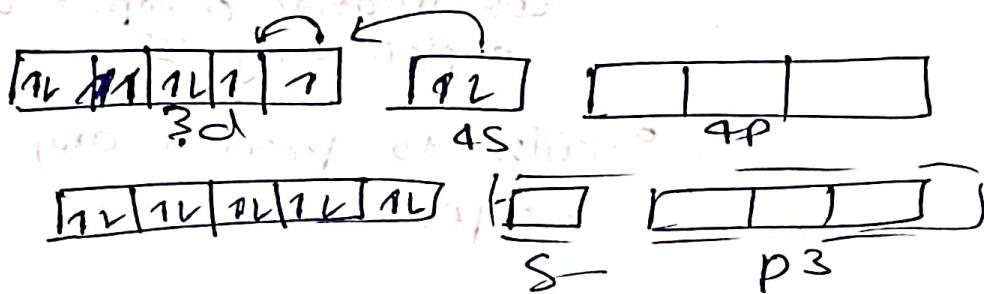
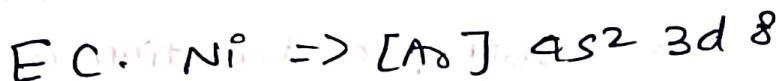
$$\begin{aligned} &+63 \\ &= 28 - 2 + 2 \times 4 \\ &= 34 \end{aligned}$$

Colourless



$$\text{ON} = 0$$

$$CN = 4$$



(8p<sub>3</sub>)



Tetrahedral

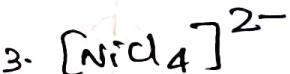
$$\text{NFE} = 0$$

$$n = 0$$

Diamagnetic

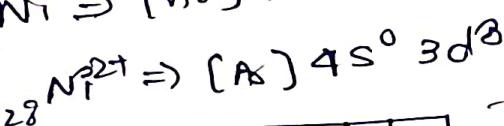
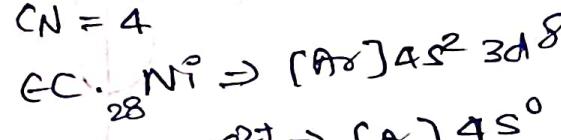
$$\begin{aligned} m \cdot M &= 0 \\ \text{EAN} &= \text{AN} - \text{DN} + 2 \times \text{C.N} = 28 - 0 + 2 \times 4 \\ &= 36 \end{aligned}$$

colourless

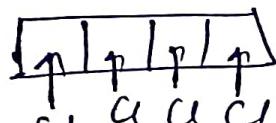


$$\text{ON} = 4$$

$$CN = 4$$



(8p<sub>3</sub>)



Tetrahedral

$$\begin{aligned} \text{unpaired e} &= 2 \\ n &= 2 \end{aligned}$$

$$m \cdot M = 18$$

Paramagnetic  
coloured.

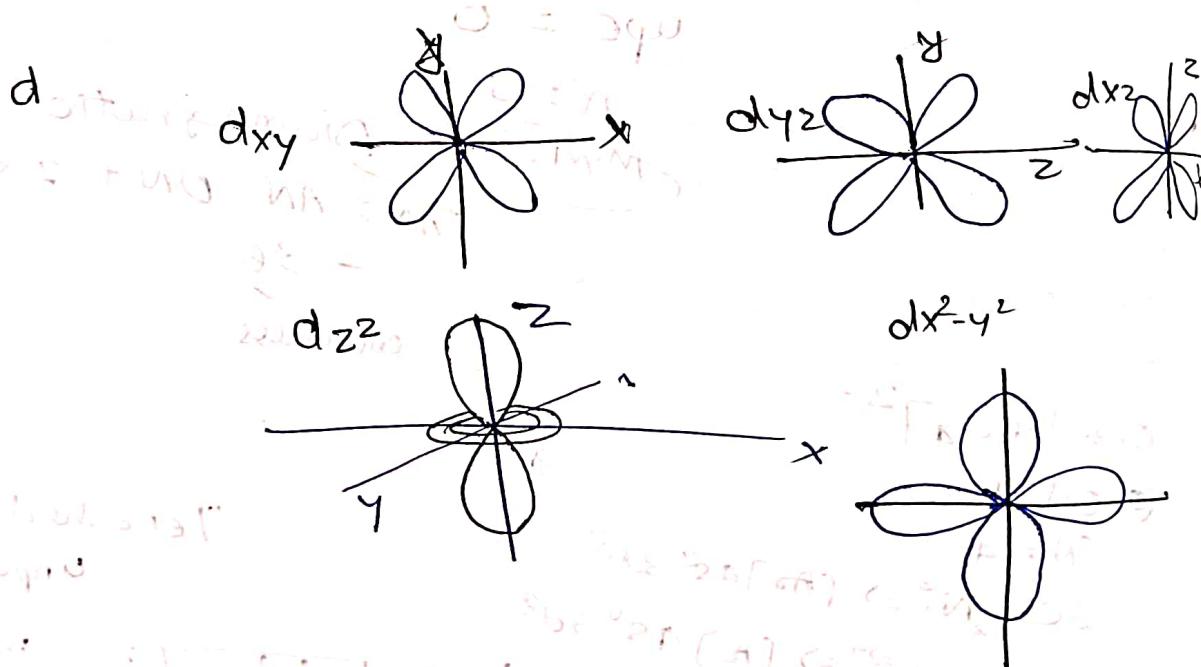
## # Limitation of VBT

Limitations

- Fails to explain colour & characteristic of absorption spectra of complex compound.
- Orbital contribution & temperature dependency on magnetic moment of coordination complex are not properly explained by VBT.
- Failed to predict any distortion in shapes.

## # Crystal field theory (CFT) :-

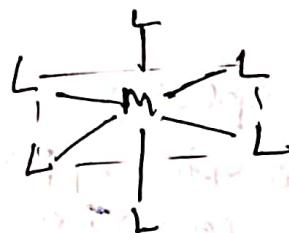
The energies of d orbitals of metal ions are splitted by Electrostatic field & approximate values for these energies can be calculated



$\Delta_o \rightarrow \text{CFSE}$  (Crystal field splitting energy)

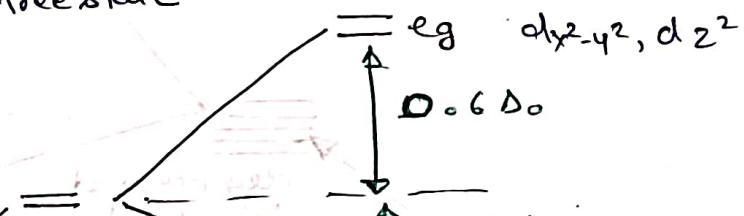
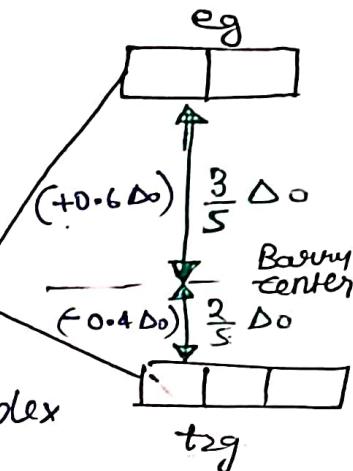
case-① in octahedral field

