

Module-1 : Chemical Bonding

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

Metallic Bond : Valence bond and Band 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, Jahn 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 CoCl_3 & NH_3

<u>compound</u>	<u>colour</u>	<u>Name according to colour</u>	<u>Coordinate formula</u>
$\text{CoCl}_3 \cdot 6\text{NH}_3$	Yellow	luteo complex	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Purple	Purpureo complex	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	Praseo complex	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	violet	violet complex	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

} isomers

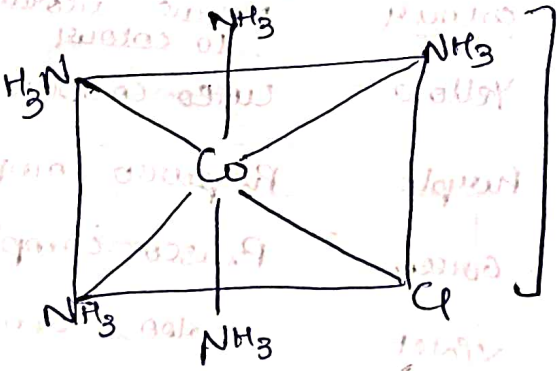
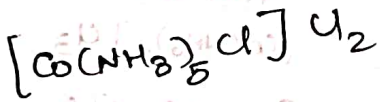
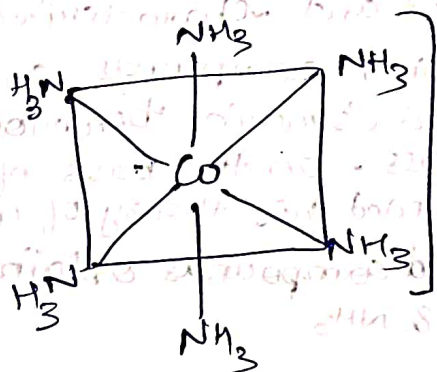
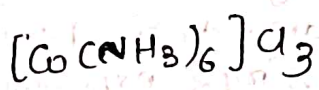
Vgpp

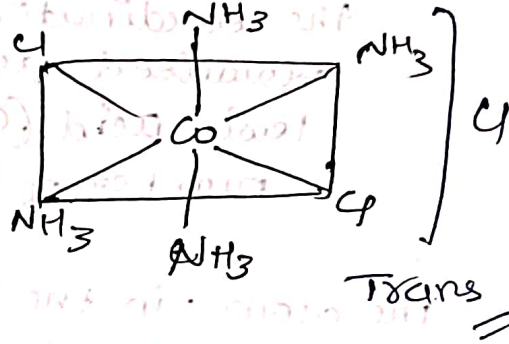
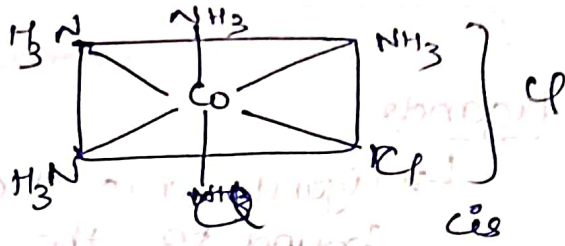
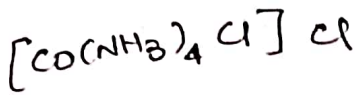
The main postulates of Werner's Theory are :-

In a coordination complex, a metal ion is engaged two types of linkages or valence.

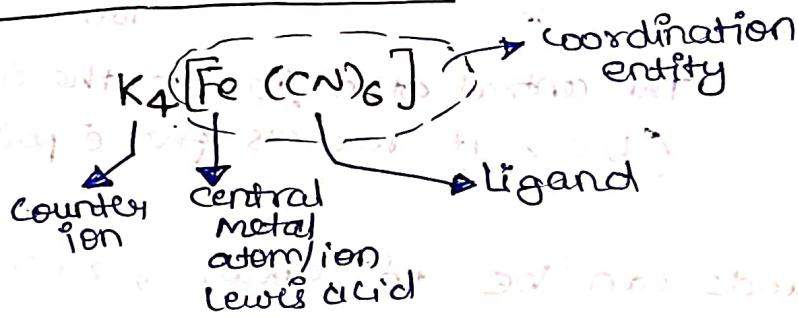
- (i) Primary or Ionisable linkage which are satisfied by negative ions & equal the oxidation state of the metal
- (ii) Secondary or non-ionisable linkage which can be satisfied by neutral or negative ions/groups. The secondary linkages equal to the coordination number of central metal atom/ion.

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

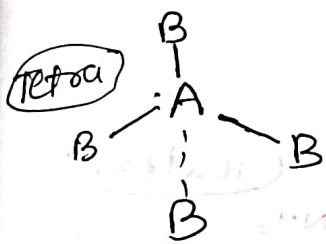




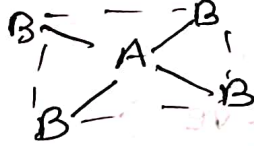
Some imp. terms of C.C.



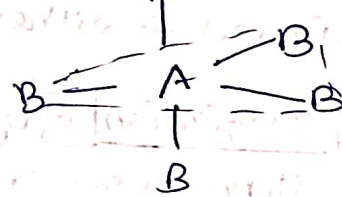
AB_4



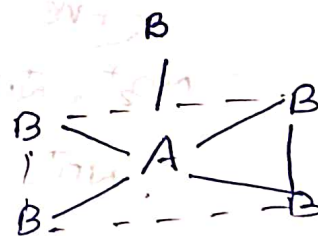
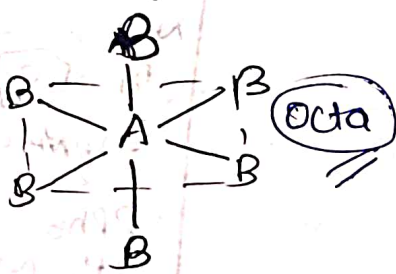
sq planar



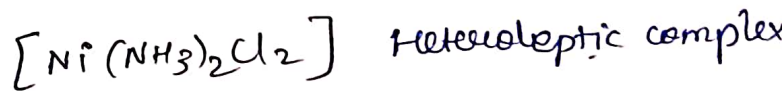
AB_5 TBP



AB_6



square Pyramidal



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** (b'coz it donates the pair of electrons required for bond formation)

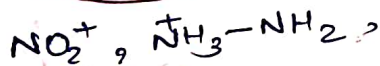
The central atom/ion is the **acceptor atom/ion** (b'coz it receives the e^- pairs from ligands).

- ① Ligands can be σ donor, π donor, π acceptor & π donor.
- ② Ligand is either Lewis base or not

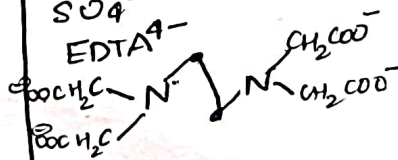
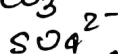
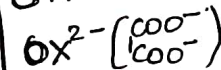
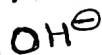
Classification of Ligands

① Based on charge

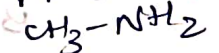
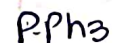
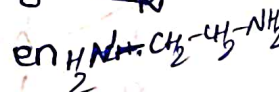
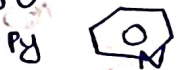
+ve



-ve



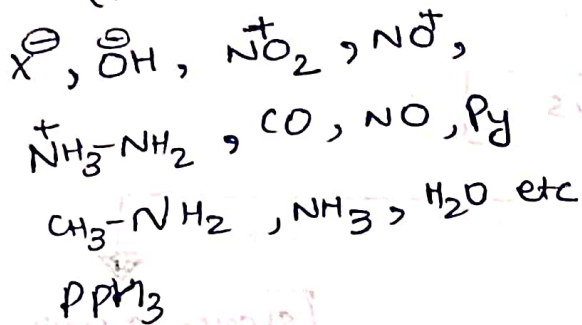
Neutral



② Based on donation (dentistry)

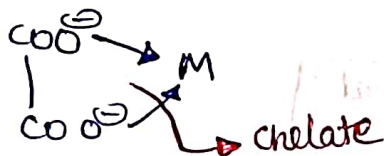
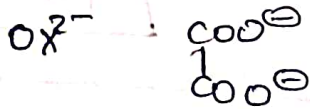
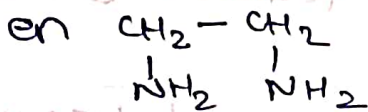
Monodentate

(1 atom donor)



Bidentate

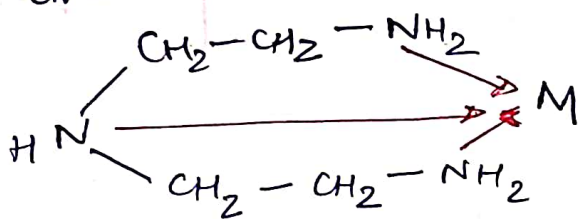
(2 donor atom)



Tridentate

(3 donor atom)

dien



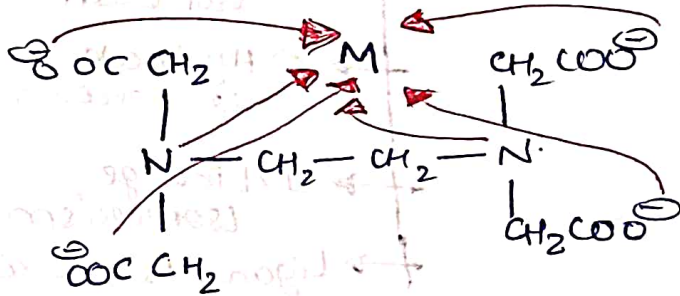
2-chelate forms

Polydentate

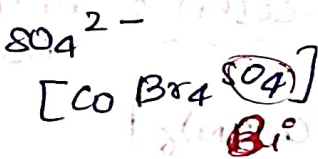
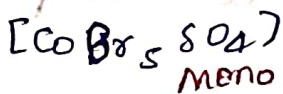
Hexadentate

(6 donor atom)

