



* Coordination Compounds. *

→ Transition metals have tendency to form large no. of complex compound (coordination compd)

→ comp. in which [metal atom] is bonded to [anion / neutral molecule by coordinate bond is coordinate comp.

chlorophyll - Mg
Haemoglobin - Fe
vitamin B₁₂ - Co

* Werner's Theory.

First scientist to study about the structure.

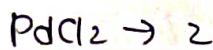
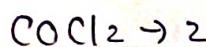
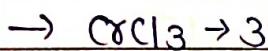
Postulates of Werner theory

i) metals have 2 types of valency

i) Primary valency

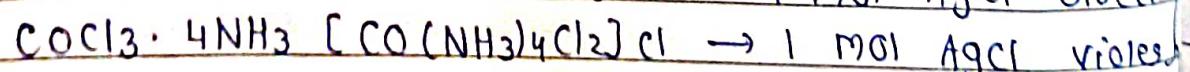
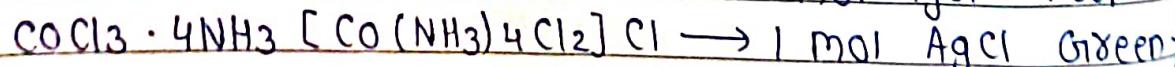
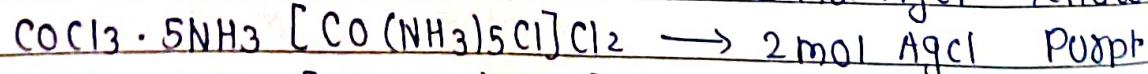
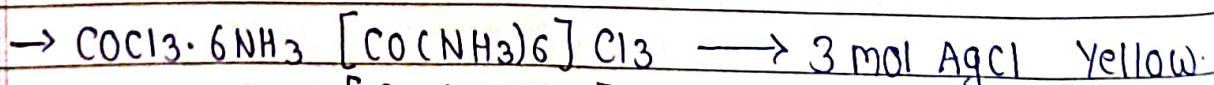
→ (oxidation no, ionizable, satisfied by -ve ligand).

non-directional

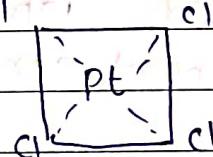
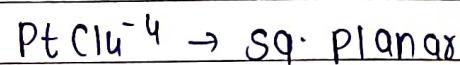
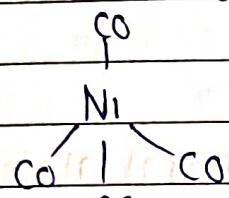
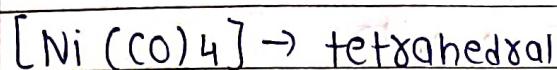
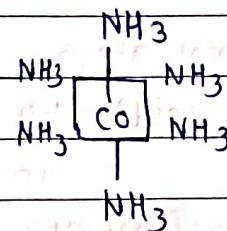
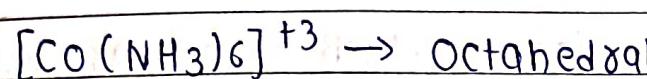
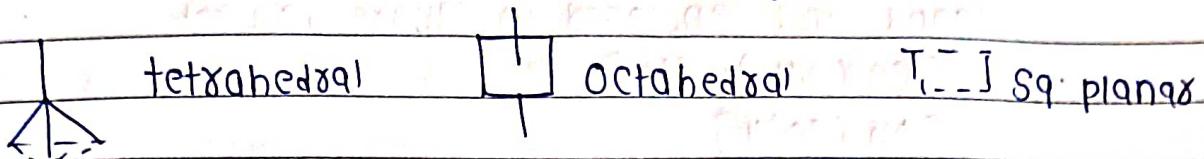


ii) Secondary valency

→ coordination no., non-ionizable, satisfied by -ve charge, neutral directional, gives definite geometry



coordination polyhedra - ion / Group bonded by secondary linkage with central atom have different spatial arrangement called coordination polyhedra

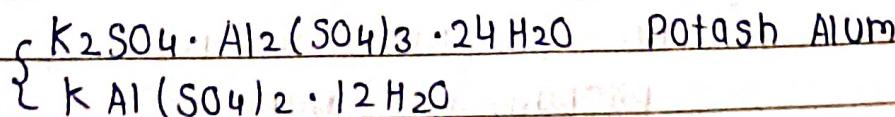
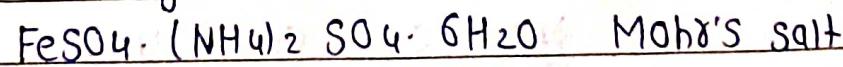
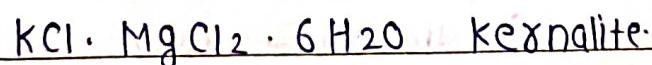


coordination entity \rightarrow species inside sq. bracket

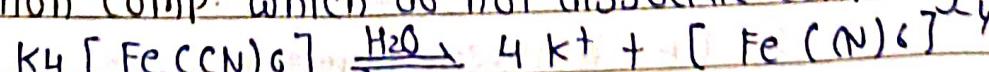
counter ion \rightarrow outside the sq. bracket

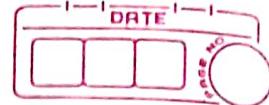
Difference betn double salt & coordination comp

Double salt - when dissolved in water - completely breaks down into ions



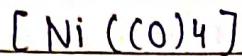
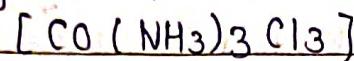
coordination comp. which do not dissociate completely into H_2O



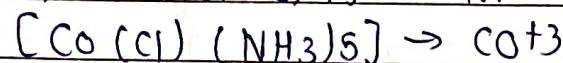
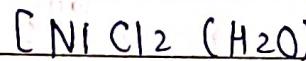


* Imp definition

1) Coordination Entity - central metal atom/ion bonded to ligand and enclosed in square bracket



2) Central atom - atom/ion to which ligands are bonded (lewis acid) by coordinate bond in a definite geometry inside coordination entity



