

COORDINATION COMPOUNDS

Transition metals have tendency to form large no. of complex compound.

→ Coordination Compound

→ Compound in which metal atom is bonded to anion/neutral molecule by coordinate bond is called Coordination compound.

→ metal atom → Central metal atom

→ anion/neutral → ligand.

→ Chlorophyll → Mg

→ Haemoglobin → Fe

→ Vitamin B-12 → Co

Werner's Theory

1st Scientist → to study about structure.

→ postulates of Werner Theory →

① Metals have 2 types of Valency.

1^o Valency

Oxidation number.

Ionizable

Satisfied by -ve ligand.

Non Directional

$\text{CrCl}_3 \rightarrow 3$

$\text{CoCl}_3 \rightarrow 2$

$\text{PdCl}_2 \rightarrow 2$

2^o Valency

Coordination number.

Non-ionizable.

Satisfied by -ve charge, neutral.

Directional

Gives definite geometry.

$\text{CoCl}_3 \cdot 6\text{NH}_3$ $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightarrow 3 \text{ mol AgCl (Yellow)}$

$\text{CoCl}_3 \cdot 5\text{NH}_3$ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow 2 \text{ mol AgCl (purple)}$

$\text{CoCl}_3 \cdot 4\text{NH}_3$ $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightarrow 1 \text{ mol AgCl (green)}$

$\text{CoCl}_3 \cdot 4\text{NH}_3$ $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightarrow 1 \text{ mol AgCl (violet)}$

Isomers → Trans
→ Cis

Coordination polyhedra →

Ion/group bonded by secondary linkage, with central atom have different spatial arrangement. → Tetrahedral



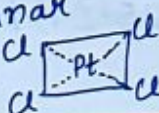
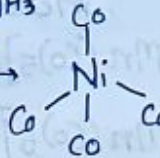
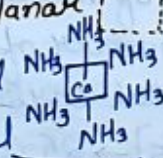
→ Octahedral

→ Square planar

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

$[\text{Ni}(\text{Co})_4] \rightarrow \text{Tetrahedral}$

$\text{PtCl}_4^{-4} \rightarrow \text{Square planar}$



Coordination entity → Species inside sq. bracket
Counter ion → Outside the sq. bracket.

Difference b/w Double Salt and Coordination Compound →

Double Salt → When dissolved in water, completely break down into ions.

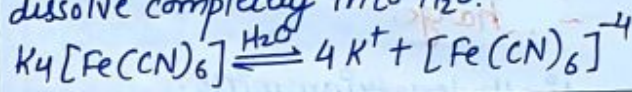
KCl. MgCl₂. 6H₂O (Kernalite).

FeSO₄. (NH₄)₂SO₄. 6H₂O (Mohr's Salt)

K₂SO₄. Al₂(SO₄)₃. 24H₂O (potash Alum)

KAl(SO₄). 12H₂O

Coordination Compound → Which do not dissolve completely into H₂O.



Important Definition

① Coordination Entity → Central metal atom/ion bonded to ligand and enclosed in square bracket.

e.g. - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ $[\text{Ni}(\text{Co})_4]$

② Central atom → atom/ion to which, ligands are bonded by coordinate bond in a definite geometry inside coordination entity (Lewis Acid)

e.g. - $[\text{NiCl}_2(\text{H}_2\text{O})_4] \rightarrow \text{Ni}^{+2}$

$[\text{Co}(\text{Cl})(\text{NH}_3)_5] \rightarrow \text{Co}^{+3}$

③ Ligand → Ion/molecule, bonded to central atom through coordinate bond, in coordination entity. (Lewis Base)

Unidentate → Single Donor atom

Cl⁻ (chlorido), H₂O (aqua), NH₃ (ammine), F⁻ (fluoro/fluorido), OH⁻ (hydroxo), O²⁻ (oxido), O₂²⁻ (peroxido), O₂⁻ (superoxido), NH₂⁻ (amido), NH⁻ (imido), N₃⁻ (azido), NO₂⁻ (nitro).