$EDTA^{4-}$



Flexidentate



Ambidentate

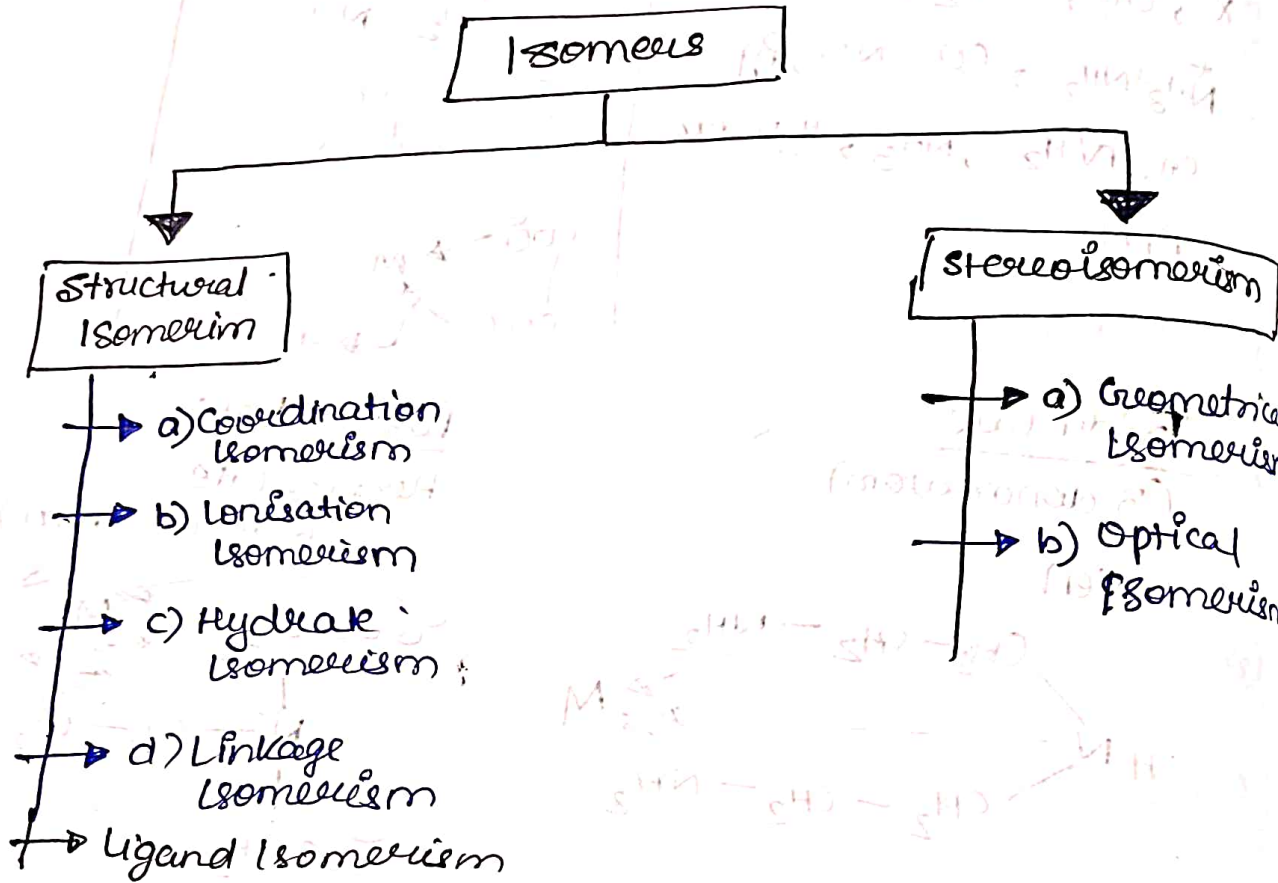
(2 donor atoms)

but only one can donate at a time



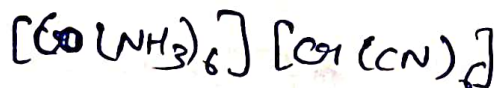
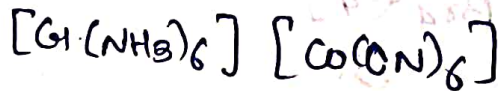
Isomerism

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

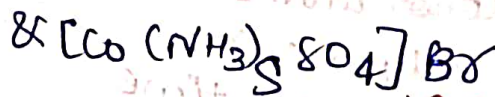
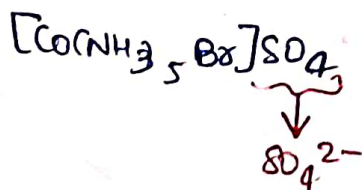


(i) Structural

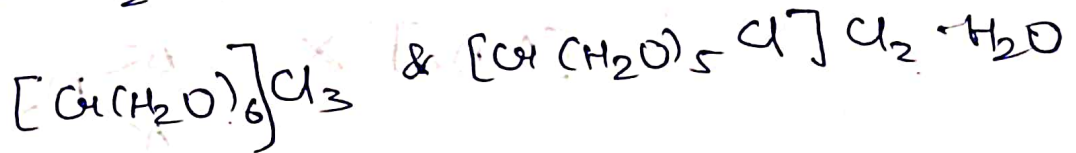
a) Coordination Isomerism: when cation & anion both are complex,



b) Ionisation Isomerism compound which give different ion in soln

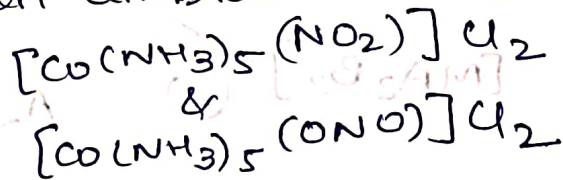


c) Hydrate Isomerism
when H_2O acts as ligand & water of crystallization



d) Linkage Isomerism

↳ when ambidentate ligand is present.



* Ligand Isomerism

eg. 1,2-diaminopropane
1,3-diaminopropane

or ortho, meta & para-toluidine ($CH_3C_6H_4NH_2$)

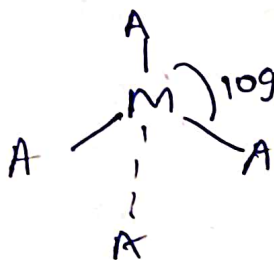
② Stereoisomerism

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 in $CN = 4$

a) Tetrahedral Geometry (MA_4)



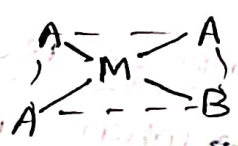
Does not exhibit GI

b) In square planar geometry:

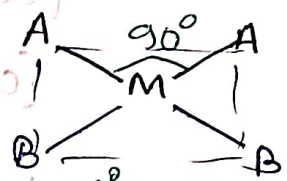
$[MA_4]$ X



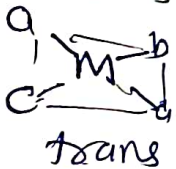
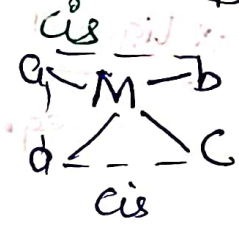
$[MA_3B]$ X



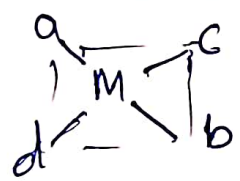
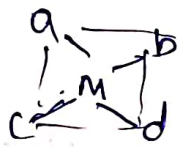
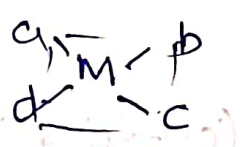
$[MA_2B_2]$ ✓ (2)



$[MA_2BC]$ ✓ (2)



$[MABCD]$ ✓ (3)



$[M(AA)_2]$ X

$[M(AB)_2]$ ✓ (2)

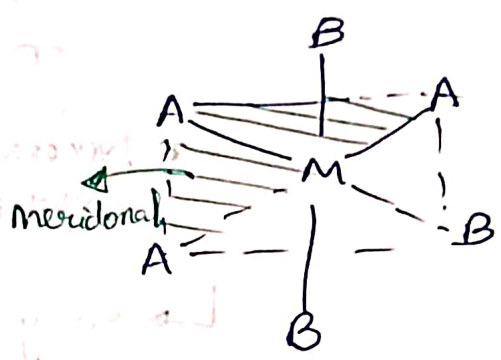
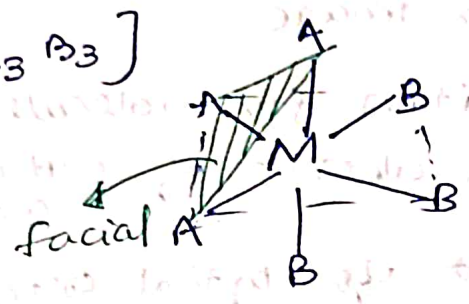
(Faint handwritten notes and diagrams at the bottom of the page, including a diagram of a square planar complex with two A and two B ligands.)

Case-2

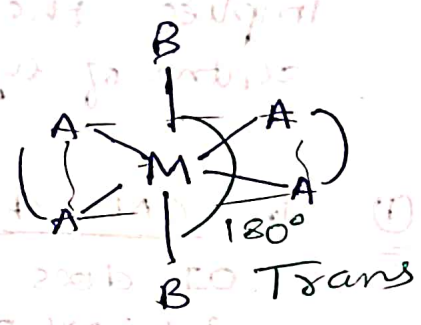
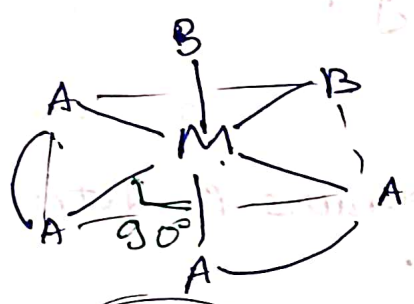
In $C.N = 6$
Octahedral

$MA_6, MA_5B \rightarrow 1$ Geometric form

$[MA_3B_3]$



$[M(AA)_2B_2]$



cis

Complexes

No. of GI

- $[MA_4B_2] \rightarrow 2$
- $[MA_4BC] \rightarrow 2$
- $^* [MA_3B_3]^* \rightarrow 2$
- $[MA_3B_2C] \rightarrow 3$
- $[MA_3BCD] \rightarrow 4$
- $[MA_2B_2C_2] \rightarrow 5$
- $[MA_2B_2CD] \rightarrow 6$
- $[MA_2BCDE] \rightarrow 9$
- $[MABCDEF] \rightarrow 15$
- $[M(AA)_2B_2] \rightarrow 2$
- $[M(AA)_2BC] \rightarrow 2$
- $[M(AB)_3] \rightarrow 2$

$M(AA)_3$

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

In CN = 4

OI does not exhibit in Tetrahedral & Square planar.

Tetra ~~X~~

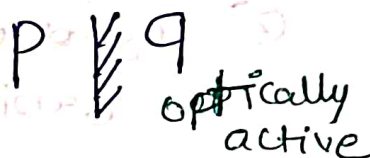
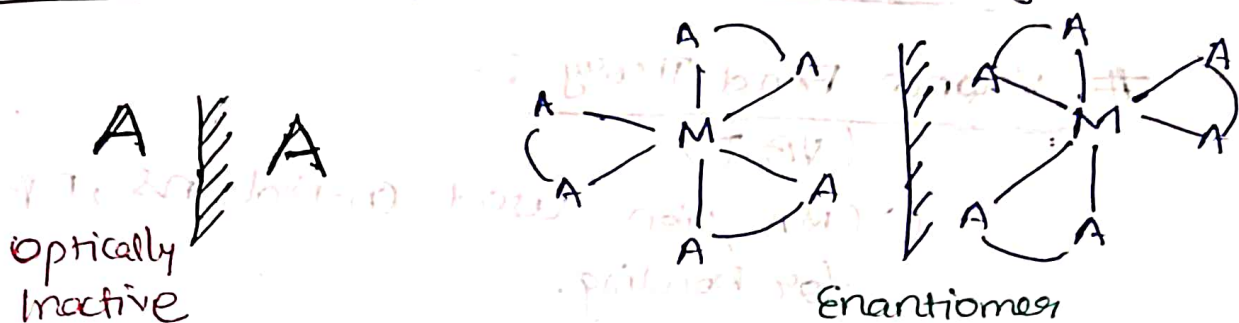
Sq. Planar ~~X~~

Sq. planar complexes → generally optically inactive due to POS ✓

b'coz of presence of asymmetric ligand

↳ optical isomerism may appear.

* Enantiomer → Non-superimposable Mirror Images.