3) Ligand - ion/molecule bonded to central atom through (lewis base) coordinate bond in coordination entity

Unidentate \rightarrow Single donor atom - Cl^- , H_2O , NH_3 , F^- , OH^- , O^{+2} ,
 O_2^{-2} , O_2^- , NH_2^- , $\text{N}^{\bar{H}}_2$, N^{-3} , N_3^-

Peroxido Super amido Imido Nitroso Oxo

chlorido aqua ammonia florofluorido hydroxido oxido

Didentate - two donor atom

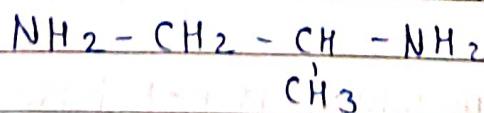
① en - ethylenediammine

(ethane 1,2-diammine)



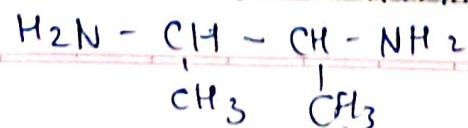
② Pn - propylene diammine

propane 1,2-diammine



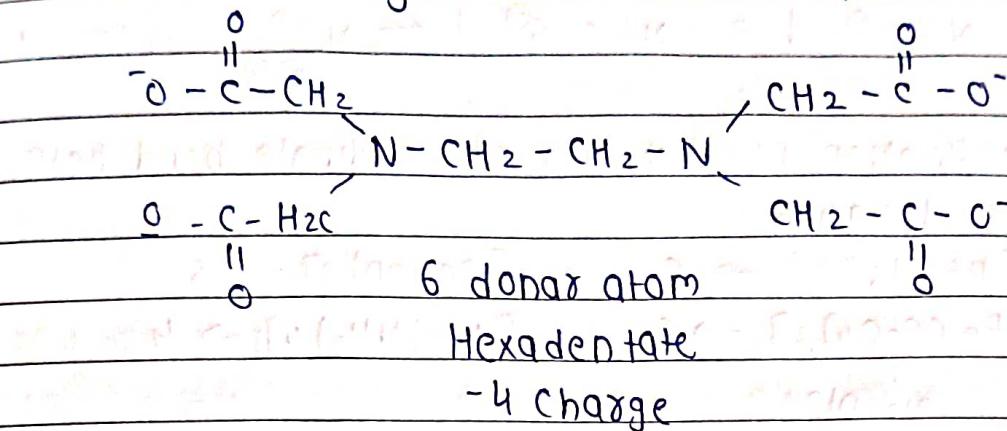
③ bn - butylenediammine

butane 2,3-diammine

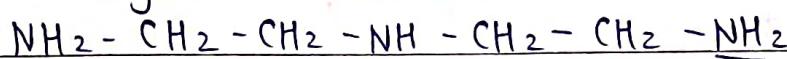


Polydentate - Several donor atom

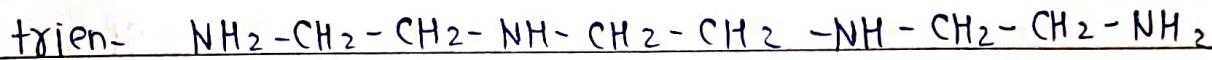
(EDTA)⁻⁴ ethylenediaminetetraacetate



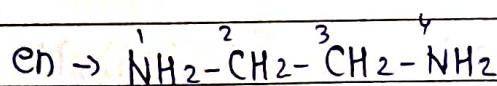
dien - diethylenetriamine



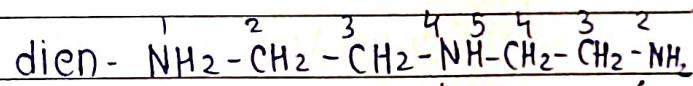
Tridentate



Chelate ligand → bidentate / polydentate which forms 5-6 member ring after donation (stable)

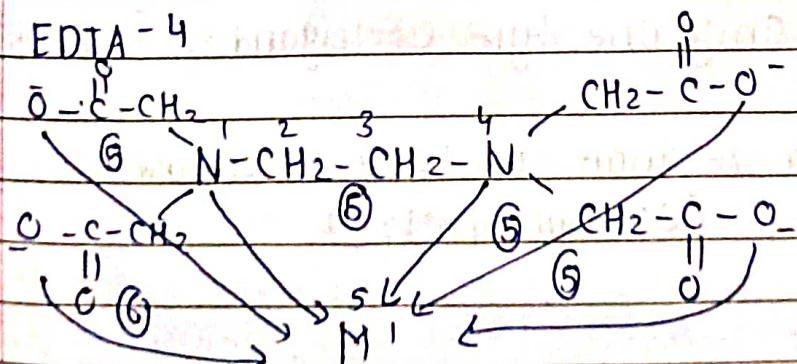


5 member ring

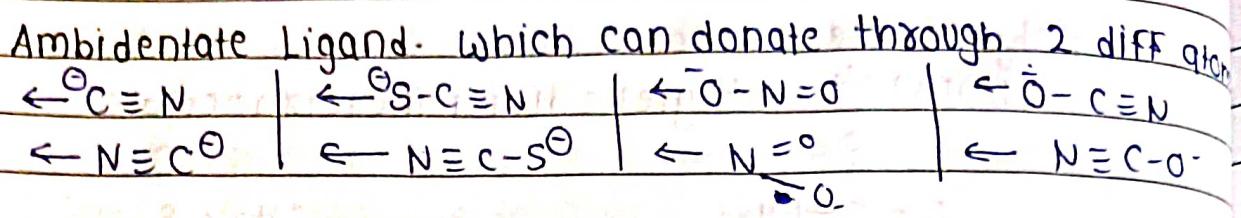
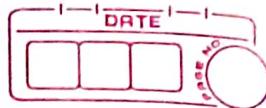