Didentate → Two Donor atom

en → (ethylene diammine)
Cethane, 1-2-diammine

NH₂-CH₂-CH₂-NH₂

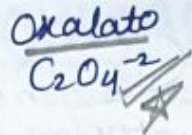
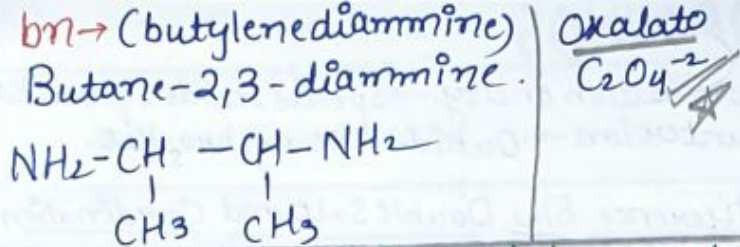
pn → (propylene diammine)

propane-1,2-diamine

NH₂-CH₂-CH(NH₂)-CH₃

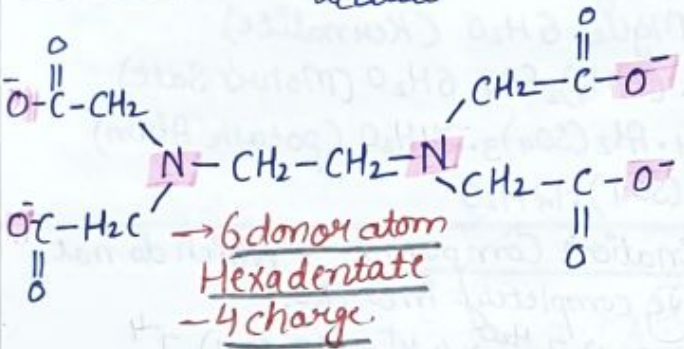
gly (glycinato)
NH₂-CH₂-C(=O)-O⁻

dmg⁻ dimethylglyoximate
CH₃-C(=O)-N-O⁻H
CH₃-C(=O)-N-O⁻



③ polydentate → Several donor atom.

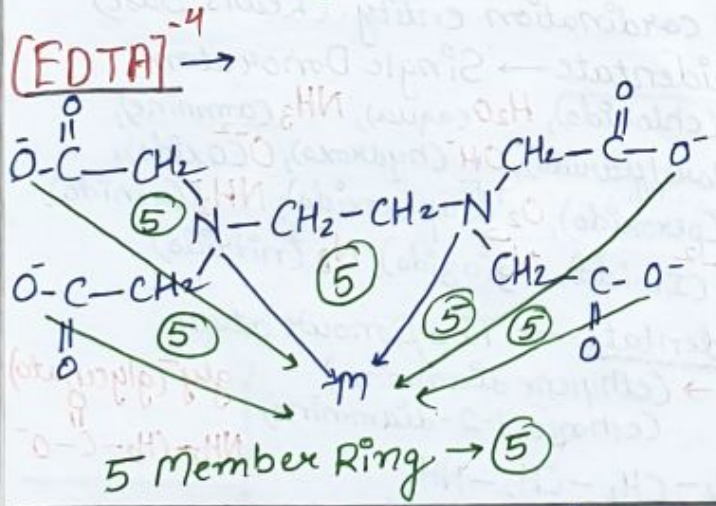
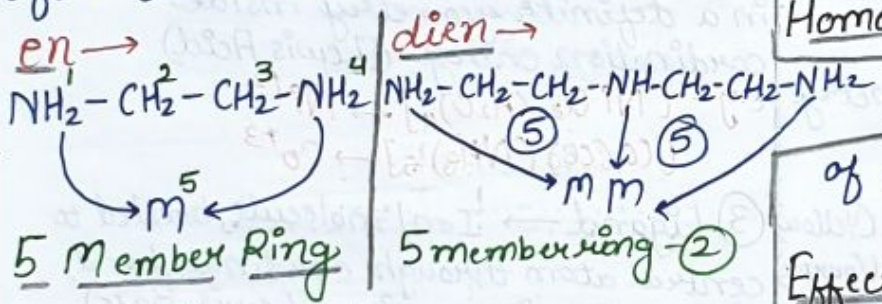
(EDTA)⁻⁴ - ethylene diammine tetra acetato



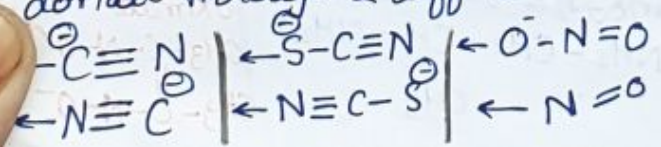
dien - diethylenetriammine.
 $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

trien - Tridentate
 $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

Chelate Ligand → didentate/polydentate, which forms 5-6 member ring, after donation. (Stable)

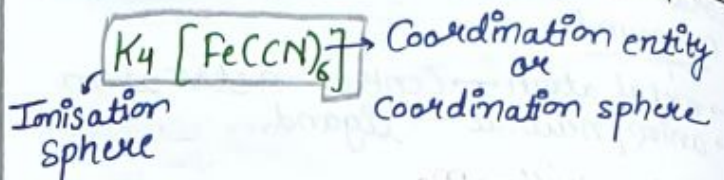


Ambidentate Ligand → which can donate through 2 diff. atom.