* Diastereomers - Stereoisomers which do not possess mirror image relation.

* Asymmetric molecule : A molecule without any symmetry.

$M(AA)_3$ exhibits OI ✓
Not GI OT ✓
GI ✗

Case - (2) i.n. $CN = 6$

Complexes	GI	Enantiomer Pair	Stereoisomers
$[MA_4B_2]$	2	0	2
$[MA_4BC]$	2	0	2
$[MA_3B_3]$	2	0	3
$[MA_3B_2C]$	3	0	5
$[MA_3B_2D]$	4	1	6
$[MA_2B_2C_2]$	5	2	8
$[MA_2B_2CD]$	6	6	15
$[MA_2B_1C_1D_1E_1]$	9	15	30
$[MAB_1C_1D_1E_1F_1]$	15	1	3
$[M(AA)_2B_2]$	2	1	3
$[M(AA)_2BC]$	2	1	3
$[M(AA)_3]$	2	2	4

Bonding Theories

Valence Bond Theory :-

(VBT)

① CMA / ion used $(n-1)d, ns, np$ or $ns, np, (n-1)d$ for bonding.

② ligand will donate LP to the vacant orbital of CMA / ion

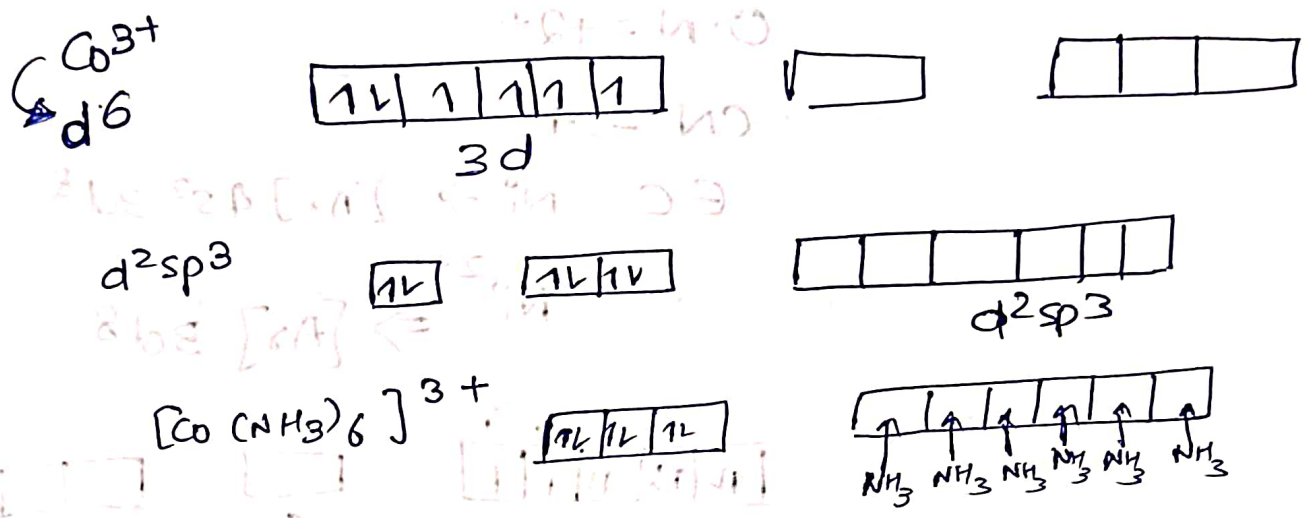
③ Pairing occurs when strong field ligands like NH_3, CN^{\ominus}, CO etc are present

Some Hybridisation schemes for complex comp.

CN	Geometry	Hybridisation	Orbitals Involved
2	Linear	sp	(s, p _z)
3	Trigonal Planar	sp ²	(s, p _x , p _y)
4	Tetrahedral	sp ³ d ³ s	sp ³ (s, p _x , p _y , p _z) d ³ s (d _{xy} , d _{yz} , d _{xz})
	Square planar	dsp ²	(d _{z²} , s, p _x , p _y)
5	Trigonal bipyramid	dsp ³	dsp ³ (d _{z²} , s, p _x , p _y , p _z)
	Square pyramid	dsp ³	dsp ³ (d _{x²-y²} , s, p _x , p _y , p _z)
6	Octahedral	d ² sp ³ sp ³ d ²	d _{z²} , d _{x²-y²} , s, p _x , p _y , p _z
	trigonal prism	d ² sp ³	d _{yz} , d _{xz} , s, p _x , p _y , p _z

eg.

Diamagnetic octahedral complex $[Co(NH_3)_6]^{3+}$

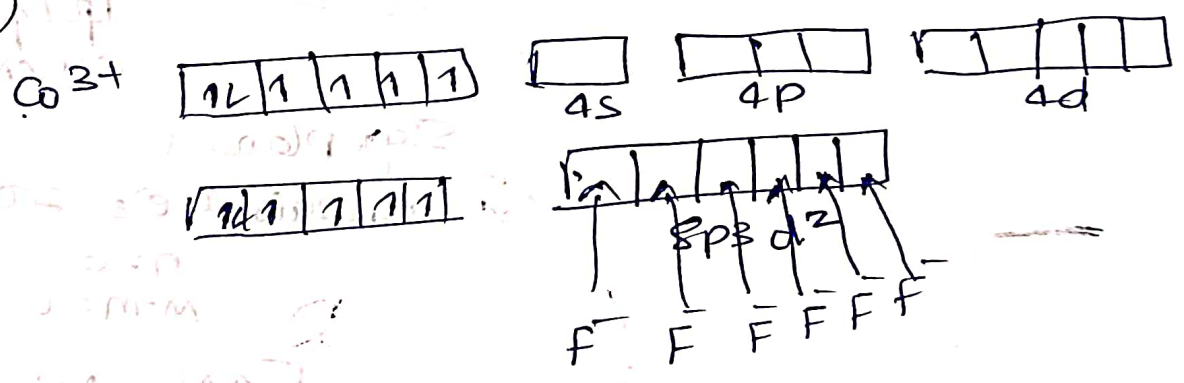


inner orbital or low spin

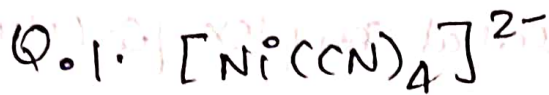
$[CoF_6]^{3-}$

outer orbital or high spin complex

(sp^3d^2)



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

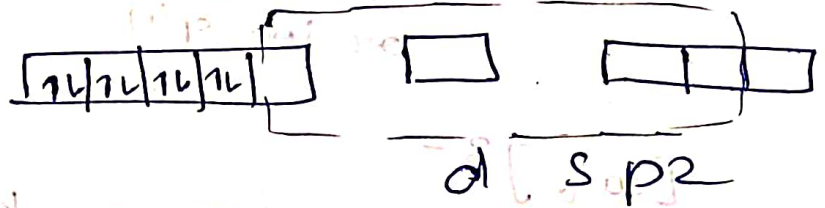
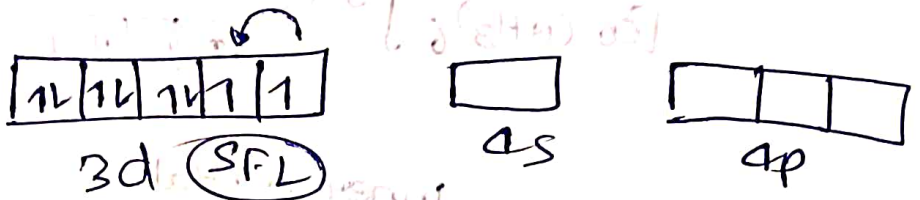


$O.N = +2$

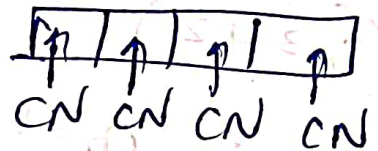
$CN = 4$

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

$\text{Ni}^{2+} \Rightarrow [\text{Ar}] 3d^8$



dsp^2



Sq. planar

unpaired $e^- \Rightarrow 0$

$n = 0$

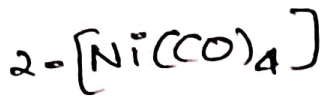
$M.M = 0$ Diamagnetic

$EAN = AN - O.N + 2 \times CN$

$= 28 - 2 + 2 \times 4$

$= 34$

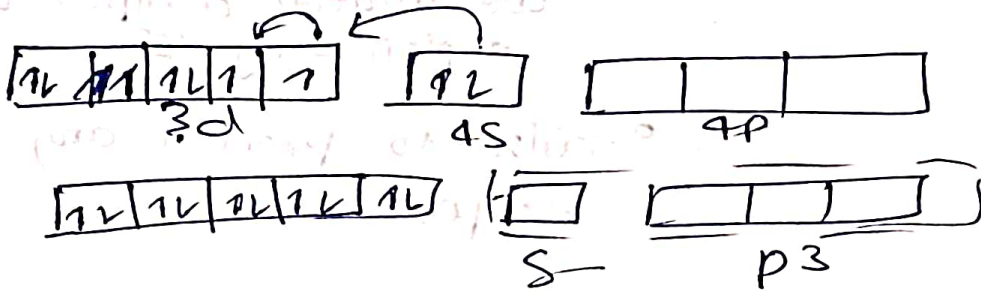
colourless



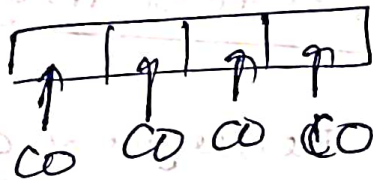
ON = 0

CN = 4

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



sp^3



Tetrahedral

unpaired e = 0

$n = 0$

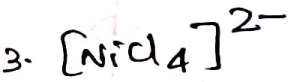
$m \cdot m = 0$

Diamagnetic

$E_{AN} = AN - DN + 2 \times C \cdot N = 28 - 0 + 2 \times 4$

$= 36$

colourless



ON = +2

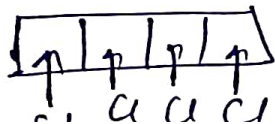
CN = 4

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

$^{28}\text{Ni}^{2+} \Rightarrow [\text{Ar}] 4s^0 3d^8$



sp^3



Tetrahedral

unpaired e = 2
 $n = 2$

$m \cdot m = 3$

Paramagnetic

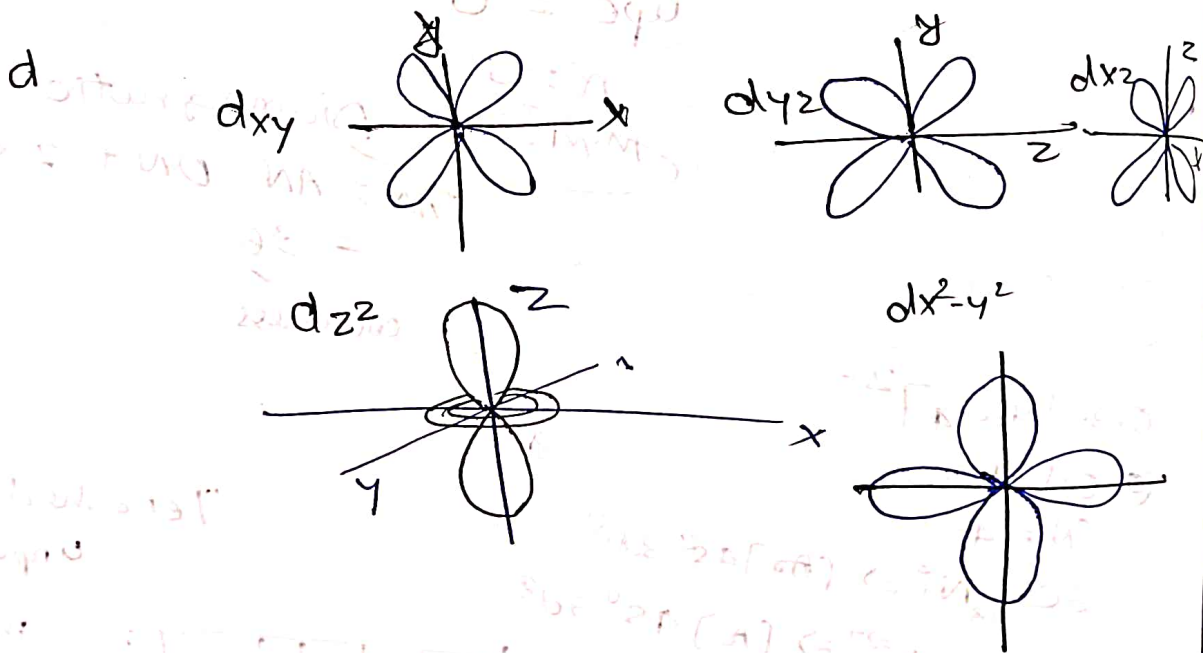
coloured.