5 member ring

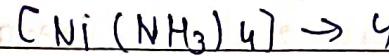
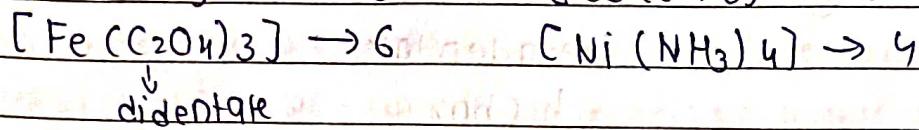
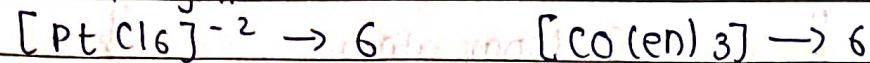
EDTA - 4



5 member Ring → [5]



Coordination number - no. of coordinate bond betn central atom & ligand

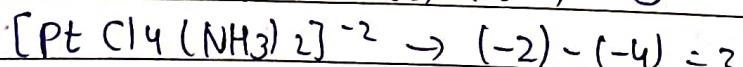
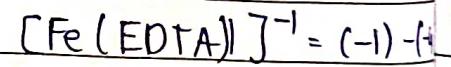
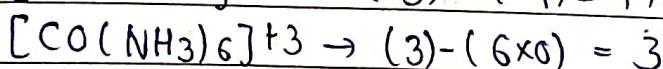
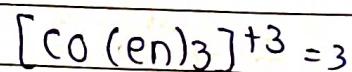
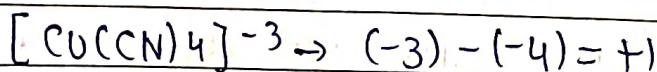


Coordination sphere $\rightarrow \text{K}_4 [\text{Fe}(\text{CN})_6]$

vs \rightarrow coordination entity

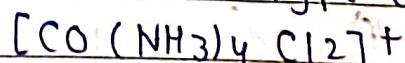
ionization Sphere ionization or coordination
Sphere Sphere

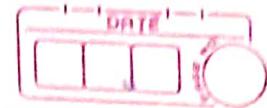
Oxidation number - charge on central atom if all ligands are removed with lone pair



Homoleptic - only one type of Ligand $\rightarrow [\text{Co}(\text{NH}_3)_6]^{+3}$

Heteroleptic - more than one type of Ligand

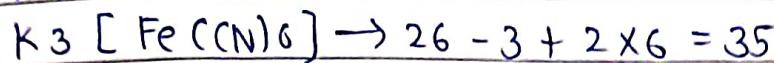
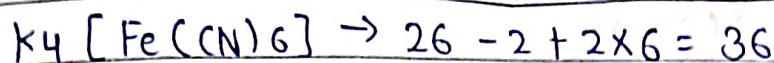




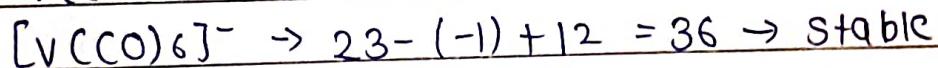
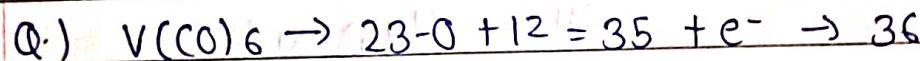
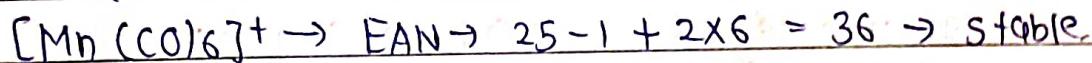
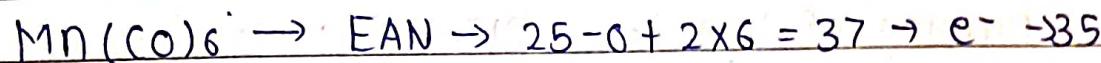
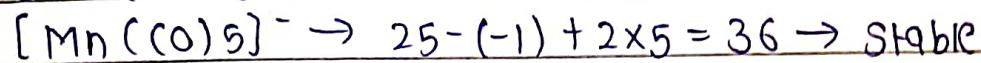
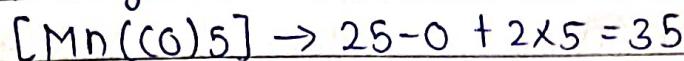
EFFECTIVE ATOMIC NUMBER (EAN)

no. of e⁻ on central metal atom forming coordinated bond with ligand

$$\text{EAN} = Z - O \cdot S + 2 \times CN$$



Sidgwick Theory - If EAN of metal carbonyl is equal to atomic no. of nearest inert gas then that metal carbonyl is stable



if EAN < atomic no. of inert gas \rightarrow oxidizing agent.

EAN > atomic no. of inert gas \rightarrow Reducing agent

* Nomenclature

Rules for writing formula.

\rightarrow identify central atom

\rightarrow write ligands in alphabetical order

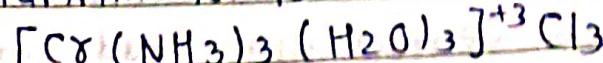
\rightarrow abbreviated ligand \rightarrow consider first letter for alphabetical order

\rightarrow write formula in sq. bracket

\rightarrow no space betw. ligand & metal

\rightarrow If counter ion is not present- charge is indicated on sq. bracket

Triammine triqua chromium (III) chloride

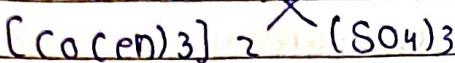
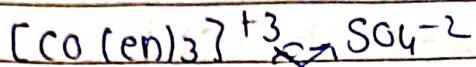