Coordination Number → No. of coordinate bond b/w central atom and ligand
 $[\text{Pt}(\text{Cl}_2)]^{-2} \rightarrow ⑥$ | $[\text{Co}(\text{en})_3] \rightarrow ⑥$
 $[\text{Fe}(\text{C}_2\text{O}_4)_3] \rightarrow ⑥$ | $[\text{Ni}(\text{NH}_3)_4]^{+2} \rightarrow ④$
 didentate

Coordination Sphere v/s Ionization Sphere



Oxidation Number → Charge on central atom, if all ligands are removed with lone pair.

$[\text{Cu}(\text{CN})_4]^{-3} \rightarrow (-3) - (-4) = 1$
 $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow (3) - (6 \times 0) = 3$
 $[\text{PtCl}_4(\text{NH}_3)_2]^{-2} \rightarrow (-2) - (-4) = 2$
 $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{-3} \rightarrow (-3) - (-6) = 3$
 $[\text{Co}(\text{en})_3]^{+3} \rightarrow 3$
 $[\text{Fe}(\text{EDTA})]^{-} \rightarrow (-1) - (-4) = 3$

Homoleptic → Only one type of ligand
 $[\text{Co}(\text{NH}_3)_6]^{+3}$

Heteroleptic → More than one type of ligand
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{+2}$

Effective Atomic Number (EAN).
 No. of e⁻ on Central Metal atom, after forming coordinate bond with ligand
 $\text{E.A.N} = Z - 0.5 + 2 \times \text{C.N.}$

$\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow 26 - 2 + 2 \times 6 = 36$
 $\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow 26 - 3 + 2 \times 6 = 35$

Sidgwick Theory →
 If EAN of metal carbonyl is equal to atomic number of nearest inert gas, then that metal carbonyl is stable.

$[\text{Mn}(\text{Co})_5] \rightarrow 25 - 0 + 2 \times 5 = 35 \xrightarrow{+e^-} \text{Unstable}$
 $[\text{Mn}(\text{Co})_5]^- \rightarrow 25 - (-1) + 2 \times 5 = 36 \rightarrow \text{Stable}$

$Mn(CO)_6 \rightarrow EAN \rightarrow 25 - 0 + 2 \times 6 = 31 - e^- \rightarrow 36$
 $[Mn(CO)_6]^+ \rightarrow EAN \rightarrow 25 - 1 + 2 \times 6 = 36 \rightarrow \text{stable}$

If $EAN < \text{atomic no. of inert gas}$ Oxidizing agent
 If $EAN > \text{atomic no. of inert gas}$ Reducing agent

Nomenclature \rightarrow

\rightarrow Rules for writing formula \rightarrow

- 1) Identify Central Atom.
- 2) Write ligands in alphabetical order.
- 3) Abbreviated ligand \rightarrow Consider first letter for alphabetical order.
- 4) Write formula in square bracket.
- 5) So space bet. ligand and metal.
- 6) If Counter is not present, charge is indicated on square bracket.

Que) Triammine triaqua chromium (III) chloride.

Sol.ⁿ $\rightarrow [Cr(NH_3)_3(H_2O)_3]^+ Cl_3^-$

Que) Tris (ethane-1,2-diammine) Cobalt (III) Sulphate.

Sol.ⁿ $\rightarrow Co$
 $Co(en)_3$
 $[Co(en)_3]^+ SO_4^{2-}$ $[Co(en)_3]_2(SO_4)_3$

Naming of Coordination Compound

\rightarrow Cation is named first, then anion.
 the LCO rule.

\rightarrow Ligands are named first (alphabetical order) then central atom is named, and then oxidation number is written in Roman.

Naming of Ligand \rightarrow

anionic ligand
 ends in o
 $Cl^- \rightarrow \text{chlorido}$
 $C_2O_4^{2-} \rightarrow \text{oxalato}$
 $O^{2-} \rightarrow \text{oxido}$
 $OH^- \rightarrow \text{hydroxido}$

neutral ligand
 as it is
 $NH_3 \rightarrow \text{ammine}$
 $H_2O \rightarrow \text{aqua}$
 $CO \rightarrow \text{carbonyl}$
 $NO \rightarrow \text{nitrosyl}$

\rightarrow Prefix: di, tri, tetra.

\rightarrow donates no. of ligands.

\rightarrow If name of ligand, already have (di, tri, tetra).
 bis $\rightarrow 2$
 tris $\rightarrow 3$
 tetrakis $\rightarrow 4$

Que) $[NiCl_2(PPh_3)_2]$

Sol.ⁿ \rightarrow dichlorobis (triphenyl phosphine) nickel(II)

Complex \rightarrow cationic \rightarrow Central atom has same name

Complex \rightarrow anionic \rightarrow Central atom \rightarrow add 'ate' in end.