Limitation of VBT

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

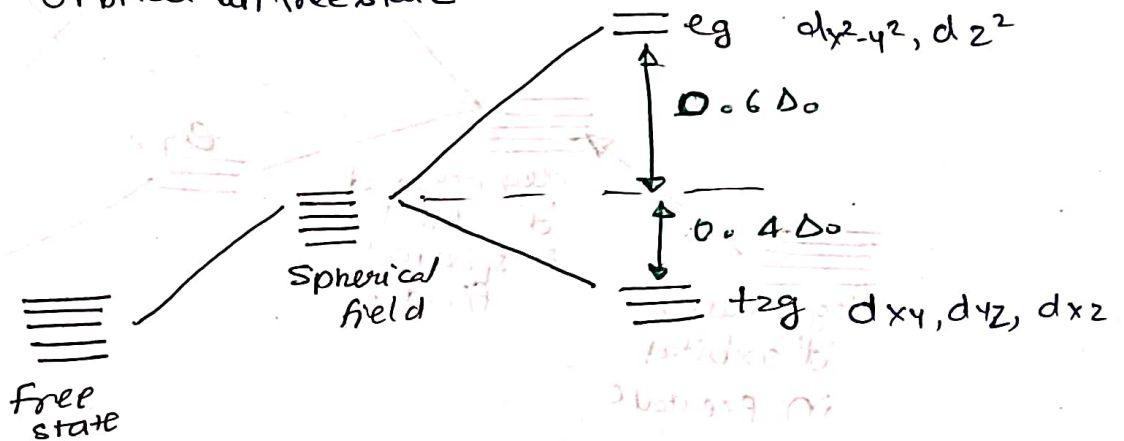
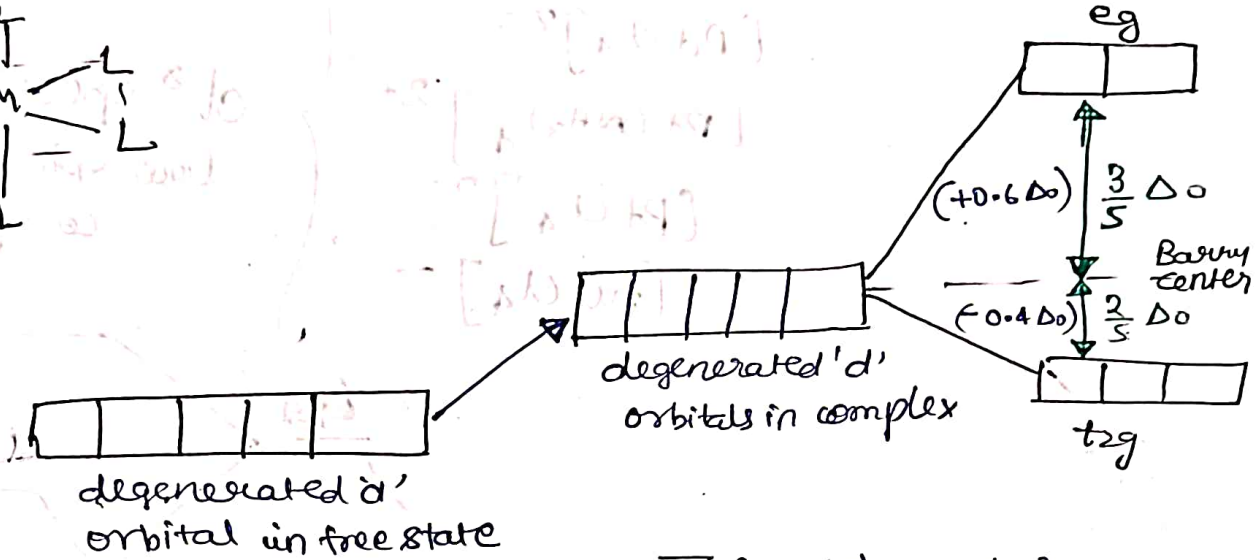
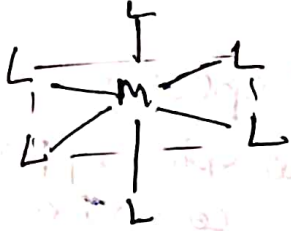
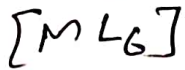
Crystal Field Theory (CFT) :-

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

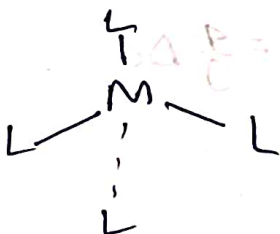


$\Delta_0 \Rightarrow$ CFSE (Crystal field Splitting energy)

Case-① in octahedral field

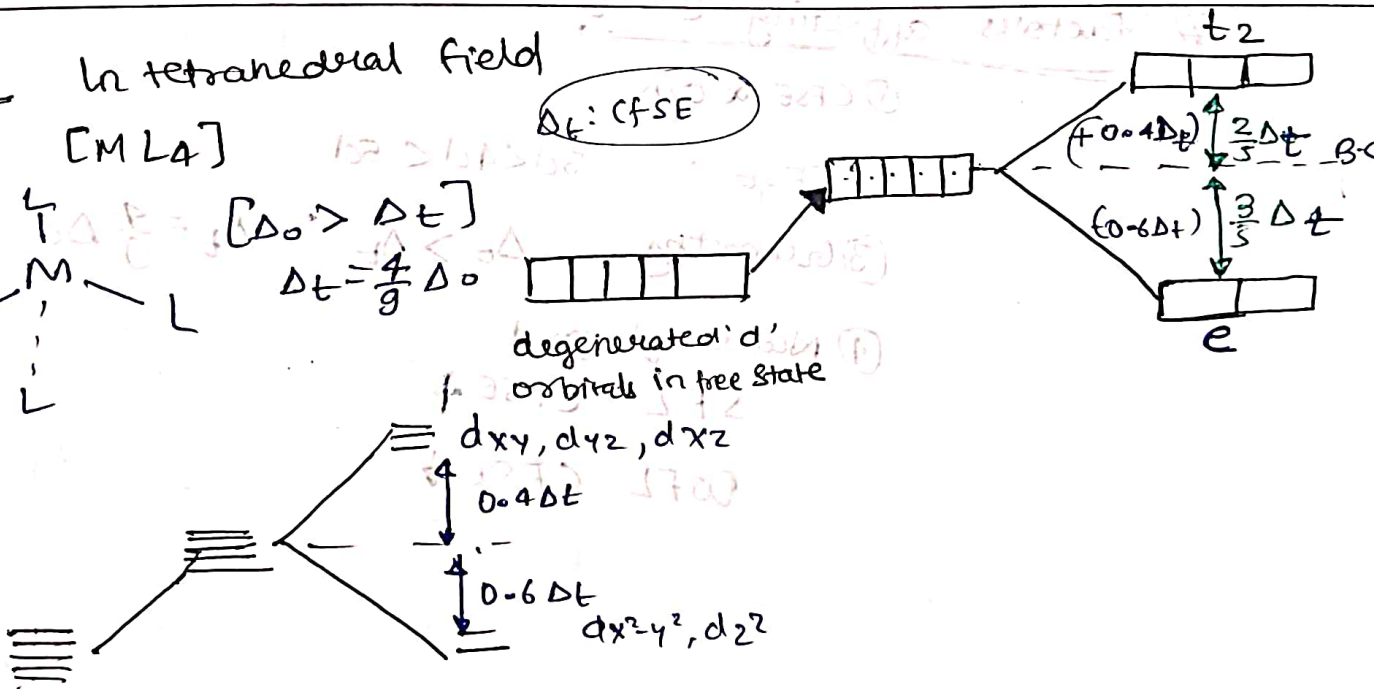


Case-② In tetrahedral field

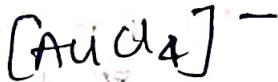
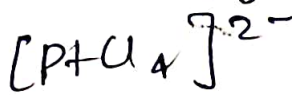
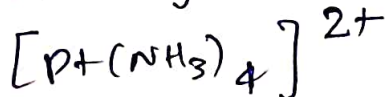
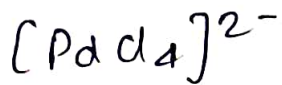
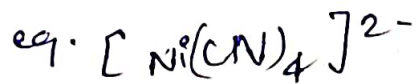