~~tris (ethane-1,2-diamine) cobalt (III) Sulphate~~

CO

CO_(en)₃



Naming of coordination compound

→ cation is named first than anion. then LCO RULE

→ Ligands are named first (alphabetical order)

then central atom is named & then oxdn. no. is written in Roman

naming of ligand - Cl⁻ → chlorido

anionic ligand C₂O₄⁻² → oxalato
ends in O. O⁻² → oxido

OH⁻ → Hydroxido

neutral ligand - NH₃ - ammine

H₂O → aquo
NO → nitrosyl
CO → carbonyl

→ Prefix - di, tri, tetra → denotes no. of ligand

→ if name of ligand already have (di, tri, tetra) then
bis - 2

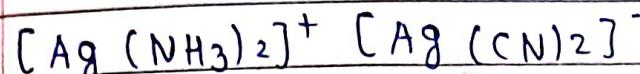
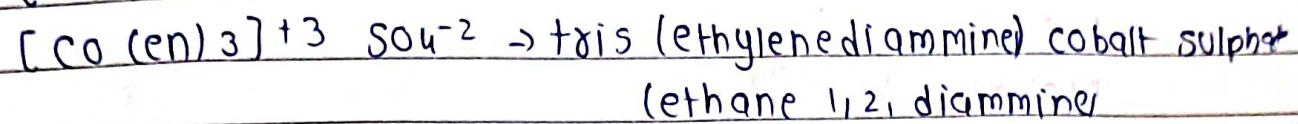
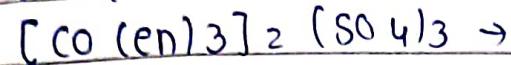
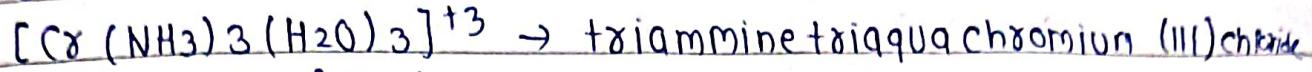
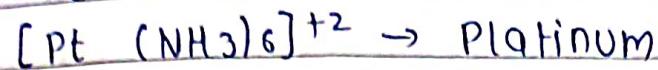
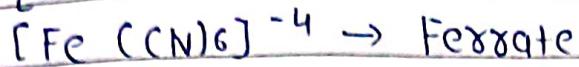
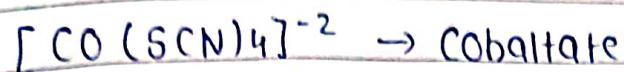
tris - 3

tetrakis - 4

[NiCl₂(PPh₃)₂]

dichloro (triphenylphosphine) nickel (III)

complex - cationic → central atom has same name
complex - anionic → central atom add rate 1 in name



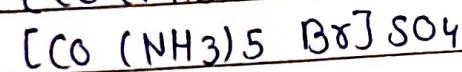
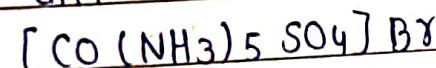
diammine silver (I) dicyanoargentate (I)

* Isomerism

* Structural isomerism

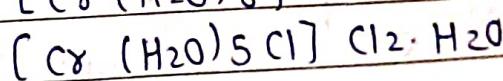
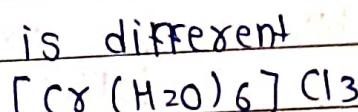
i) ionization

→ comp. which give diff. ions



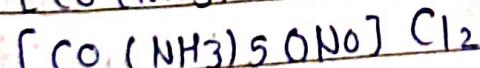
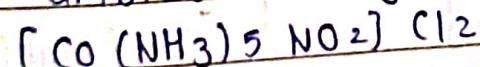
ii) Solvate

→ no. of water molecules inside & outside coordination sphere



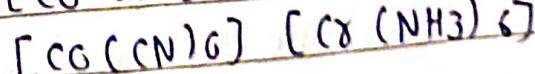
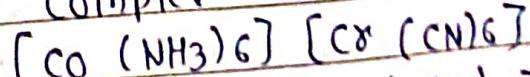
iii) Linkage

→ ambidentate ligand



iv) coordination

→ cation & anion both are complex



* Stereo isomers

i) Geometrical isomers

Tetrahedral X

Sq. planar ✓

Octahedral ✓

Coordination no. = 4

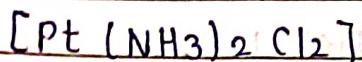
$M_{94} = 0$

$M_{36} = 0$

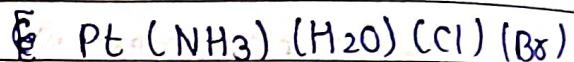
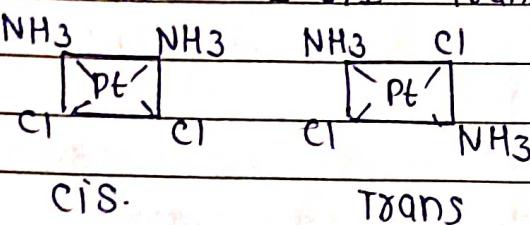
$M_{92b_2} = 2 \leq^{cis}_{trans}$

$M_{92bc} = 2 \leq^{cis}_{trans}$

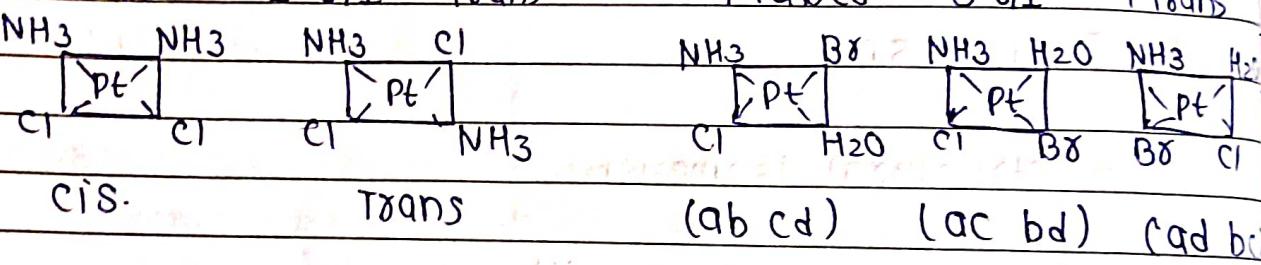
$M_{abcd} = 3 \leq^{2cis}_{trans}$



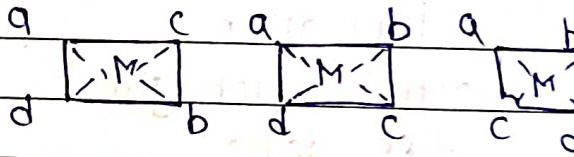
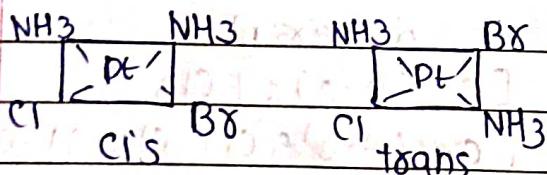
$M_{92b_2} \rightarrow 2 GI \leq^{cis}_{trans}$