$[ML_6]$



degenerated  $d'$  orbital in free state

degenerated 'd' orbitals in complex

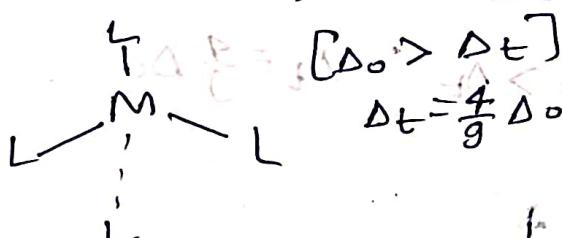


free state

Case-② In tetrahedral field

$[ML_4]$

$\Delta_t$ : CFSE

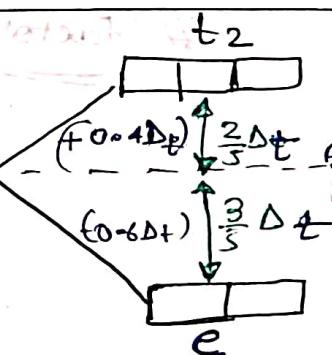


$$\Delta_t = \frac{4}{9} \Delta_o$$

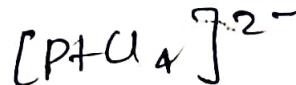
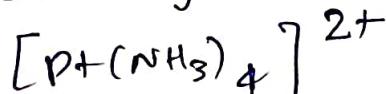
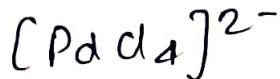
degenerated  $d'$  orbitals in free state

$d_{xy}, d_{yz}, d_{zx}$

$0.4 \Delta_t$   
 $d_{x^2-y^2}, d_{z^2}$



### Case - ③ square planar



$t_{2g}^8$  species

low spin sq planar complexes

$d_{x^2-y^2}^{2+}$

$d_{xy}$

$d_{z^2}$

$d_{xy}, d_{yz}$

degenerated d orbital in spherical field

### # factors affecting CFSE

①  $\text{CFSE} \propto \text{O.N.}$

$3d < 4d < 5d$

② CFSE :

$\Delta_o > \Delta_t$

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

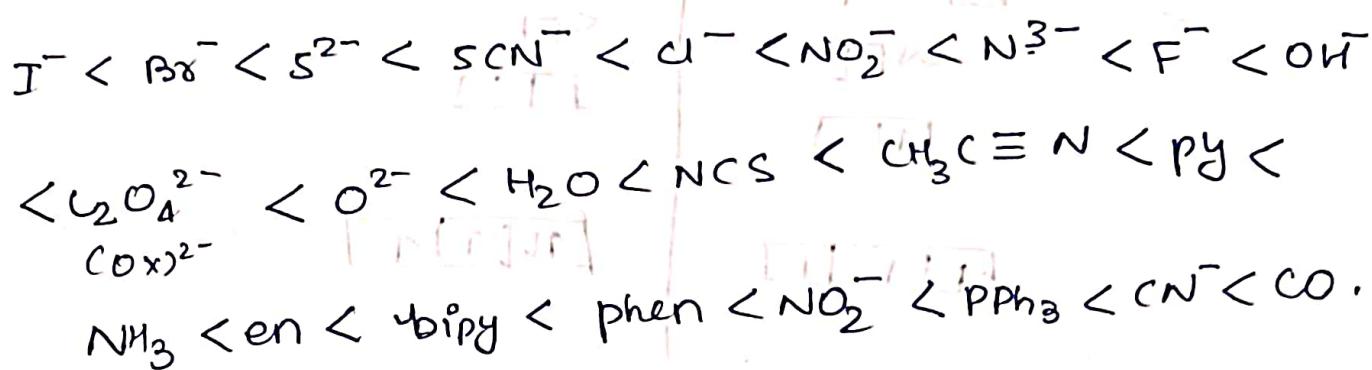
③ Geometry

④ Nature of Ligand

SFL  $\rightarrow$  CFSE  $\uparrow$

CWFL  $\rightarrow$  CFSE  $\uparrow$

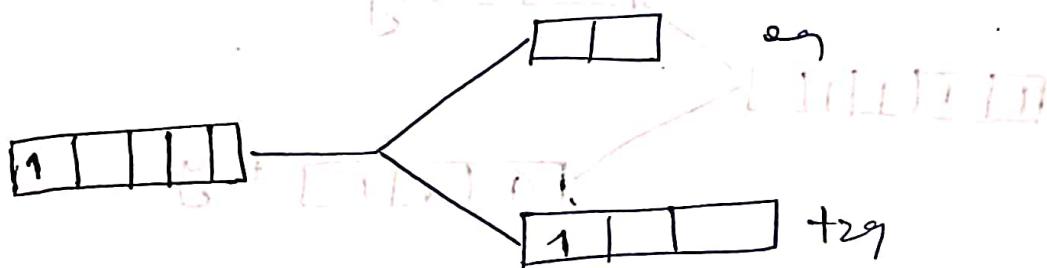
## Spectrochemical Series



calculation of CFSE in octahedral field :-

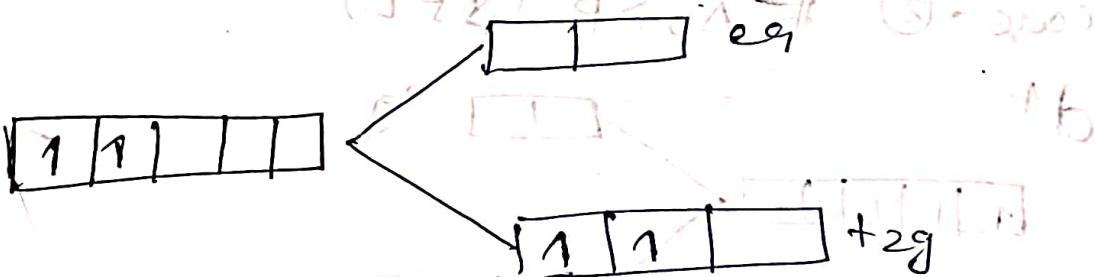
$$CFSE = x(-0.4\Delta_o) + y(0.6\Delta_o) + z(0)$$

$d^1$



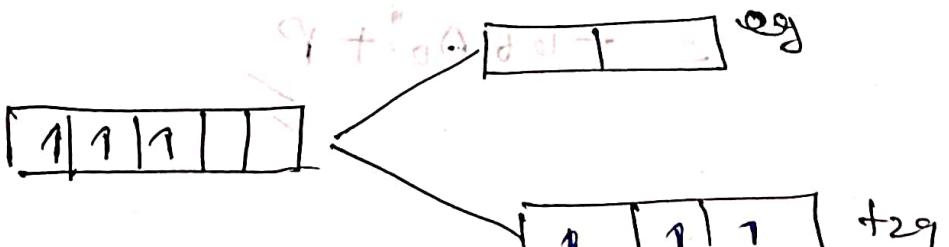
$$CFSE = 1(-0.4\Delta_o) + 0(0.6\Delta_o) + 0(0) \\ = -0.4\Delta_o$$

$d^2$



$$CFSE = 2(-0.4\Delta_o) + 0 + 0 \\ = -0.8\Delta_o$$

$d^3$



$$CFSE = 3(-0.4\Delta_o) + 0 + 0 \\ = -1.2\Delta_o$$

$d^4$

$\Delta_o < P$

WFL

$\rightarrow 01 > 11 > 11$

$\boxed{111}$

$\Delta_o > P$

SFL

$\boxed{\cdot \cdot}$

$\rightarrow 11 > 01 > 11$

$\boxed{1111}$

Case - ① If  $\Delta_o < P$  (WFL)