$\Delta_0 > \Delta_t$
 $\Delta_t = \frac{4}{9}\Delta_0$

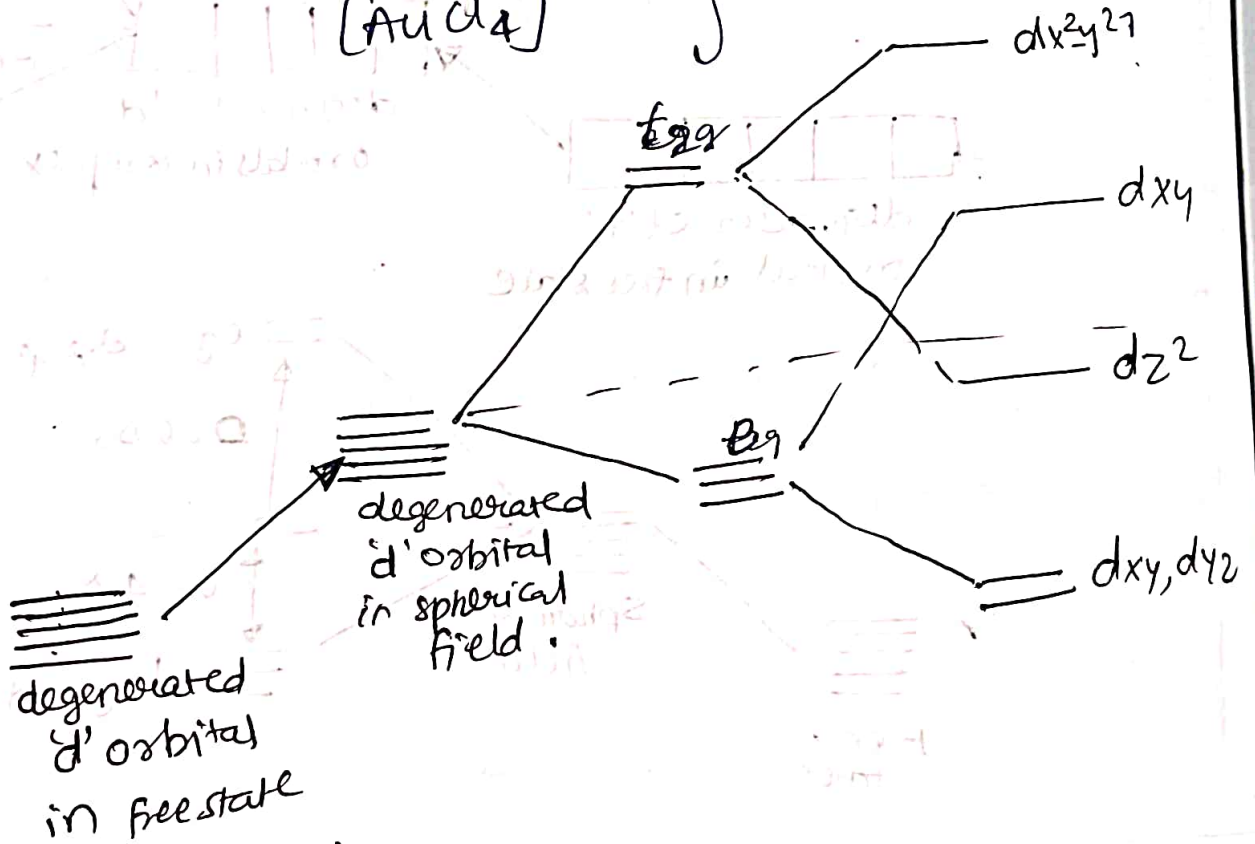
Δ_t : CFSE



Case-3 square planar



d^8 species
low spin sq planar
complexes



Factors affecting CFSE

① CFSE $\propto O.N$

② CFSE : $3d < 4d < 5d$

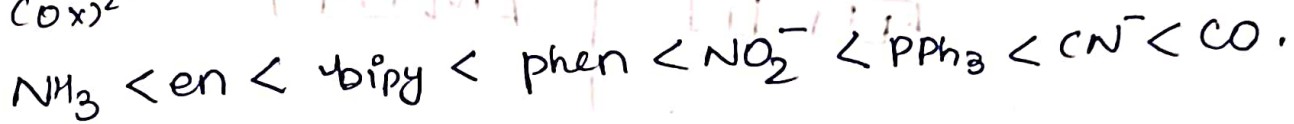
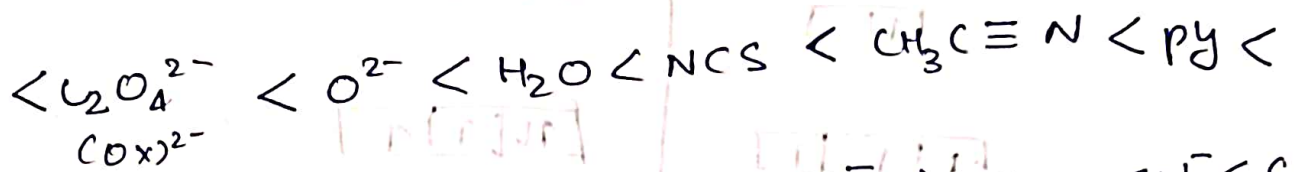
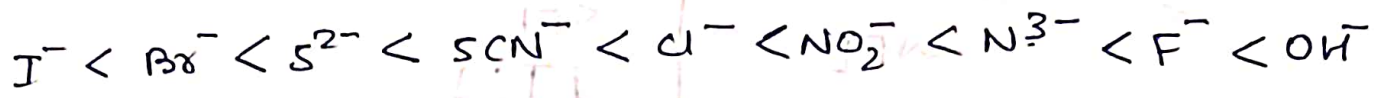
③ Geometry $\Delta_o > \Delta_t$ $\Delta_t = \frac{4}{9} \Delta_o$

④ Nature of Ligand

SFL \cdot CFSE \uparrow

WFL CFSE \downarrow

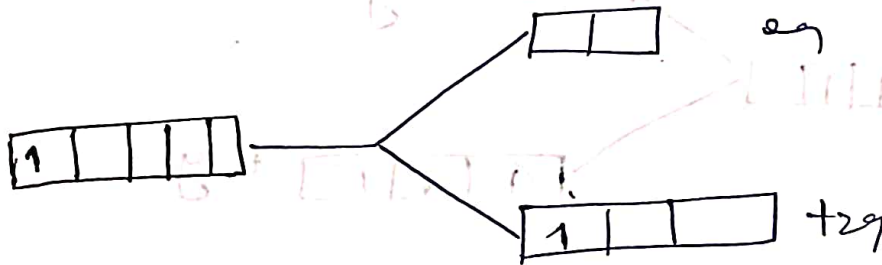
Spectrochemical Series



Calculation of CFSE in octahedral field :-

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

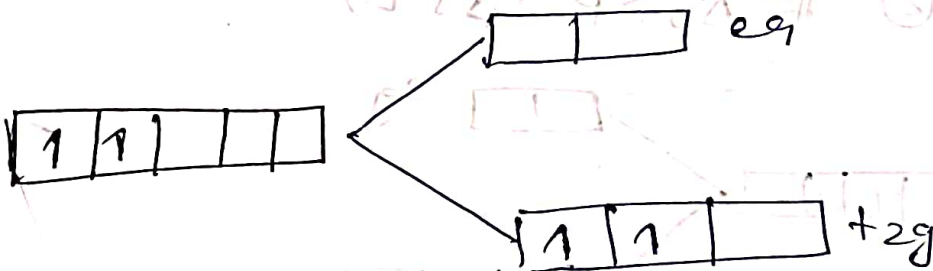
d¹



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

$$= -0.4\Delta_o$$

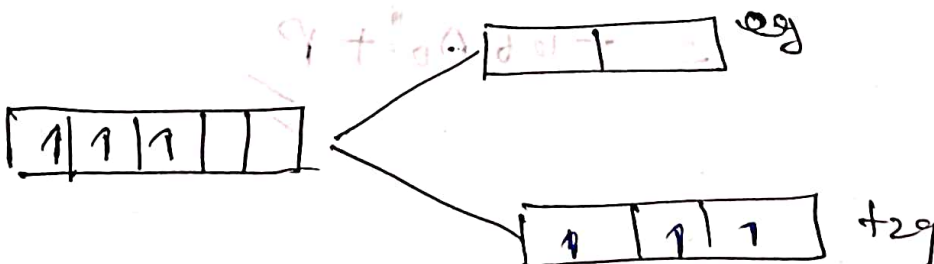
d²



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

$$= -0.8\Delta_o$$

d³

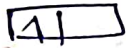


$$CFSE = 3(-0.4\Delta_o) + 0 + 0$$

$$= -1.2\Delta_o$$

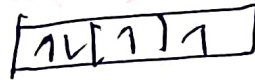
d^4

$\Delta_0 < P$
WFL



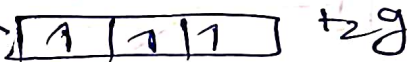
$\Delta_0 > P$

SFL



Case - (1) $\Delta_0 < P$ (WFL)

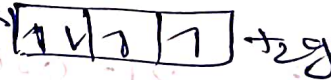
d^4



$$\begin{aligned} \text{CFSE} &= 3(-0.4\Delta_0) + 1(0.6\Delta_0) + 0 \\ &= -0.6\Delta_0 \end{aligned}$$

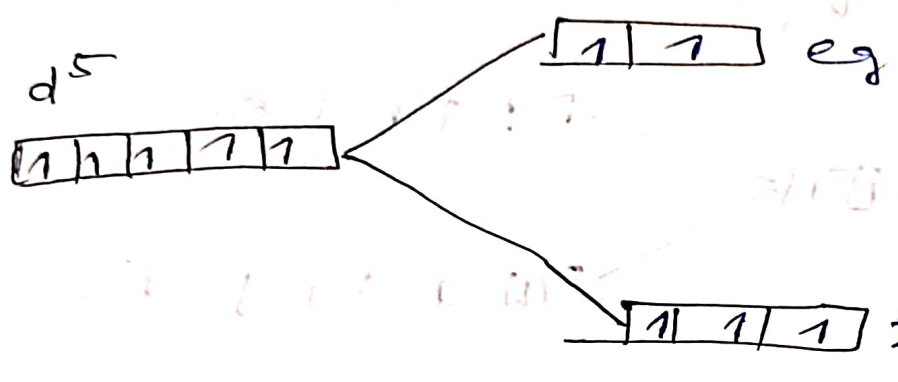
Case - (2) $\Delta_0 > P$ (SFL)

d^4



$$\begin{aligned} \text{CFSE} &= 4(-0.4\Delta_0) + 0(0.6\Delta_0) + P \\ &= -1.6\Delta_0 + P \end{aligned}$$

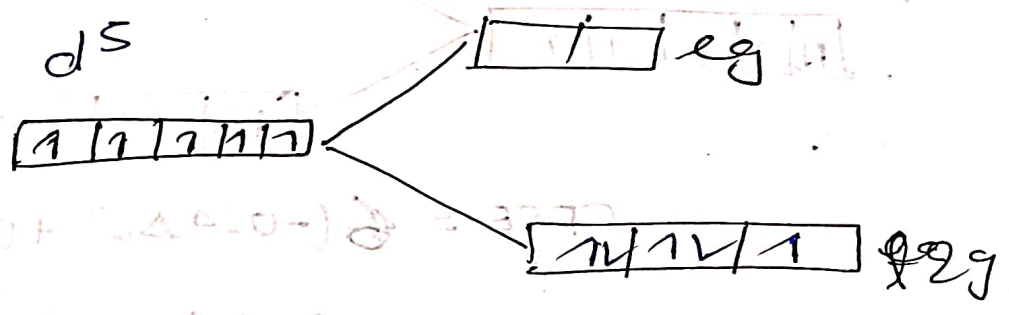
d⁵
 Case - (1) $\Delta_0 < P$ (WFL)



$$CFSE = 3(-0.4\Delta_0) + 2(0.6\Delta_0) + 0$$

$$= 0$$

Case - (2) $\Delta_0 > P$ (SFL)