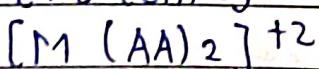
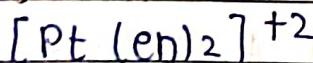
$M_{abcd} \rightarrow 3 GI \leq^{2cis}_{1trans}$



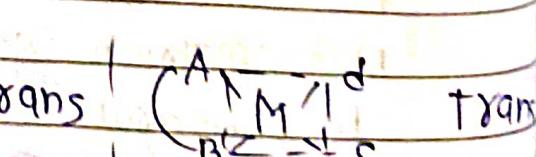
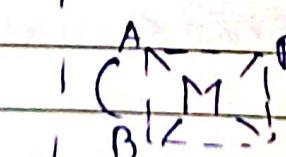
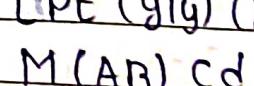
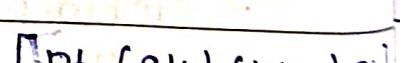
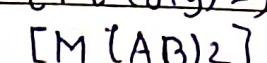
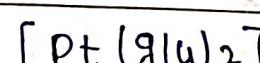
$M_{92bc} = 2 GI \leq^{cis}_{trans}$



Bidentate



2 donor atom of
bidentate ligand
never lie at 180°

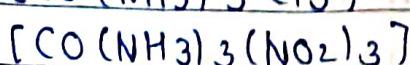
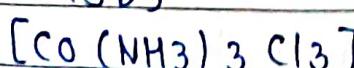
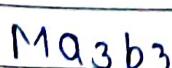
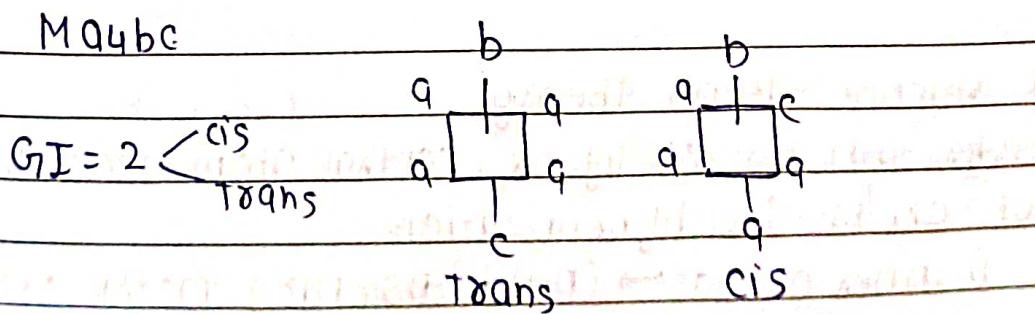
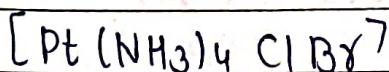
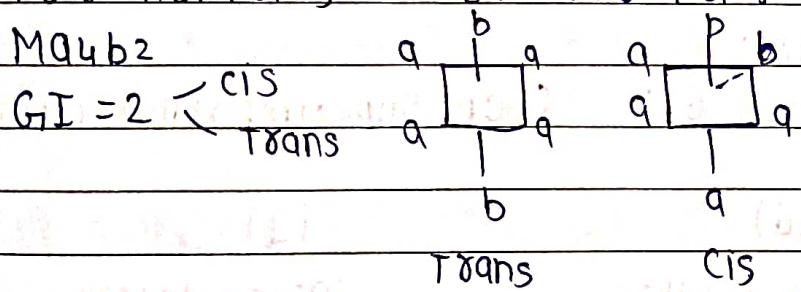
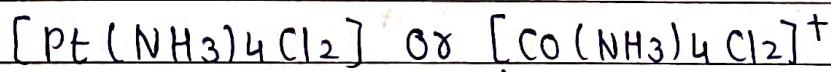


no GI

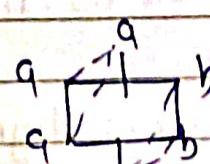


Geometrical & Optical isomer in octahedra

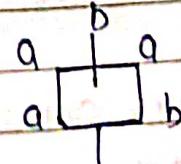
GI | Pair of enantiomer; no. of stereoisomers
O | (GI + OI)



$$2G_{\perp} - \text{fac} \rightarrow m_x$$

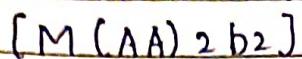
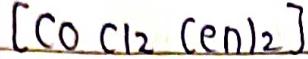


Facial isomers

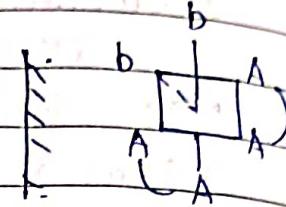
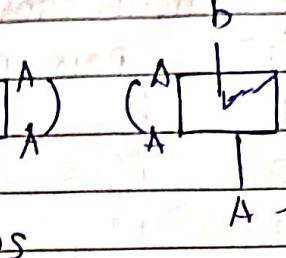
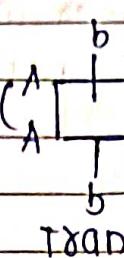


^b
meridional isomer
(mer)

Bidentate ligand



trans

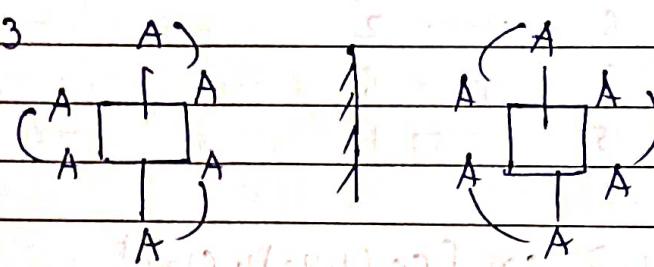
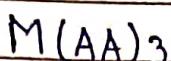


cis

(chiral molecule)

shows O.I.

non superimposable mirror image



chiral

shows G.I. (non superimposable mirror image)

(d)

dextrorotatory
PPI {+ve)
rotation

(l)

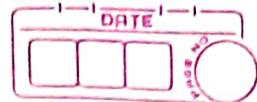
levorotatory
PPI {-ve)
rotation

* Valence - Bond Theory:

Under influence of ligand, central atom uses two types of orbital for hybridization.