$d^4$

$\rightarrow \begin{array}{|c|c|c|c|} \hline 1 & 1 & & \\ \hline \end{array}$  eg

$\rightarrow \begin{array}{|c|c|c|c|c|} \hline 1 & 1 & 1 & 1 \\ \hline \end{array}$

$\rightarrow \begin{array}{|c|c|c|c|} \hline 1 & 1 & 1 & \\ \hline \end{array}$

$$\text{CFSE} = 3(-D_0 + \Delta_o) + 1(D_0 + 6\Delta_o) + 0$$

$$= -3D_0 + 7\Delta_o$$

Case - ② If  $\Delta_o > P$  (SFL)

$d^4$

$\rightarrow \begin{array}{|c|c|c|c|c|} \hline 1 & 1 & 1 & 1 \\ \hline \end{array}$

$\rightarrow \begin{array}{|c|} \hline 1 \\ \hline \end{array}$  eg

$\rightarrow \begin{array}{|c|c|c|c|c|} \hline 1 & 1 & 1 & 1 & 1 \\ \hline \end{array}$

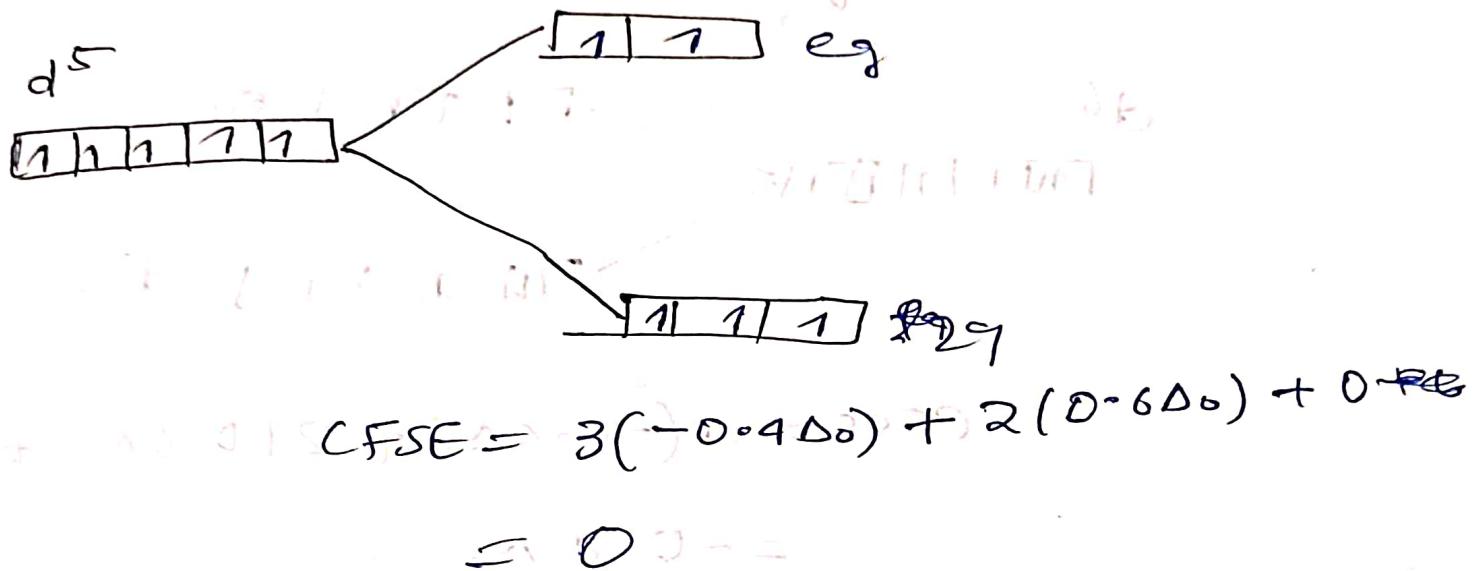
$\rightarrow \begin{array}{|c|c|c|c|} \hline 1 & 1 & 1 & 1 \\ \hline \end{array}$  eg

$$\text{CFSE} = 4(D_0 + 4\Delta_o) + 0(D_0 + 6\Delta_o) + 0 \times P$$

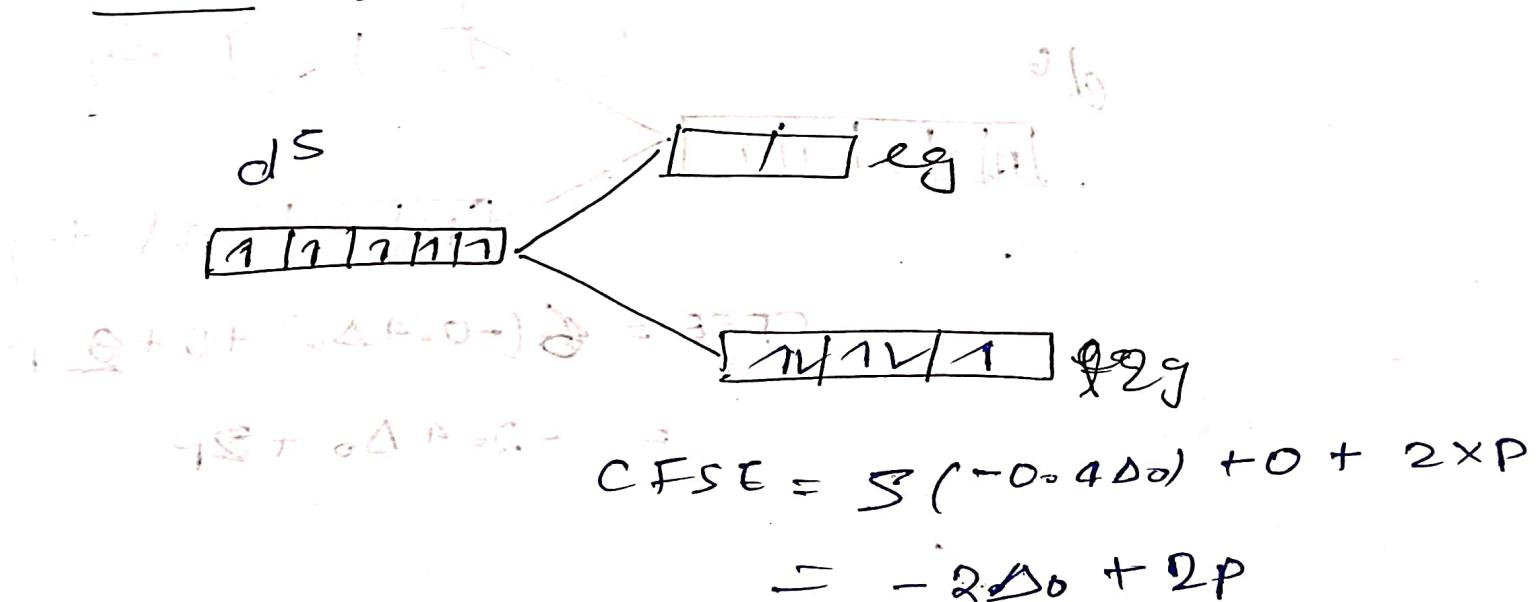
$$E_{\text{tot}} = -10.67\Delta_o + P$$

Plot  $E_{\text{tot}}$  vs  $\Delta_o$   $\Rightarrow$   $\boxed{[1111]}$

Case - ① If  $\Delta_0 < P(\text{WFL})$



Case - ② If  $\Delta_0 > P(\text{WFL})$



d<sub>6</sub>

if  $\Delta_0 > \Delta_p$  (Ex. w<sub>1</sub>)