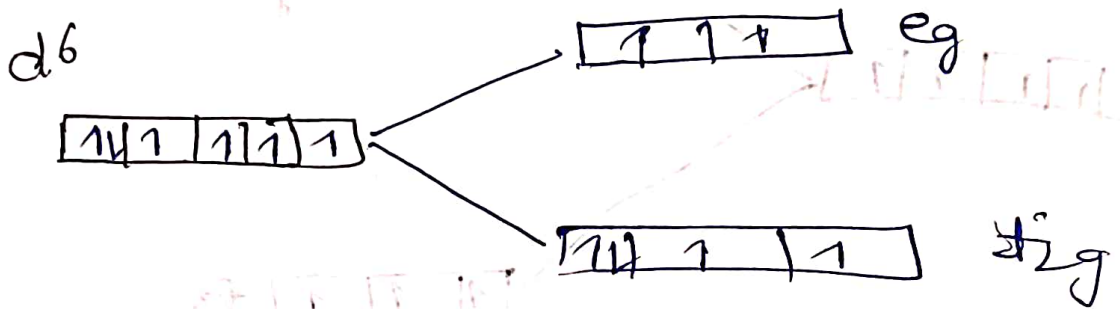


$$CFSE = 3(-0.4\Delta_0) + 0 + 2P$$

$$= -2\Delta_0 + 2P$$

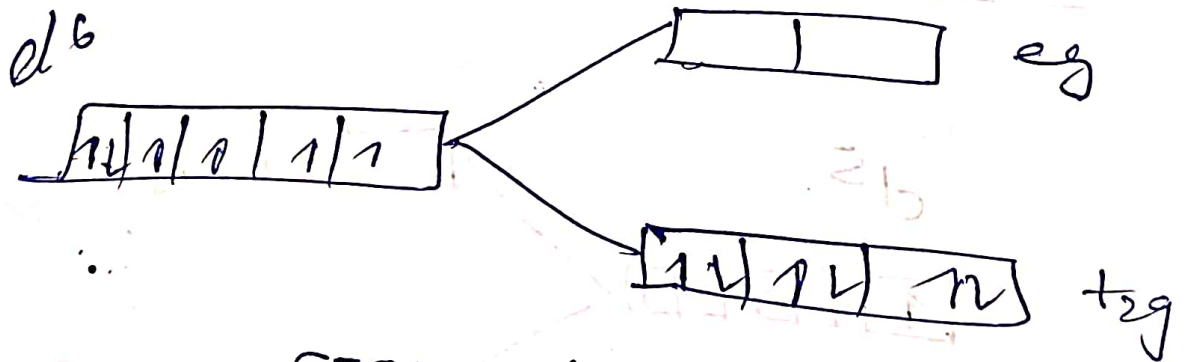
d6

case - ① $\Delta_0 < P$ (WFL)



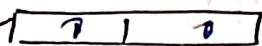
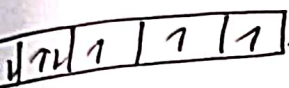
$$\begin{aligned} CFSE &= 4(-0.4\Delta_0) + 2(0.6\Delta_0) + 0 \\ &= -0.4\Delta_0 \end{aligned}$$

case - ② $\Delta_0 > P$ (WFL)

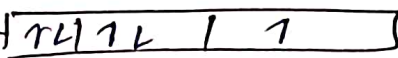


$$\begin{aligned} CFSE &= 6(-0.4\Delta_0) + 0 + 2 \times P \\ &= -2.4\Delta_0 + 2P \end{aligned}$$

Case-① If $\Delta_0 < P$ (WFL)



eg

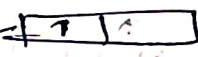
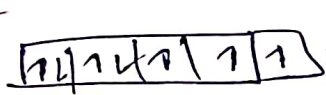


t2g

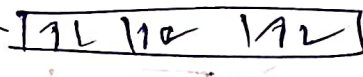
$$CFSE = 5(-0.4\Delta_0) + 0(0.6\Delta_0) + 0$$

$$= -0.8\Delta_0$$

Case-② If $\Delta_0 > P$ (SFL)



eg

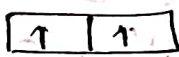
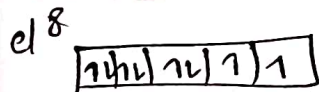


t2g

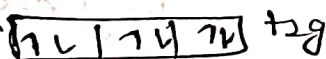
$$CFSE = 6(-0.4\Delta_0) + 1 \times (0.6\Delta_0) + P$$

$$= -1.8\Delta_0 + P$$

Case-① If $\Delta_0 < P$ (WFL)



eg

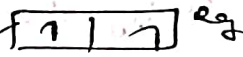
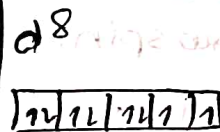


t2g

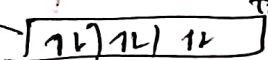
$$CFSE = 6 \times (-0.4\Delta_0) + 2 \times (0.6\Delta_0) + 0$$

$$= -1.2\Delta_0$$

Case-② If $\Delta_0 > P$ (SFL)



eg



t2g

$$CFSE = -1.2\Delta_0$$

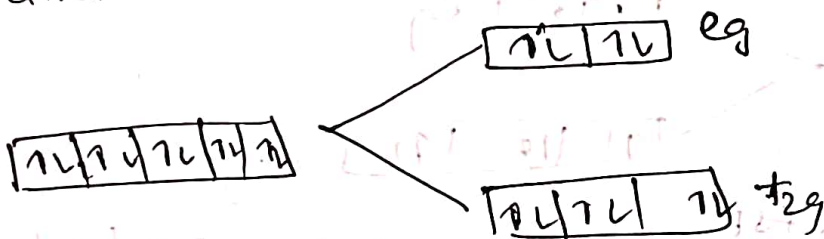
d⁹ either WFL or SFL



$$CFSE = 6(-0.4\Delta_0) + 3(0.6\Delta_0) + 0$$

$$= -0.6\Delta_0$$

d¹⁰ either WFL or SFL



$$CFSE = 6(-0.4\Delta_0) + 4(0.6\Delta_0) + 0$$

$$= 0$$

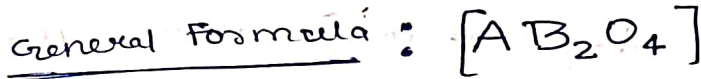
Configuration	SFL (low spin)	CFSE	WFL (High spin)	CFSE
d ¹	t _{2g} ¹ e _g ⁰	-0.4Δ ₀	t _{2g} ¹ e _g ⁰	-0.4Δ ₀
d ²	t _{2g} ² e _g ⁰	-0.8Δ ₀	t _{2g} ² e _g ⁰	-0.8Δ ₀
d ³	t _{2g} ³ e _g ⁰	-1.2Δ ₀	t _{2g} ³ e _g ⁰	-1.2Δ ₀
d ⁴	t _{2g} ⁴ e _g ⁰	-1.6Δ ₀ + P	t _{2g} ³ e _g ¹	-0.6Δ ₀
d ⁵	t _{2g} ⁵ e _g ⁰	-2Δ ₀ + 2P	t _{2g} ³ e _g ²	0
d ⁶	t _{2g} ⁶ e _g ⁰	-2.4Δ ₀ + 2P	t _{2g} ⁴ e _g ²	-0.4Δ ₀
d ⁷	t _{2g} ⁶ e _g ¹	-1.8Δ ₀ + P	t _{2g} ⁵ e _g ²	-0.8Δ ₀
d ⁸	t _{2g} ⁶ e _g ²	-1.2Δ ₀	t _{2g} ⁶ e _g ²	-1.2Δ ₀
d ⁹	t _{2g} ⁶ e _g ³	-0.6Δ ₀	t _{2g} ⁶ e _g ³	-0.6Δ ₀
d ¹⁰	t _{2g} ⁶ e _g ⁴	0	t _{2g} ⁶ e _g ⁴	0

* CFT & MOT were combined into ligand field theory by Griffiths & Orgel

spinels

↳ It is mixed-metal oxides that have very useful magnetic properties.

Normal spinel structure



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

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

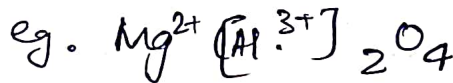
O^{2-} → FCC array

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

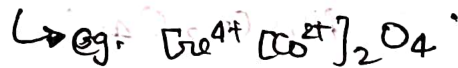
B → $\frac{1}{2}$ of octahedral holes

commonly denoted as $A[B_2]O_4$

[] → octahedral sites

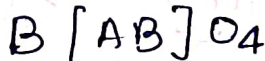


eg. exception: $A^{4+} B_2^{2+} O_4$



} high spin configuration

Inverted spinel structure



A: octahedral hole

2B: octahedral hole

B: tetrahedral hole

Mn_3O_4 → Normal spinel

Fe_3O_4 → Inverse spinel:

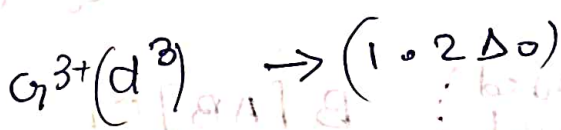
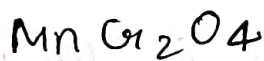
Occupation factor (λ) of a spinel is the fraction of B sites in the tetrahedral sites.

$\lambda = 0$ for a normal spinel

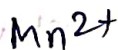
$\lambda = \frac{1}{2} = 0.5$ for an inverse spinel.

Intermediate values of λ indicate a level of disorder in the distribution.

	A	Mg ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
		d ⁰	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰
Al ³⁺ d ⁰	0	0	0	0	0	0.33	0	0
Cr ³⁺ d ³	0	0	0	0	0	0	0	0
Mn ³⁺ d ⁴	0	0	0	0	0	0	0	0
Fe ³⁺ d ⁵	0.45	0.1	0.5	0.5	0.5	0.5	0.5	0
Co ³⁺ d ⁵						0		0