- 1) inner orbital $\rightarrow (n-1)d, ns, np$ } vacant orbital
- 2) outer orbital $\rightarrow ns, np, nd$ }

vacant orbital undergo hybridization & gives octahedral tetrahedral & sq. planar geometry



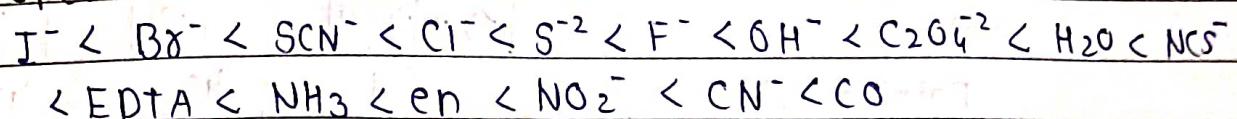
$\text{CN} = 4$ (sp^3 - Tetrahedral)
 dsp^2 - Sq. planar

$\text{CN} = 6$ ($\text{d}^2 \text{sp}^3$ - Octahedral)
 $\text{sp}^3 \text{d}^2$ - Octahedral

SFL \rightarrow Pairing occurs

WFL \rightarrow pairing do not occur

Spectrochemical Series



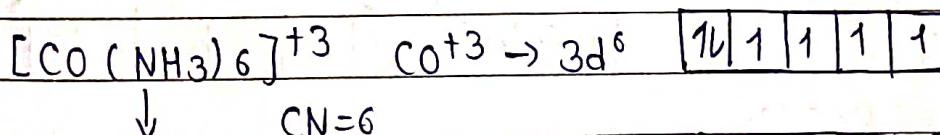
carbon / nitrogen donor - SFL

oxygen / halogen donor - WFL

Imp point

- \rightarrow All ligand act as SFL with 4d / 5d metal ions
- $\rightarrow \text{F}^-$ act as SFL with Ni^{+4}
- $\rightarrow \text{H}_2\text{O}$ & $\text{C}_2\text{O}_4^{2-}$ act as SFL Co^{+3}
- $\rightarrow \text{NH}_3 \rightarrow \text{WFL} \rightarrow \text{Fe}^{+2}$ & Mn^{+2}
- $\rightarrow \text{H}_2\text{O} \rightarrow \text{SFL} \rightarrow \text{Cu}^{+2}$ ($\text{CN} = 4$)

$\text{Co} - 3d^1 \text{hs}^2$



SFL

\downarrow Pairing V

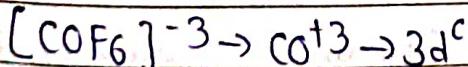
$\boxed{1}$	$\boxed{1}$	$\boxed{1}$	$\boxed{}$	$\boxed{}$	$\boxed{}$	$\boxed{}$
$(n-1) \text{ d}$			hs		np	

$d^2 \text{sp}^3$

inner orbital complex

low spin / spin paired

diamagnetic



\hookrightarrow WFL

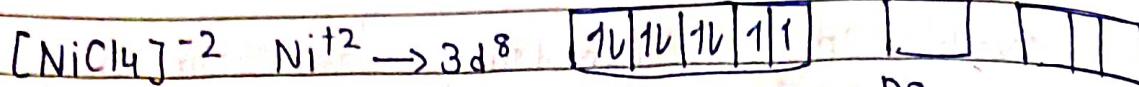
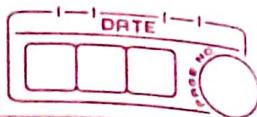
\downarrow Pairing X

$\boxed{1}$	$\boxed{1}$	$\boxed{1}$	$\boxed{1}$	$\boxed{}$	$\boxed{}$	$\boxed{}$	$\boxed{}$
ns		np		nd			

paramagnetic

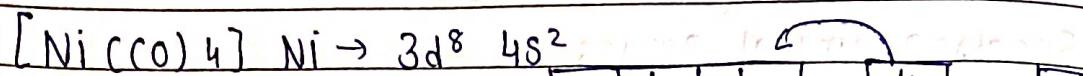
$\text{sp}^3 \text{d}^2$

outer orbital complex / high spin /
spin free complex



↳ WFL → 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ ns np

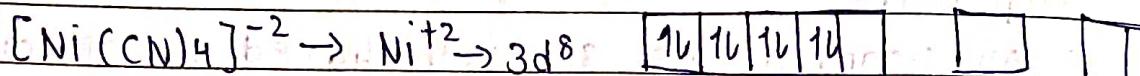
Pairing ✗ sp³ + tetrahedral paramagnetic



↳ SFL → 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s² np

Pairing ✓ 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s² 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s² 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s²

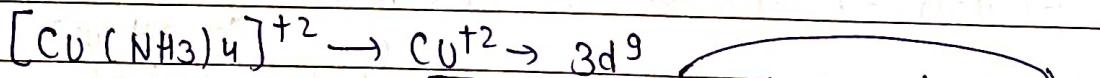
sp³ + tetrahedral diamagnetic



SFL 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ dsp²

Pairing ✓ 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ Sq. planar

diamagnetic



SFL 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹

d e⁻ excites

1	1	1	1						
---	---	---	---	--	--	--	--	--	--

1	1	1	1						1
---	---	---	---	--	--	--	--	--	---

dsp²

Sq. planar paramagnetic

Magnetic property of c.c.