case -① If  $\Delta_0 < p$  (WFL)

d<sub>6</sub>

111 111 1

111

eg

111 1 11

+<sub>2g</sub>

$$\text{CFSE} = 4(-\Delta_0 + 4\Delta_0) + 2(\Delta_0 + 6\Delta_0) + 0 \\ = -0.4 \Delta_0$$

case -② If  $\Delta_0 > p$  (WFL)

d<sub>6</sub>

111 110 111

11

eg

111 111 111

+<sub>2g</sub>

$$\text{CFSE} = 6(-0.4 \Delta_0) + 0 + 9 \times p$$

$$= -2.4 \Delta_0 + 9p$$

case-① If  $\Delta_o < P$  (WFL)

$$\begin{array}{c} \text{eg } \boxed{1 \ 1 \ 1 \ 0} \\ \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \xrightarrow{\text{f}_1 + f_2} \boxed{1 \ 1 \ 1 \ 1 \ 1} +_{2g} \boxed{1 \ 1 \ 1 \ 1 \ 1} \\ \text{CFSE} = 5(-0.4\Delta_o) + 2(0.6\Delta_o) + 0 \\ = -0.8\Delta_o \end{array}$$

case-② If  $\Delta_o > P$  (GFL)

$$\begin{array}{c} \text{eg } \boxed{1 \ 1 \ 1 \ 1 \ 0} \\ \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \xrightarrow{\text{f}_1 + f_2} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} +_{2g} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \\ \text{CFSE} = 6(-0.4\Delta_o) + 1 \times (0.6\Delta_o) + P \\ = -1.8\Delta_o + P \end{array}$$

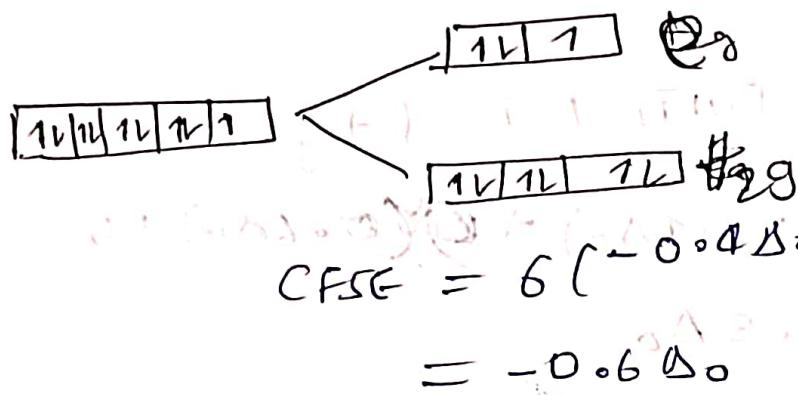
Case-① If  $\Delta_o < P$  (WFL)

$$\begin{array}{c} \text{eg } \boxed{1 \ 1 \ 1 \ 0} \\ \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \xrightarrow{\text{f}_1 + f_2} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} +_{2g} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \\ \text{CFSE} = 6 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) + 0 \\ = -1.2\Delta_o \end{array}$$

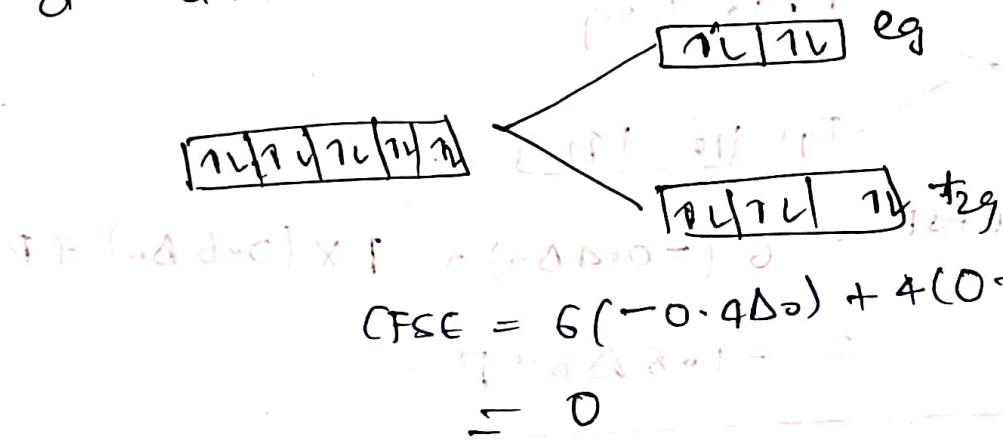
Case-② If  $\Delta_o > P$  (GFL)

$$\begin{array}{c} \text{eg } \boxed{1 \ 1 \ 1 \ 1 \ 0} \\ \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \xrightarrow{\text{f}_1 + f_2} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} +_{2g} \boxed{1 \ 1 \ 1 \ 1 \ 1 \ 1} \\ \text{CFSE} = -1.2\Delta_o \end{array}$$

$d^9$  either SiFL or SFL



$d^{10}$  either WFL or SFL



Configuration	SFL (low spin)	CFSE	WFL (High spin)	CFSE
$d^1$	t <sub>2g</sub> <sup>1</sup> e <sub>g</sub> <sup>0</sup>	-0.4Δ <sub>o</sub>	t <sub>2g</sub> <sup>1</sup> e <sub>g</sub> <sup>0</sup>	= 0.4Δ <sub>o</sub>
$d^2$	t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>0</sup>	-0.8Δ <sub>o</sub>	t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>0</sup>	-0.8Δ <sub>o</sub>
$d^3$	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>0</sup>	-1.2Δ <sub>o</sub>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>0</sup>	-1.2Δ <sub>o</sub>
$d^4$	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>0</sup>	-1.6Δ <sub>o</sub> + P	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup>	-0.6Δ <sub>o</sub>
$d^5$	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>0</sup>	-2Δ <sub>o</sub> + 2P	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>2</sup>	0
$d^6$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>0</sup>	-2.4Δ <sub>o</sub> + 2P	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>2</sup>	-0.4Δ <sub>o</sub>
$d^7$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>1</sup>	-1.8Δ <sub>o</sub> + P	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup>	-0.8Δ <sub>o</sub>
$d^8$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	-1.2Δ <sub>o</sub>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	-1.2Δ <sub>o</sub>
$d^9$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>3</sup>	-0.6Δ <sub>o</sub>	t <sub>2g</sub> <sup>6</sup> t <sub>2g</sub> <sup>3</sup>	-0.6Δ <sub>o</sub>
$d^{10}$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>4</sup>	0	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>3</sup>	0

\* CFT & MOT were combined into ligand field theory by van Vleck & Orgel

# spinels  $\rightarrow$  it is mixed-metal oxides that have many useful magnetic properties.

General formula:  $[AB_2O_4]$

Normal  
Spinel  
Structure

A: Bivalent metal ion ( $A^{2+}$ )

B: Trivalent metal ion ( $B^{3+}$ )

$O^{2-} \rightarrow$  FCC Array

A  $\rightarrow$   $\frac{1}{8}$  th of tetrahedral holes

B  $\rightarrow$   $\frac{1}{2}$  of octahedral holes

Commonly denoted as  $A[B_2]O_4$

$[ ] \rightarrow$  octahedral sites

e.g.  $Mg^{2+}[Al^{3+}]_2O_4$

e.g. exception:  $A^{4+}B_2^{2+}O_4$

(e.g.  $Ti^{4+}[Co^{2+}]_2O_4$ )

high  
spin  
config.