↳ octahedral



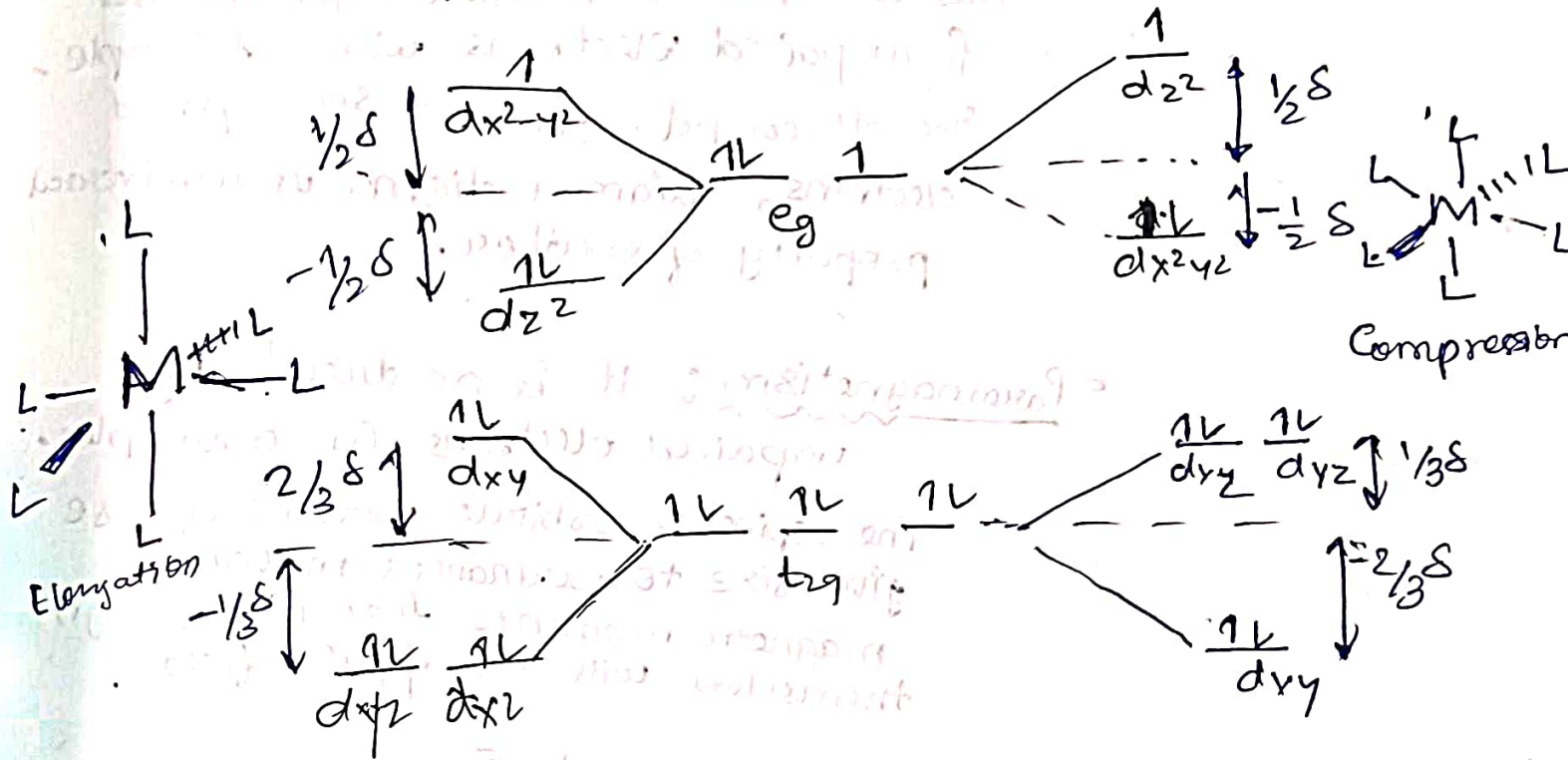
↳ tetrahedral

} 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 unfavourable electronic configurations molecules distort (lowering their symmetry) to render these orbitals no longer degenerate.



In short Jahn-Teller Distortion (JTD)

↳ # In symmetrical octahedral field

JTD is absent

Half filled

Fully filled

HF + FF

- d¹ ✓
- d² ✓
- d³ ✗
- d⁴ ✓
- d⁵ ✗ (WFL)
- d⁶ ✓ (SFL)

- d⁶ (WFL) ✓
- d⁶ (SFL) ✗
- d⁷ ✓
- d⁸ ✗
- d⁹ ✓
- d¹⁰ ✗

JTD is absent in d³, d⁵, d⁶, d⁸, d¹⁰
 (WFL), (SFL)

3, 5, 6, 8, 10

JTD is present in d¹, d², d⁴, d⁵, d⁶, d⁷, d⁹
 (SFL), (WFL)

Magnetic Properties

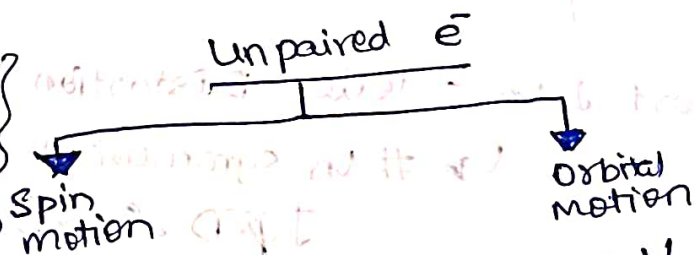
◦ Diamagnetism: when any substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in opposition to the applied field. This is the diamagnetic effect it arises from paired electrons within a sample. Since all compds. contain 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 - then $\mu = [4S(S+1) + L(L+1)]^{1/2}$

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

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

J: Total angular momentum quantum no.

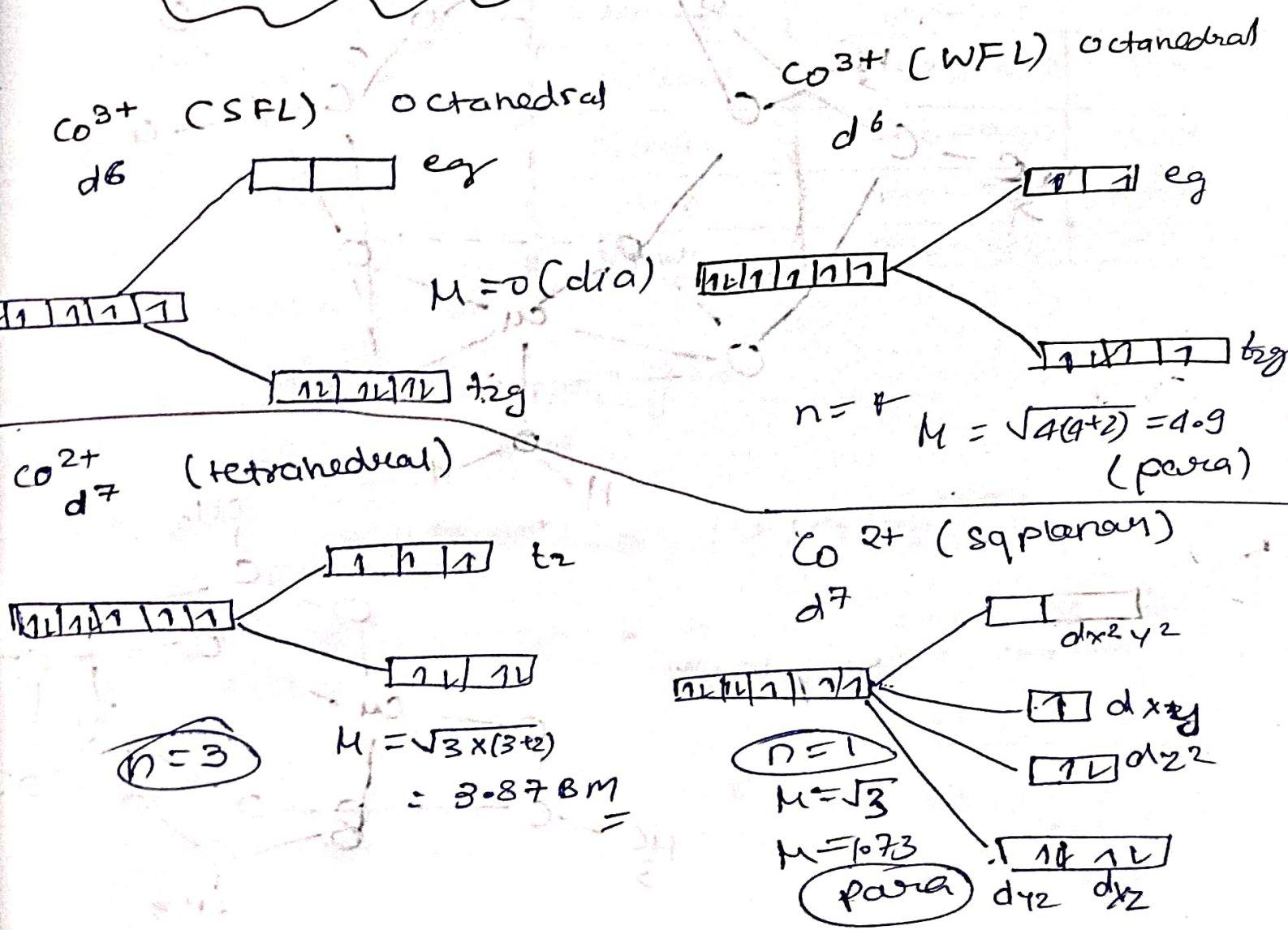
g: g-factor

L: Orbital angular momentum quantum no.

S: Spin angular momentum quantum no.

Central metal	No. of 'f' electrons	Ground state	Compound	μ (expt) BM	μ (Calc) BM
Ce^{3+}	1	$^2F_{5/2}$	$Ce_2Mg(NO_3)_6 \cdot 24H_2O$	2.28	2.54
Gd^{3+}	7	$^8S_{7/2}$	$Gd_2(SO_4)_3 \cdot 8H_2O$	7.91	7.94
Yb^{3+}	13	$^2F_{7/2}$	$Yb_2(SO_4)_3 \cdot 8H_2O$	4.86	4.50