$[Co(SCN)_4]^{2-} \rightarrow \text{Cobaltate}$

$[Fe(CN)_6]^{4-} \rightarrow \text{ferrate}$

$[Pt(NH_3)_6]^{+2} \rightarrow \text{platinum}$

$[Cr(NH_3)_3(H_2O)_3]^+ Cl_3^- \rightarrow$
 triamminetriaquachromium (III) chloride

$[Co(en)_3]^+ [SO_4]^{2-} \rightarrow$
 tris (ethylenediammine) cobalt sulphate.

$[Ag(NH_3)_2]^+ [Ag(CN)_2]^- \rightarrow$
 diamminesilver (I) dicyanoargentate (I).

Isomerism

Structural Isomerism

① Ionization \rightarrow Compound which give diff. ions. e.g. $[Co(NH_3)_5SO_4]Br$
 $[Co(NH_3)_5Br]SO_4$

② Solvate \rightarrow No. of water molecules inside and outside coordination sphere is different. e.g. $[Cr(H_2O)_6]Cl_3$
 $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

③ Linkage \rightarrow Ambidentate ligand.
 e.g. $[Co(NH_3)_5NO_2]Cl$
 $[Co(NH_3)_5ONO]Cl$

④ Coordination \rightarrow Cation and anion, both are complex.
 e.g. $[Co(NH_3)_6]^+ [Cr(CN)_6]^-$
 $[Co(CN)_6]^- [Cr(NH_3)_6]^+$

Stereoisomer

Geometrical Isomerism

Tetrahedral X
Square Planar ✓
Octahedral ✓

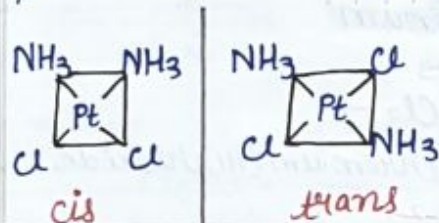
CN=4

G.I

$Ma_4 \rightarrow 0$
 $Ma_3b \rightarrow 0$
 $Ma_2b_2 \rightarrow 2$ (cis, trans)
 $Ma_2bc \rightarrow 2$ (cis, trans)
 $Mabcd \rightarrow 3$ (2 cis, 1 trans)

eg $[Pt(NH_3)_2Cl_2]$

solⁿ $\rightarrow Ma_2b_2 \rightarrow 2$ G.I. (cis, trans)



eg for abcd - 3 G.I. (2 cis, 1 trans)

(ab cd) (ac bd) (ad bc)



Geometrical Isomerism and Optical Isomerism in Octahedral \rightarrow

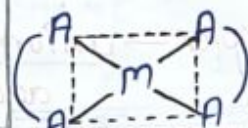
Optical Isomerism

Bidentate

$[Pt(en)_2]^{+2}$

$[M(AB)_2]^{+2}$

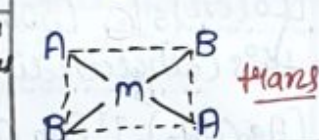
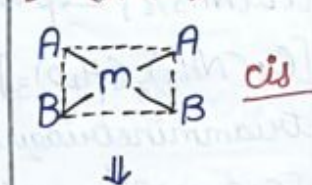
2 donor atom of bidentate ligand never lie at 180°



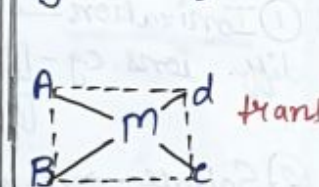
no Geometrical Iso...

$[Pt(gly)_2]$

$[M(AB)_2]$



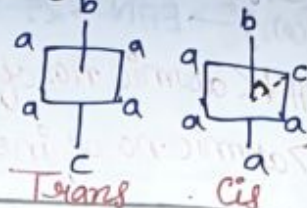
$[Pt(gly)(NH_3)Cl]$
 $M(AB)cd$



Que) $[Pt(NH_3)_4Cl_2]$

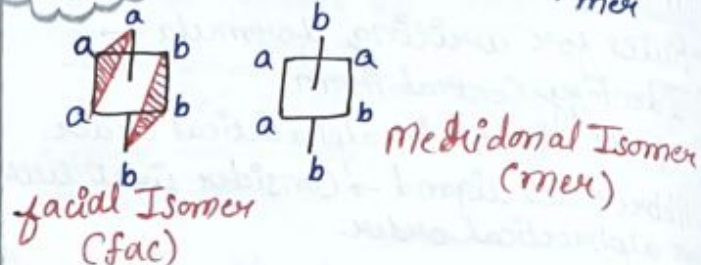
solⁿ $\rightarrow Ma_4b_2$

G.I = 2 (cis, trans)