Inverted  
Spinel  
Structure

$B[AB]O_4$

A: Octahedral hole

2B: Octahedral hole

B: tetrahedral hole

$Mn_3O_4 \rightarrow$  Normal spinel

$Fe_3O_4 \rightarrow$  Inverse spinel

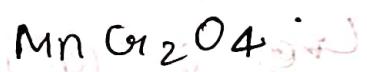
occupation factor ( $\lambda$ ) of a spinel is the fraction of ions in the tetrahedral sites in a normal spinel

$$\lambda = \frac{1}{2} = 0.5$$

for an inverse spinel.

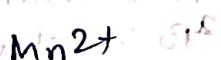
Intermediate values of  $\lambda$  indicate a level of disorder in the distribution.

	A	Mg <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
Al <sup>3+</sup>	d <sup>0</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	0.38	0	0
Cr <sup>3+</sup>	d <sup>3</sup>	0	0	0	0	0	0	0
Mn <sup>3+</sup>	d <sup>4</sup>	0	0	0.5	0.5	0.5	0.5	0
Fe <sup>3+</sup>	d <sup>5</sup>	0.45	0.1	0.5	0.5	0	0	0
Co <sup>3+</sup>	d <sup>5</sup>	0.5	0.5	0.5	0.5	0.5	0.5	0



octahedral

Octahedral site A



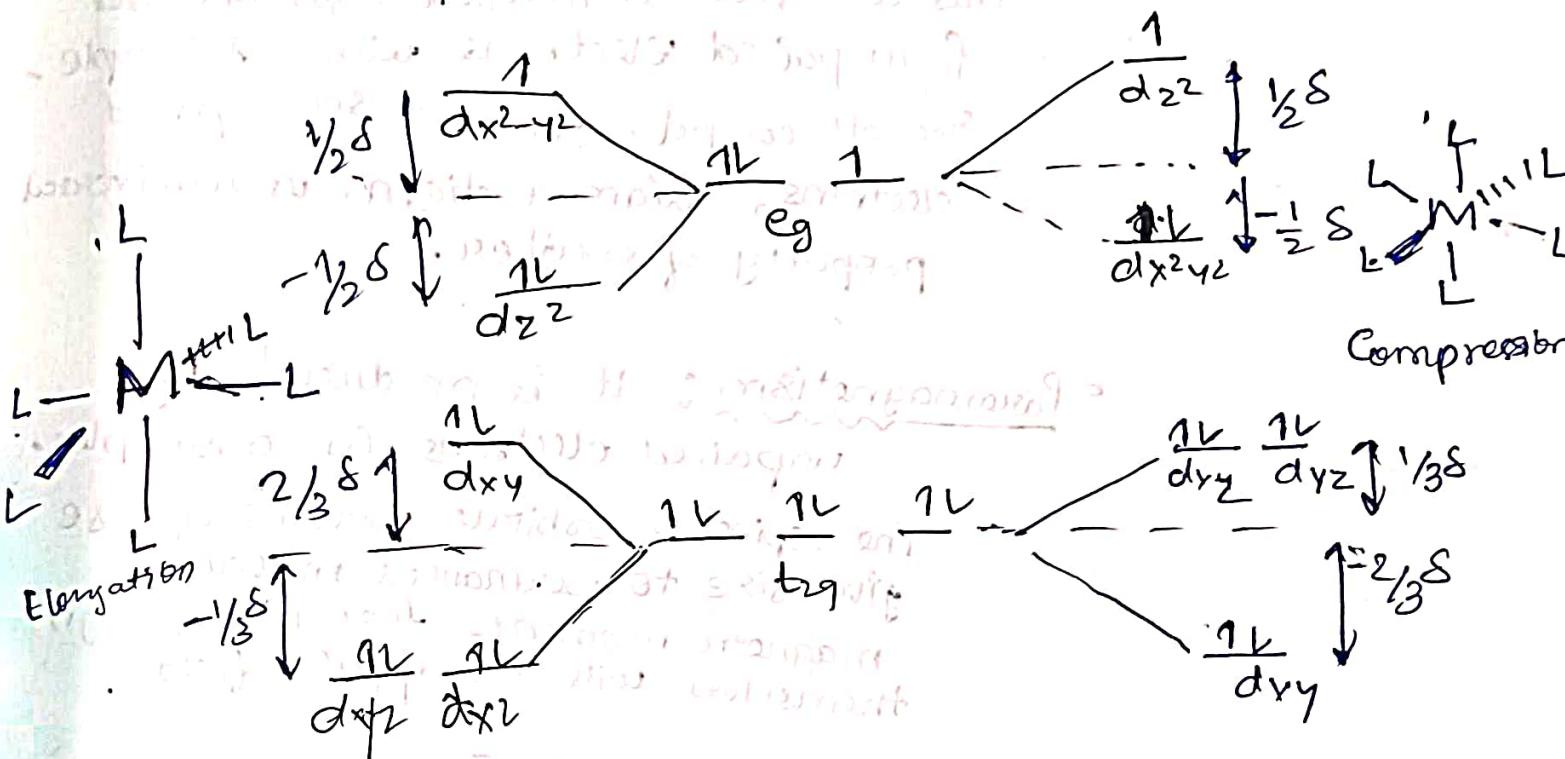
Tetrahedral site B

Normal spinel structure

## # Jahn-Teller Effect :-

The Jahn-Teller effect states that degenerate orbitals (those with identical energies) cannot be unequally occupied.

To avoid these unfavorable electronic configurations molecules distort (lowers their symmetry) to render these orbitals no longer degenerate



In short Jahn-Teller Distortion (JTD)

↳ # In symmetrical octahedral Field

J.T.D is absent

# Half filled

# Fully filled

# HF + F<sup>-</sup>

d <sup>1</sup> ✓	
d <sup>2</sup> ✓	
d <sup>3</sup> ✗	
d <sup>4</sup> ✓	
d <sup>5</sup> ✗	
(WFL)	
d <sup>6</sup> ✓	

d<sup>6</sup> ✓  
(WFL)

d<sup>6</sup> ✗  
(CSFL)

d<sup>7</sup> ✓

d<sup>8</sup> ✗

d<sup>9</sup> ✓

d<sup>10</sup> ✗

| J.T.D is absent in  
d<sup>3</sup>, d<sup>5</sup>, d<sup>6</sup>, d<sup>8</sup>, d<sup>10</sup>  
(WFL), (CSFL)

3, 5, 6, 8, 10

| J.T.D is present in  
d<sup>1</sup>, d<sup>2</sup>, d<sup>4</sup>, d<sup>5</sup>, d<sup>6</sup>, d<sup>7</sup>, d<sup>9</sup>  
(WFL), (CSFL)

## # Magnetic Properties

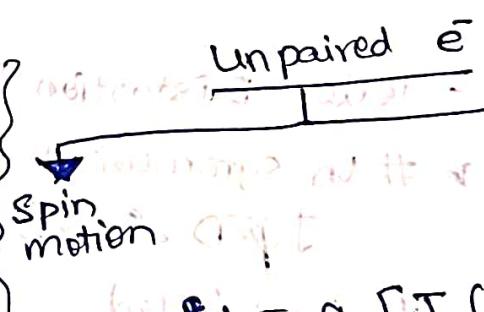
Diamagnetism: when any substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in opposition to the applied field. This is the diamagnetic effect it arises from paired electrons within a sample. Since all compd. contain some paired electrons, diamagnetism.. is a universal property of matter.