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

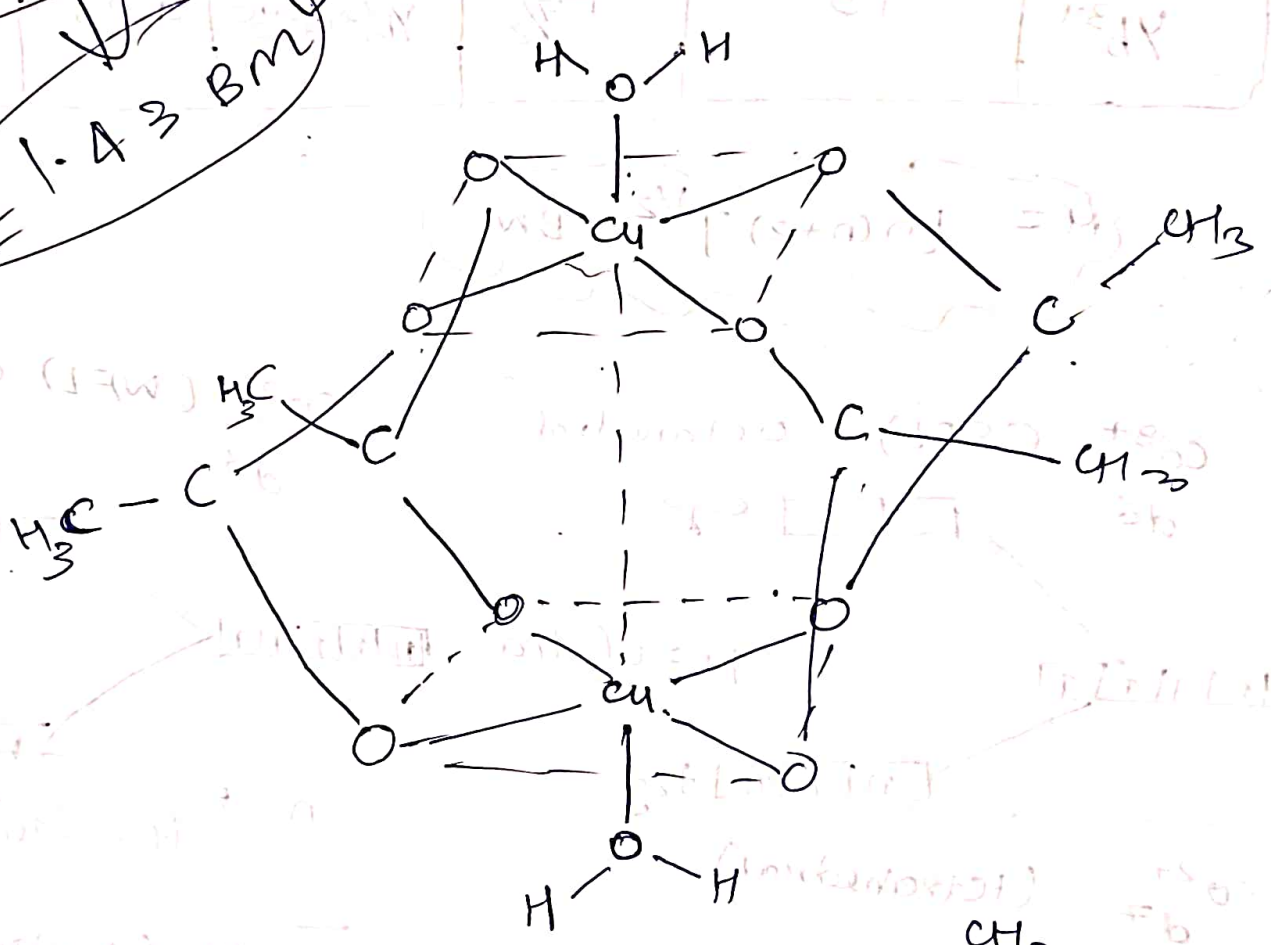


special case of copper acetate monohydrate :-

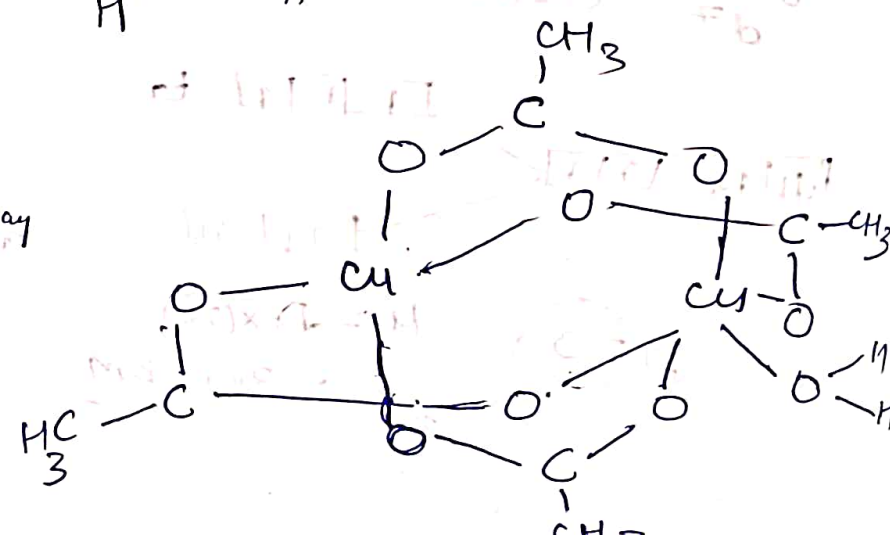


exists as dimer the magnetic moment of compound is

~~$\mu = 1.073 \text{ BM}$~~
 $\mu = 1.43 \text{ BM}$



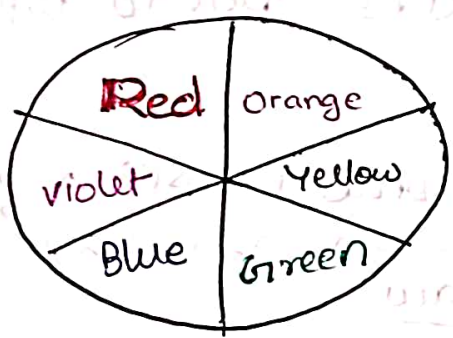
Simple way



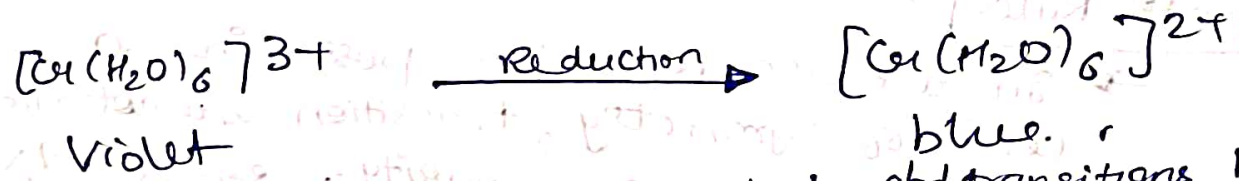
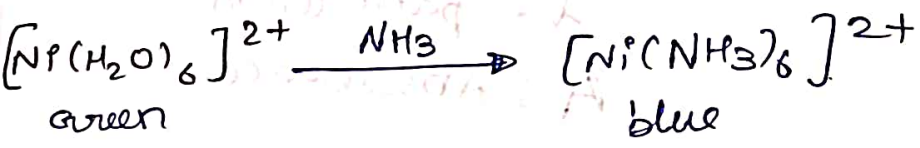
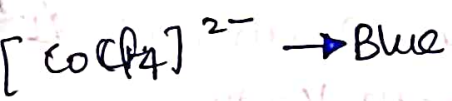
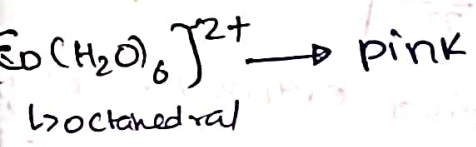
In its structure, the acetate groups act as bidentate bridging groups between the two copper atoms. Each copper atom is surrounded by 4 oxygen atoms in a square planar arrangement. The 5th position around each Cu atom is occupied by the O-atom from a water molecule. The other Cu atom occupies 6th of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

There is weak coupling of spin of unpaired e⁻ on the two copper atoms in the dimeric structure.

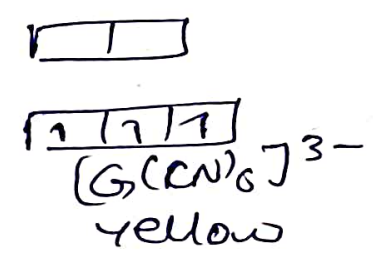
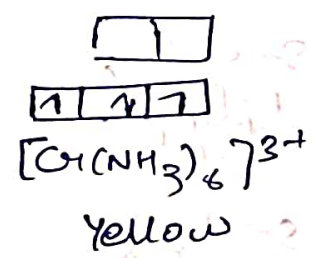
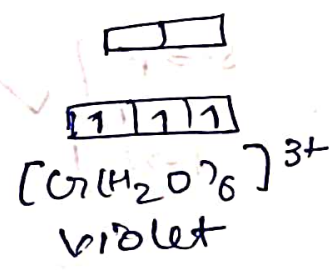
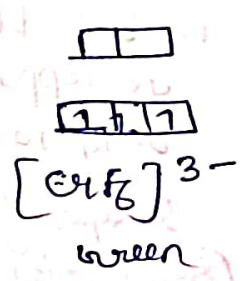
Electronic Spectra of Transition metal complex :-

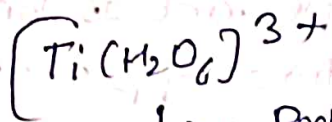


Colour of light absorbed	Approx. λ ranges (nm)	Colour of light transmitted
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow



These color transitions are referred to as d-d transitions because they involve molecular orbitals that are mainly d in character.





↳ Perfectly octahedral

should give only one d-d transition.

Here distortion occurs to eliminate the degeneracy of system.

* complex of d^{10} e config. \Rightarrow colourless

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

The complexity arises due to interelectron repulsions.

Selection Rules for Electronic Transitions :-

The Beer-Lambert Law

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon c l$$

ϵ : Molar extinction coefficient

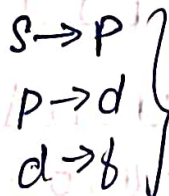
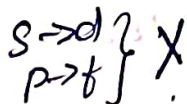
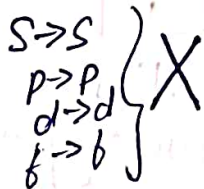
c : concn in mole L^{-1}

l : path length

A : Absorbance.

Laporte Rule

↳ In a molecule or ion possessing a centre of symmetry, transition are not allowed b/w orbital of same parity. eg. d to d
 $\Delta l = \pm 1$. Quantum no. should differ by 1.



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

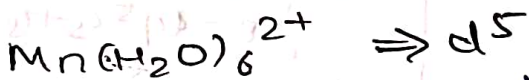
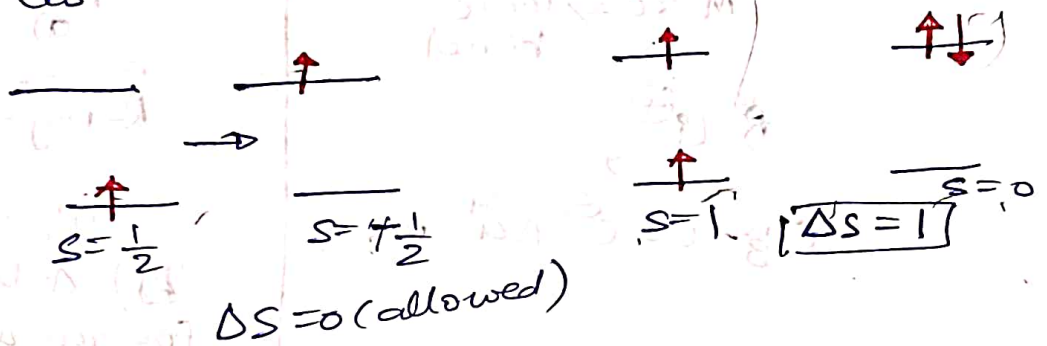
$\epsilon(Td)$ is a 100 times greater than $\epsilon(O_h)$

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.

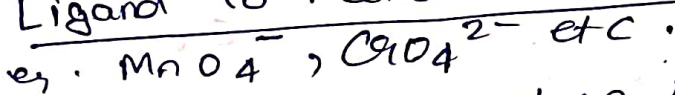


For this complex electronic transition is not only Laporte forbidden but also spin forbidden therefore its dilute solⁿ are colourless

Charge Transfer (CT) band :-

Relative energy levels of d-orbitals :-

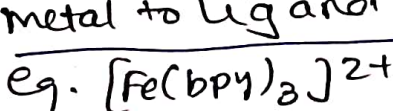
i) Ligand to Metal Charge Transfer (LMCT)



for MnO_4^- d⁰ count on Mn(VII) is d⁰.

⇓
 so color is not due to d-d transition rather charge transfer from O²⁻ to Mn(VII) described as LMCT band.

ii) Metal to Ligand Charge Transfer (MLCT)



charge transfer from Fe(II) to empty π^* orbitals of bpy ligands

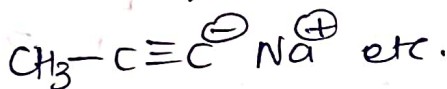
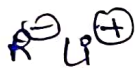
* organometallic compound :-

comps in which metal is directly bonded with carbon.

OMC

Ionic

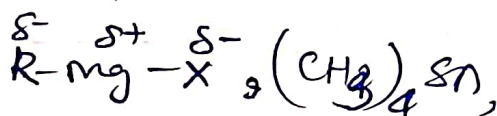
M & C \Rightarrow ionic bond



Covalent

M & C \Rightarrow covalent

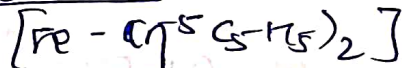
a) σ bonded



Al_2Me_6 etc

b) π -bonded

ferrocene



ON = +2
Fe

c) σ & π both