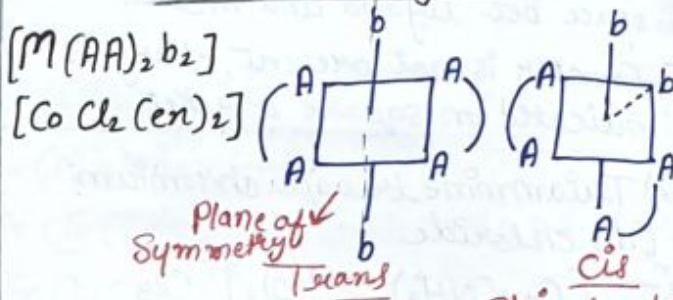


Special Case

$Ma_3b_3 \rightarrow 2$ G.I. (fac, mer)

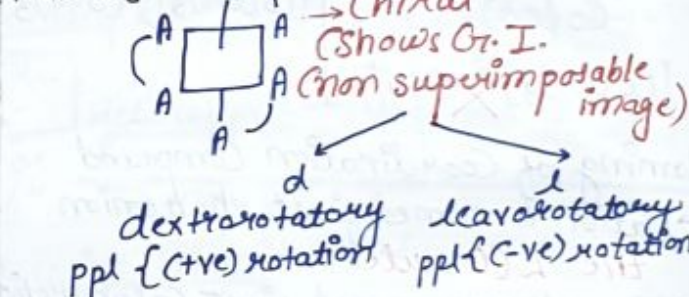


Bidentate Ligand



(chiral molecule) + Shows Optical Iso. (non-superimposable image)

$M(AA)_3$



Valence Bond Theory

Under influence of ligand, Central atom uses 2 types of Orbital for hybridisation.

- Inner Orbital $\rightarrow (n-1)d, ns, np$ { Vacant orbital
- Outer Orbital $\rightarrow ns, np, nd$ { orbital

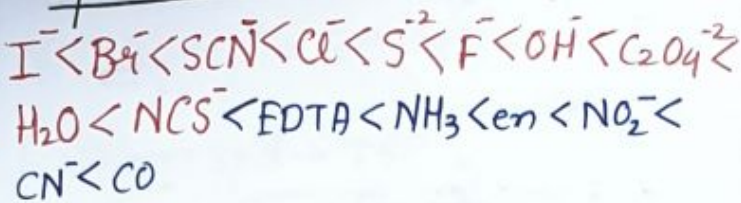
Vacant orbital undergo hybridisation and gives, octahedral, tetrahedral and square planar geometry.

CN=4 $(sp^3 - \text{Tetrahedral})$
 $(dsp^2 - \text{Sq. planar})$
CN=6 $(d^2sp^3 - \text{Octahedral})$
 $(sp^3d^2 - \text{Octahedral})$

Strong field Ligand - pairing occurs
Weak field Ligand - pairing do not occur.

	G.I	Pair of enantiomer	no. of stereoisomer
Ma_6	0		
Ma_5b	0		
Ma_4b_2	2		
Ma_4bc	2		
Ma_3b_3	2		
Ma_3b_2c	3		
Ma_3bcd	4	1	5
$Ma_2b_2c_2$	5	1	6
Ma_2b_2cd	6	2	8
Ma_2bcde	9	6	15
$Mabcdef$	15	15	30

Spectrochemical Series



C/N donor \rightarrow Strong field ligand.

O/X donor \rightarrow Weak field ligand.

Important Point \rightarrow

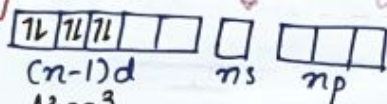
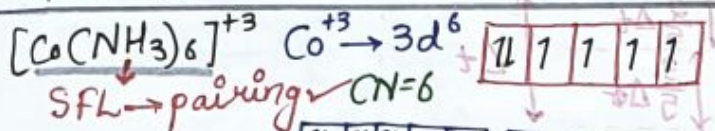
\rightarrow All ligands act as SFL with 4d/5d metal ions.