Paramagnetism: It is produced by unpaired electrons in a sample. The spins & orbital motions of these give rise to permanent molecular magnetic moments that tend to align themselves with an applied field.

There are 3 possible modes of coupling b/w these components

① spin-spin coupling  
② orbital-orbital coupling

③ spin-orbital coupling



$$\mu = g [J(J+1)]^{1/2}$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

The complex in which spin orbit coupling is negligible

$$\text{then } \mu = [4S(S+1) + L(L+1)]^{1/2}$$

$$\text{for } L=0 \quad \mu = [4S(S+1)]^{1/2}$$

$$\mu = 2[S(S+1)]^{1/2} BM$$

$J$ : Total angular momentum quantum no.

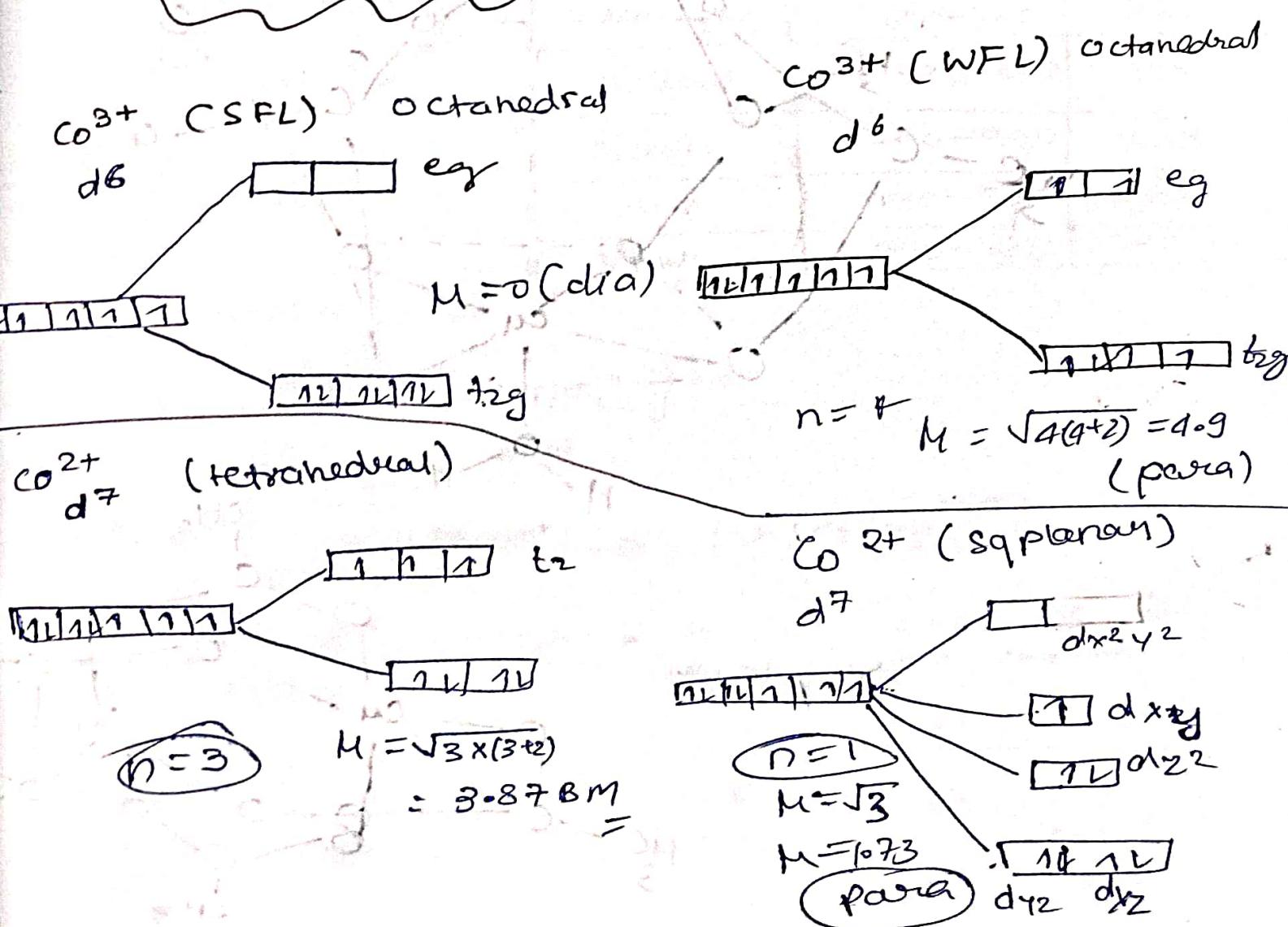
$g$ : g-factor

$L$ : Orbital angular momentum quantum no.

$S$ : Spin Angular momentum quantum no.

Central metal	No. of 'f' electrons	Ground State	Compound	$\mu_{(exp)}$ BM	$\mu_{(calc)}$ BM
$Ce^{3+}$	1	$^2F_{5/2}$	$Ce_2Mg_3(NO_3)_6 \cdot 24H_2O$	2.28	2.54
$Gd^{3+}$	7	$^8S_{3/2}$	$Gd_2(SO_4)_3 \cdot 3H_2O$	7.91	7.94
$Yb^{3+}$	13	$^2F_{7/2}$	$Yb_2(SO_4)_3 \cdot 3H_2O$	4.88	4.50

$$\mu = [n(n+2)]^{1/2} \cdot BM$$

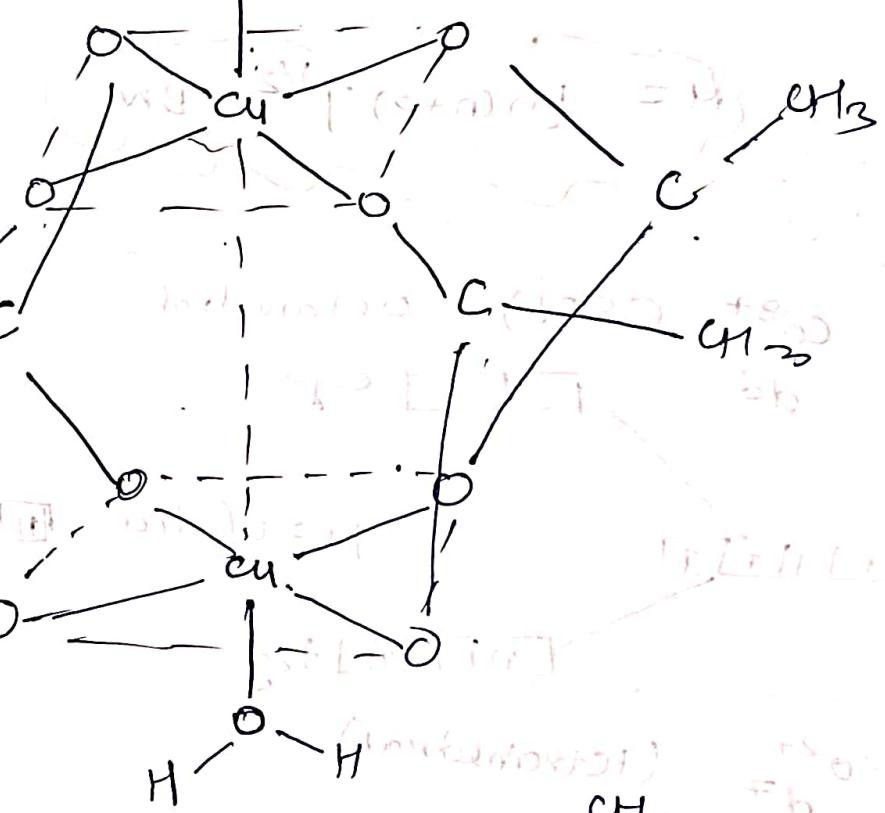
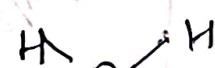