Octahedral case

d¹, d², d³

1			
---	--	--	--

SFL | WFL → always d² sp³
inner orbital

1	1		
---	---	--	--

no pairing complex
is needed

1	1	1	
---	---	---	--

$d^8 d^9 d^{10}$

1L	1L	1L	1	1
----	----	----	---	---

 SFL/WFL, always sp^3d^2

↓

1L	1L	1L	1L	1
----	----	----	----	---

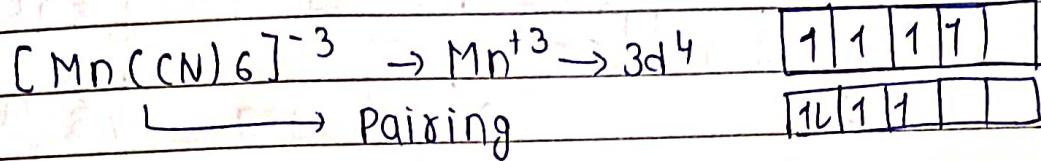
 no pairing outer orbital

occurs

1L	1L	1L	1L	1U
----	----	----	----	----

 complex

Magnetic moment

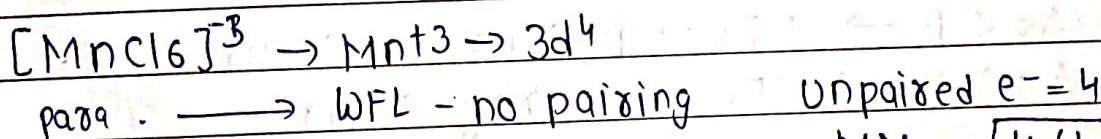


Unpaired $e^- = 2$

$$MM = \sqrt{n(n+2)} BM$$

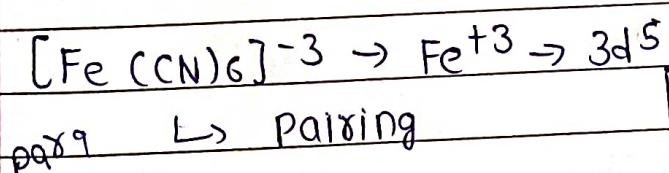
$$= \sqrt{2 \times 4}$$

$$= \sqrt{8} BM$$



$$MM = \sqrt{4(4+2)} BM$$

$$= \sqrt{24} BM$$



1	1	1	1	1
---	---	---	---	---

1L	1L	1		
----	----	---	--	--

$n=1$ $MM = \sqrt{3} BM$

* CFT

→ electrostatic Model

→ central metal → +ve charge } electrostatical

→ Ligand → -ve charge

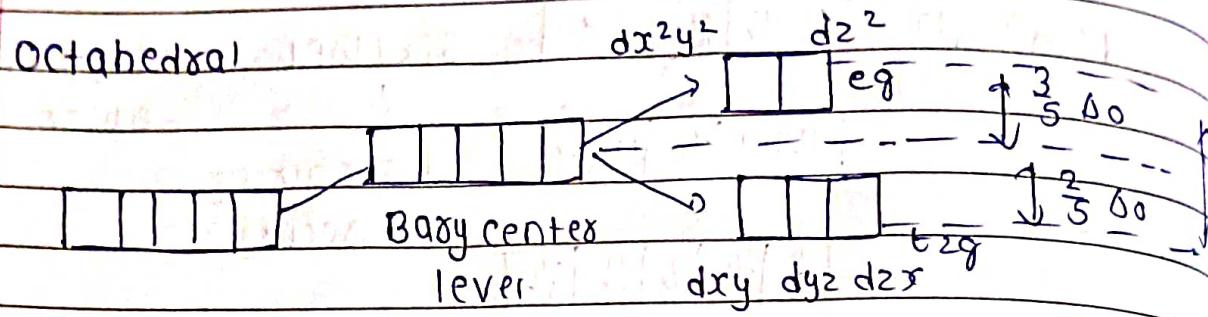
→ Degeneracy of d orbital breaks when ligand approaches central atom