$\rightarrow F^-$ acts as SFL with Ni^{+4}

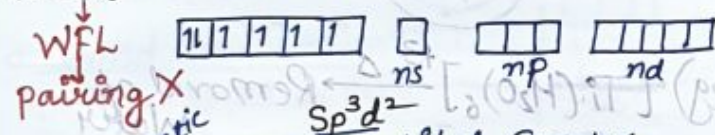
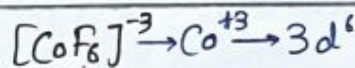
$\rightarrow H_2O$ and $C_2O_4^{2-}$ act as SFL (Co^{+3})

$\rightarrow NH_3 \rightarrow WFL \rightarrow Fe^{+2}$ and Mn^{+2}

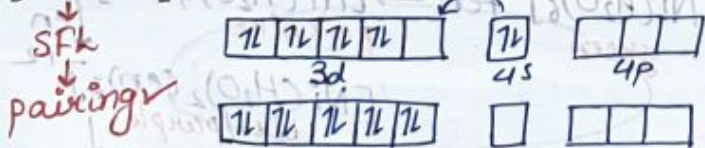
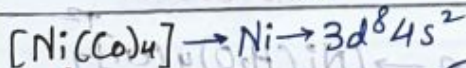
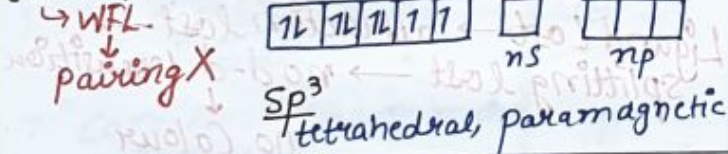
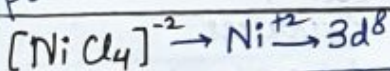
$\rightarrow H_2O \rightarrow SFL \rightarrow Cu^{+2}$ (CN=4)



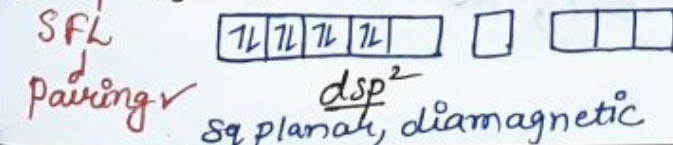
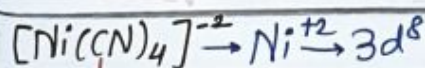
inner orbital complex
low spin / spin paired
 \rightarrow diamagnetic



outer orbital complex
high spin / spin free complex

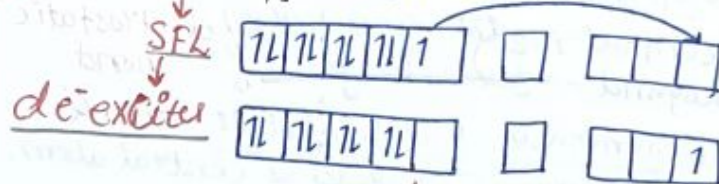
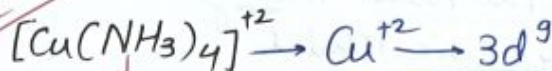


Tetrahedral, diamagnetic



Sq planar, diamagnetic

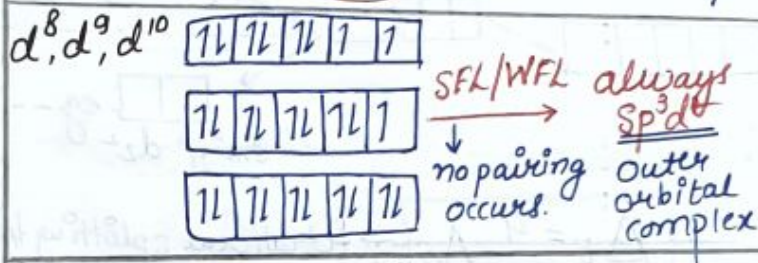
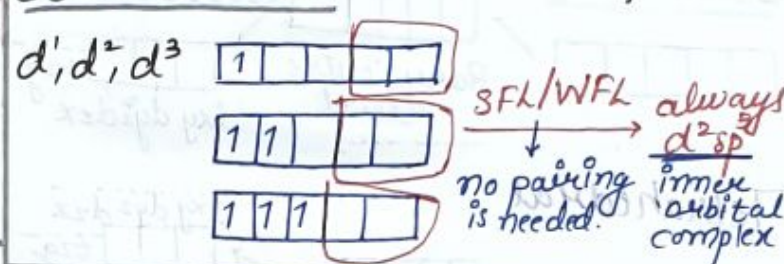
Special Case