# special case of copper acetate

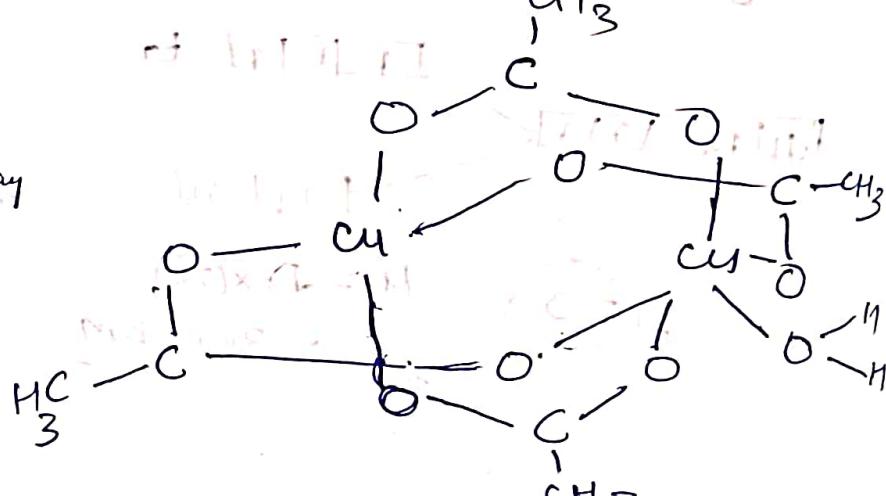
monohydrate  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$



$\downarrow$   
exists as dimer the magnetic moment of compound is



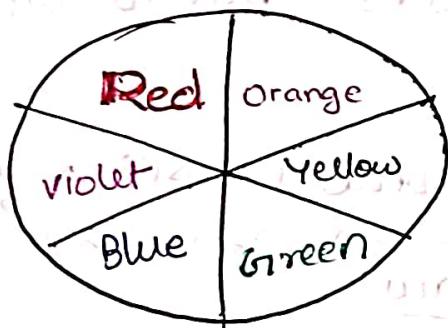
Simple way



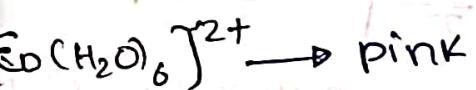
In its structure, the acetate groups act as bidentate bridging groups between the two copper atoms. Each copper atom is surrounded by 4 oxygen atoms in a square planar arrangement. The 5th position around each Cu atom is occupied by the O-atom from a water molecule. The other Cu atom occupies 6th of octahedral positions.

There is weak coupling of spin of unpaired e<sup>-</sup> on the two copper atom in the dimeric structure.

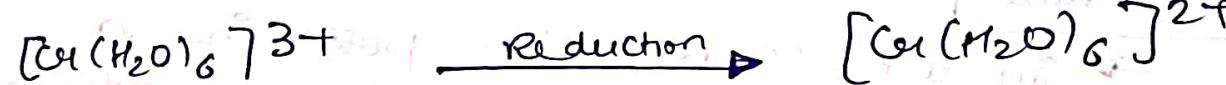
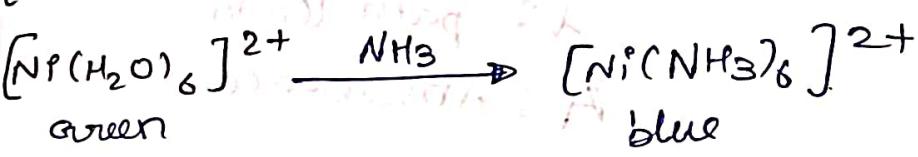
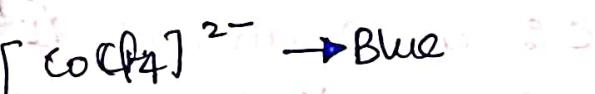
### # Electronic Spectra of Transition metal complex :-



Colour of light absorbed	Approx. λ ranges / nm	Colour of light transmitted
Red	700 - 620	Green
Orange	620 - 580	Blue
Yellow	580 - 560	Violet
Green	560 - 490	Red
Blue	490 - 480	Orange
Violet	480 - 380	Yellow

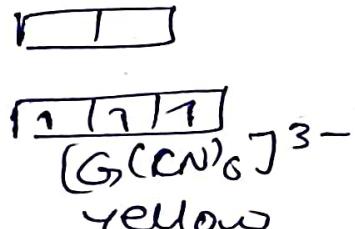
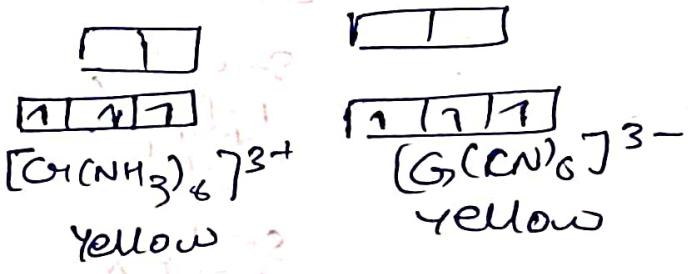
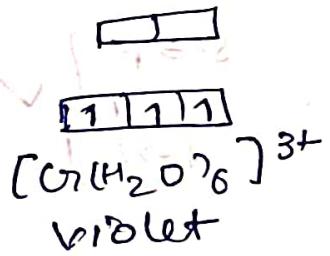
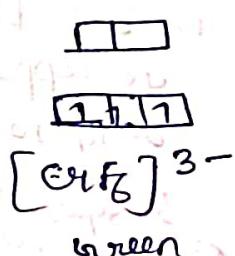


b'octahedral



Violet

These color transitions referred to d-d transitions b'coz they involve Molecular orbitals that are mainly d in character.



$\text{[Ti}(\text{H}_2\text{O})_6]^3+$

- Perfectly octahedral
- should give only one  $\sigma$ -d transition.
- if there distortion occurs to eliminate the degeneracy of system.

→ to begin → complex of  $d^{10}$  e config.  $\Rightarrow$  colourless

→ transitions ab initio  $\rightarrow$  multiple transitions

\* multi-e systems exhibit multiple transitions & assignment of the absorption bands is not straight forward.

The complexity arises due to interelectro repulsions.