repulsion betw. of d orbital

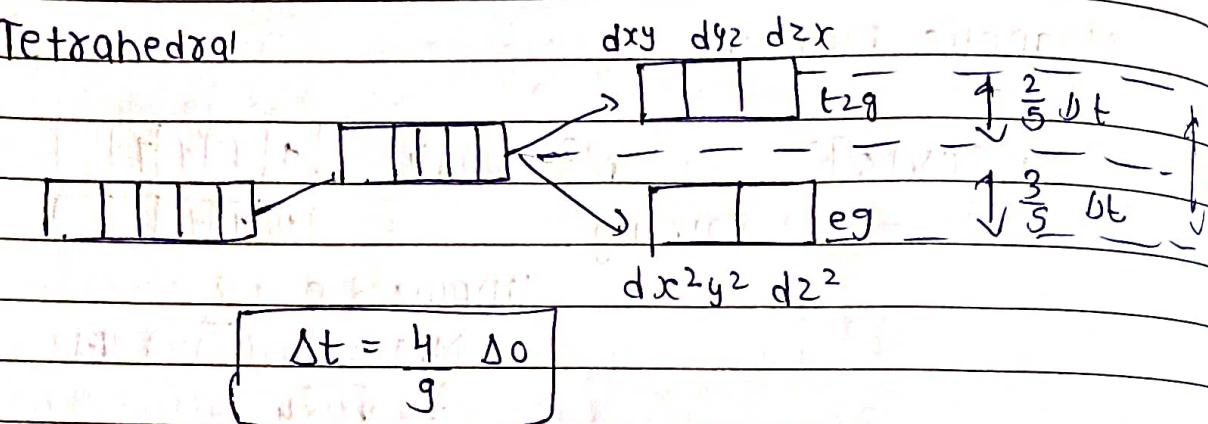
4 lone pair of ligand

so d orbital splitting occurs

Octahedral



Tetrahedral



$\Delta_0 < P \rightarrow$ WFL \rightarrow pairing not occur

$\Delta_0 > P \rightarrow$ SFL \rightarrow pairing occur

Factors affecting CFSE

$\Delta_0 \propto$ charge on CMA

$\Delta_0 \propto$ Z_{eff} of CA

3d < 4d < 5d \rightarrow CFSE

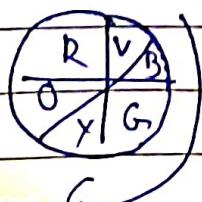
$\Delta_0 \propto$ Strength of ligand

Octahedral > tetrahedral $(\Delta t = \frac{4}{8} \Delta_0)$

Color

e⁻ jump ($t_{2g} - e_g$) } d-d transition
($e_g - t_{2g}$) } color

\rightarrow It always shows complementary colors

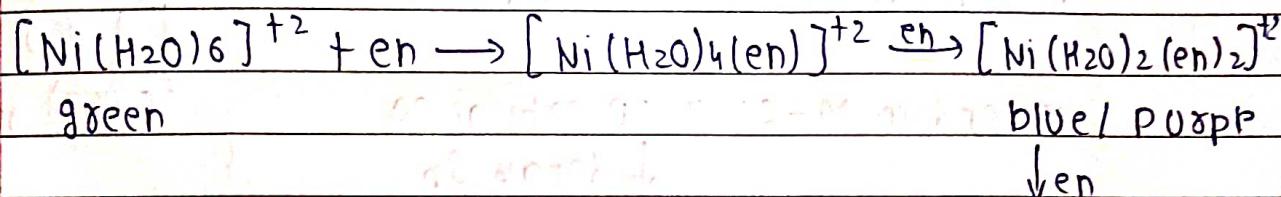


$\lambda \uparrow$



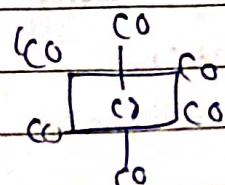
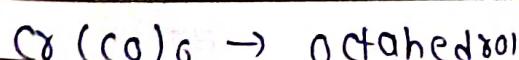
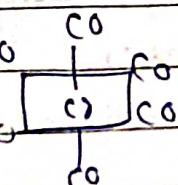
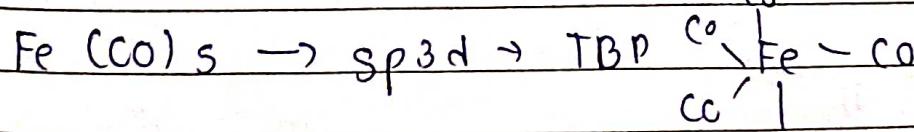
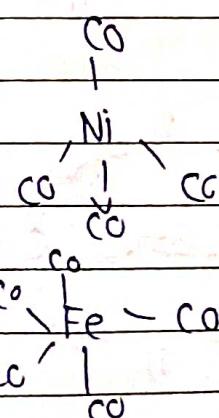
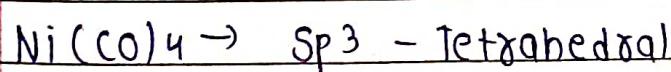
eg - $[\text{Ti}(\text{H}_2\text{O})_6]^{+3} \xrightarrow{\Delta}$ Removal of water
 violet colorless
 (ligand is lost)
 (attraction is lost)
 (splitting is lost)
 (no -dd transition)
 no colour

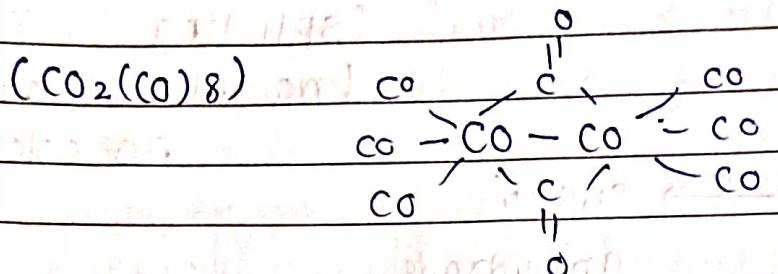
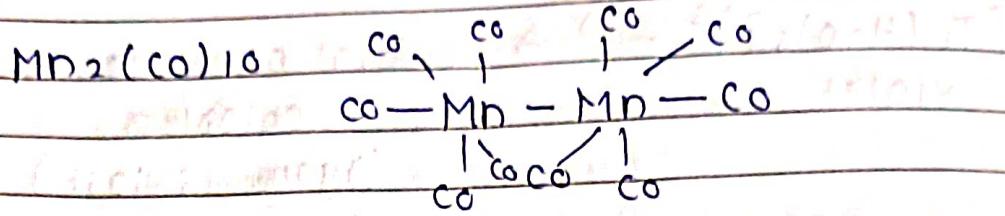
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{\Delta} \text{CuSO}_4$
 Blue violet anhydrous
 $4\text{H}_2\text{O} \rightarrow$ Ligand colorless
 coordinate bond
 $\rightarrow \text{H}_2\text{O} \rightarrow \text{H bond}$



Ans. $\text{EN} \rightarrow \text{SFL}$ $[\text{Ni}(\text{en})_3]^{+2}$
 $\text{SFL} \uparrow \text{CFSE} \uparrow$ violet
 $\text{EN} \uparrow \lambda \downarrow$

Bonding in metal carbonyls





Synergic bond.

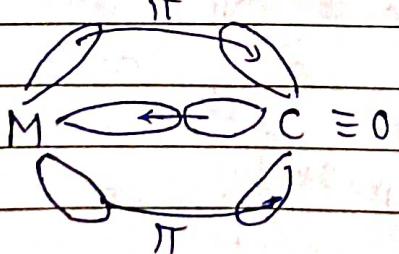
metal-carbon bond in metal carbonyl
has both σ and π bond.

σ bond in M-C: π -2p orbital CO
 \downarrow double dp

vacant orbital of metal

π bond in M-C \rightarrow Filled d orbital of M
 \downarrow donate

π^* (antibonding) molecular orbital of CO



Synergic bond
Strong