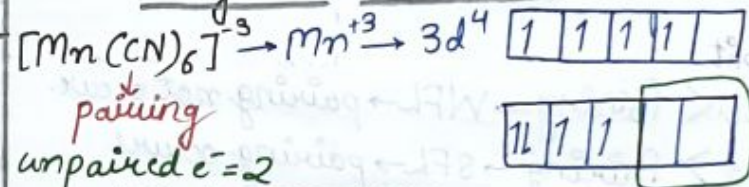
Sq. planar, paramagnetic

Magnetic property of Coordination Compound

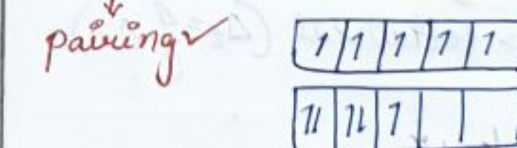
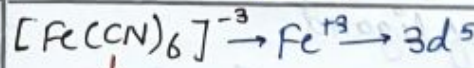
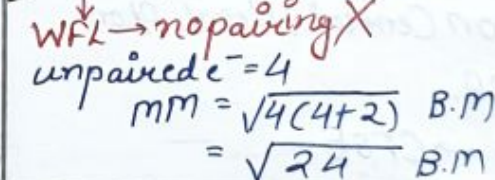
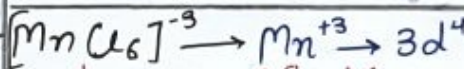
Octahedral Case



Magnetic Moment



$MM = \sqrt{n(n+2)} \text{ BM}$
 $= \sqrt{2 \times 4} = \sqrt{8} \text{ BM}$

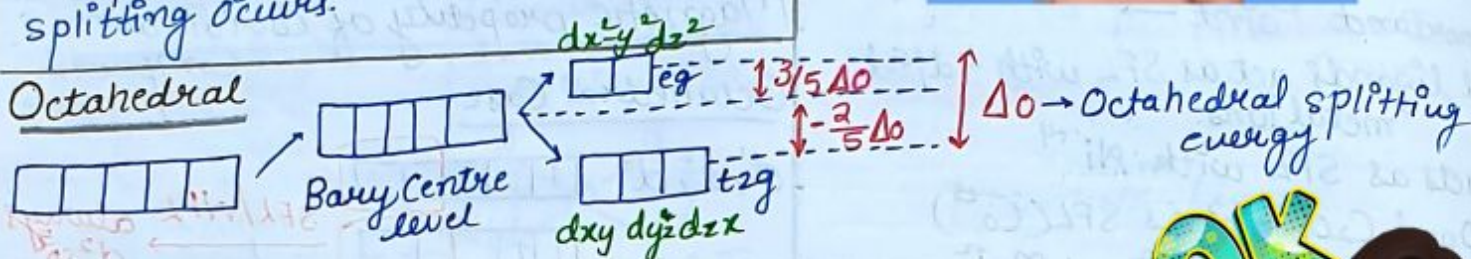


$unpaired e^- = 1$
 $MM = \sqrt{3} \text{ BM}$

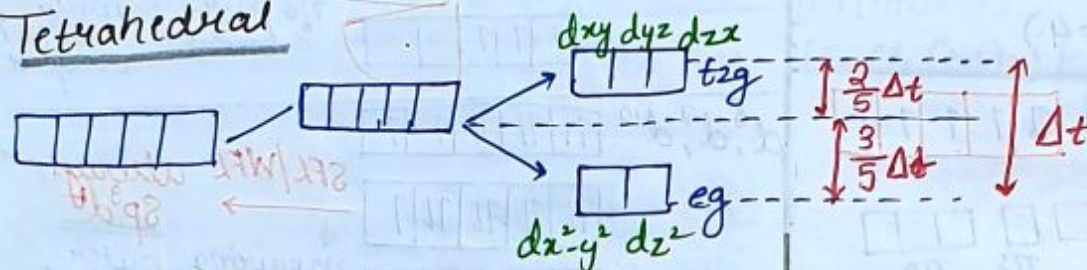
Crystal Field Theory

- Electrostatic Model
- Central metal $\rightarrow (+ve)$ charge
- Ligand $\rightarrow (-ve)$ charge
- Degeneracy of D orbitals break when ligands approach central atom.
- Repulsion b/w e⁻ of d orbital and lone pair of ligand. So, D orbital splitting occurs.