# selection Rules for Electronic Transitions :-

The Beer - Lambert Law

$$\rightarrow A = \log_{10} \left( \frac{I_0}{I} \right) = \epsilon cl.$$

$\epsilon$ : molar extinction coefficient

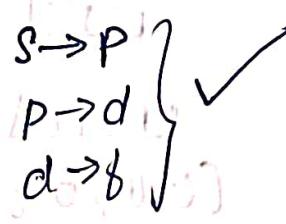
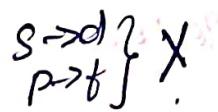
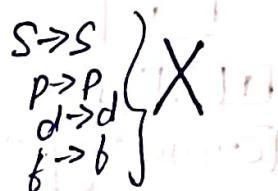
c: concn in mole/l

l: path length

A: Absorbance

### Laporte Rule

→ In a molecule or ion possessing a center of symmetry, transitions are not allowed b/w orbital of same parity. e.g.  $d$  to  $d$  x  $\Delta l = \pm 1$ . Quantum no. should differ by 1.



totally

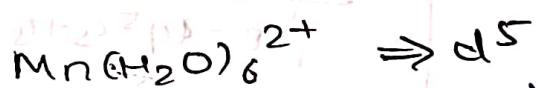
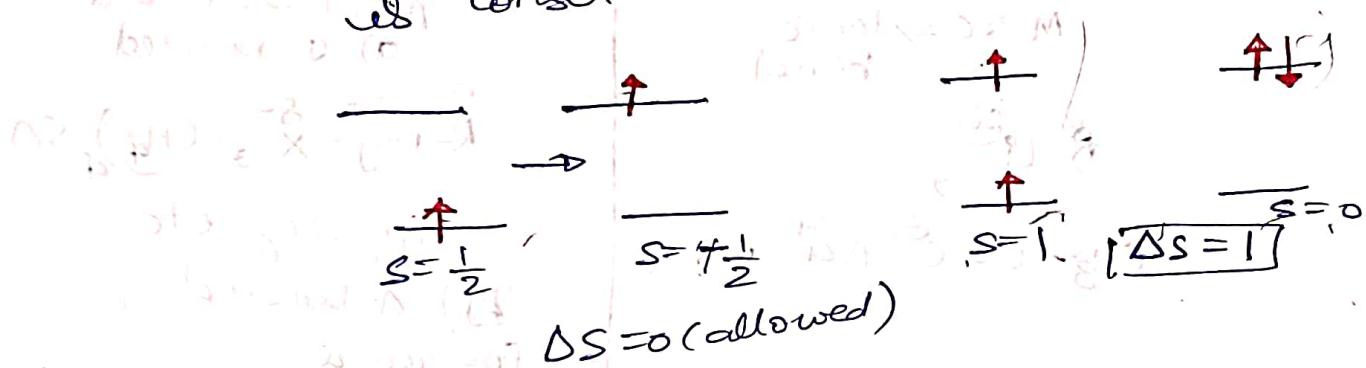
This rule is applied only to octahedral & square planar (Symmetrical geometry)

$E(T_d)$  is a 100 times greater than  $E(O_h)$

Spin - allowed & spin forbidden

spin allowed transition must involve no change in spin state ( $\Delta S = 0$ )

↓  
Promotion of an electron can only proceed if the spin orientation is conserved.



For this complex electronic transition is

not only Laporte forbidden but also spin forbidden there its dilute soln are colourless

Charge Transfer (CT) band :-

Relative energy levels of d-orbitals

i) Ligand to Metal Charge Transfer (LMCT)

e.g.  $MnO_4^-$ ,  $CrO_4^{2-}$  etc.

for  $MnO_4^-$  d<sup>-count</sup> on  $Mn(VII)$  is d<sup>0</sup>.

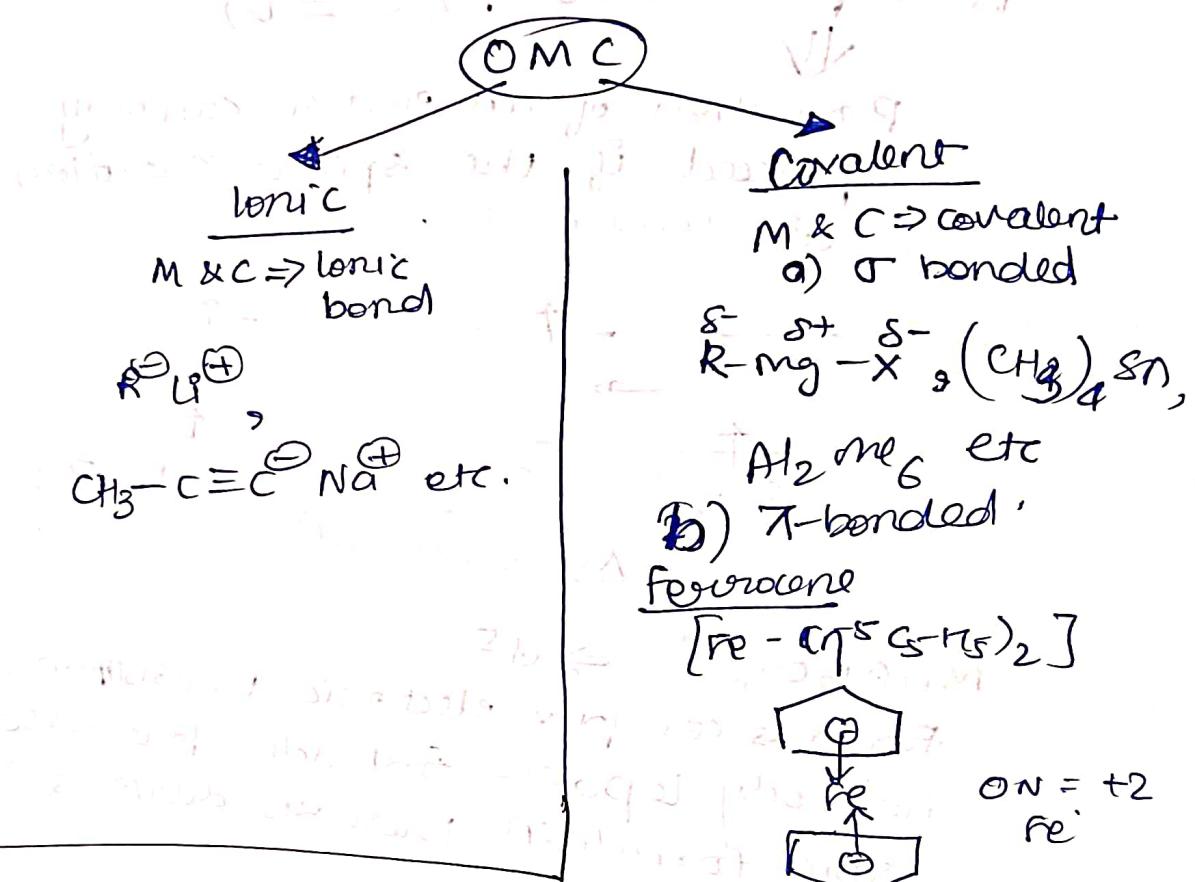
↓  
so color is not due to d-d transition  
but charge transfer from O<sup>2-</sup> to  
 $Mn(VII)$  described as LMCT band.

ii) metal to ligand charge Transfer (MLCT)

e.g.  $[Fe(bpy)_3]^{2+}$  charge transfer from Fe(II) to empty  $\pi^*$  orbitals of bpy ligands

\* organometallic compound,  $\text{O}^-$

compds in which metal is directly bonded with carbon.



C)  $\sigma$  &  $\pi$  bond