Octahedral



Tetrahedral



$$\Delta_t = \frac{4}{9} \Delta_o \rightarrow \text{tetrahedral splitting} \downarrow \text{Octahedral} \uparrow$$

- split
- $\Delta_o < \text{Pairing} \rightarrow \text{WFL} \rightarrow \text{pairing not occur.}$
 - $\Delta_o > \text{Pairing} \rightarrow \text{SFL} \rightarrow \text{pairing occurs.}$

Factors Affecting CF Splitting energy

$\Delta_o \propto \text{Charge on Central Metal Atom}$

$\Delta_o \propto Z_{\text{eff}} \text{ of CA.}$

$3d < 4d < 5d \rightarrow \text{CFSE}$

$\Delta_o \propto \text{Strength of ligand}$

Octahedral $>$ tetrahedral ($\Delta_t = \frac{4}{9} \Delta_o$)

Colour

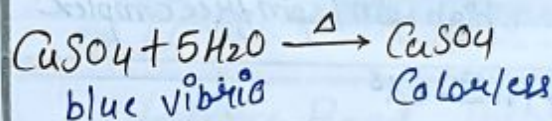
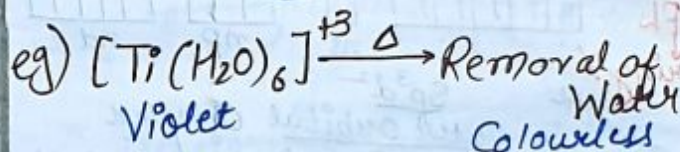
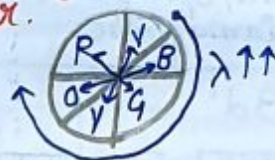
$e^- \text{ jump } (t_{2g} \rightarrow e_g) \left\{ \begin{array}{l} \text{Ceg} - t_{2g} \end{array} \right\} \rightarrow \text{d-d transition} \rightarrow \text{Colour}$



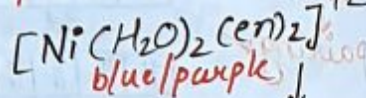
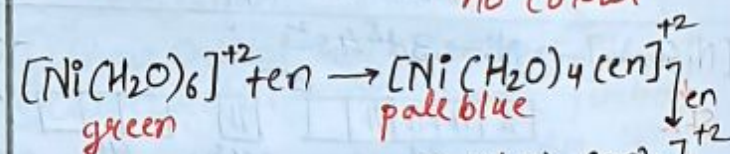
OK



* It always shows Complementary Colour.



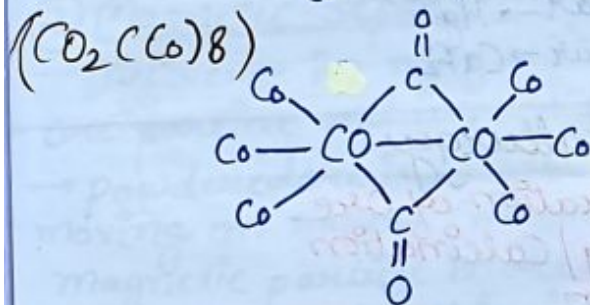
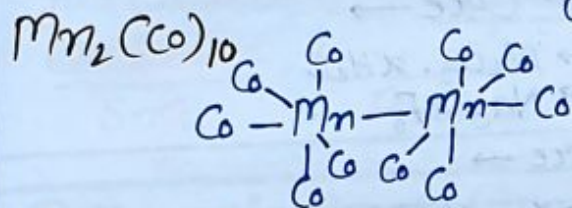
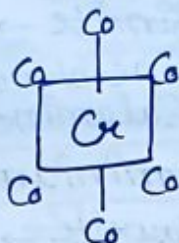
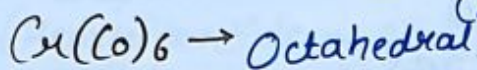
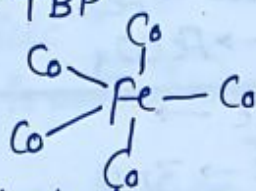
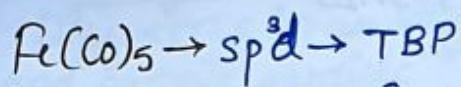
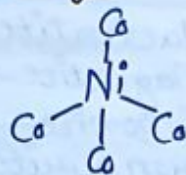
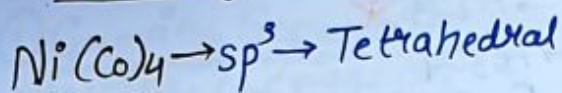
Ligand Lost \rightarrow attraction lost \rightarrow Splitting lost \rightarrow no d-d transition \rightarrow no Colour



Ans $\rightarrow \text{en} \rightarrow \text{SFL}$
SFL \uparrow , CFSE \uparrow
en \uparrow , $\lambda \downarrow$



Bonding in metal Carbonyl



Synergic Bond $[Co \rightarrow MO]$

(Metal \rightarrow Carbon) bond in metal carbonyl has both σ and π bond.

σ bond in $M-C \rightarrow$
 $\pi 2p$ orbital of Co
 \downarrow donate p

Vacant orbital of metal.

π bond in $M-C \rightarrow$

Filled d orbital of M
 \downarrow donate

π^* (anti bonding) molecular orbital of Co

