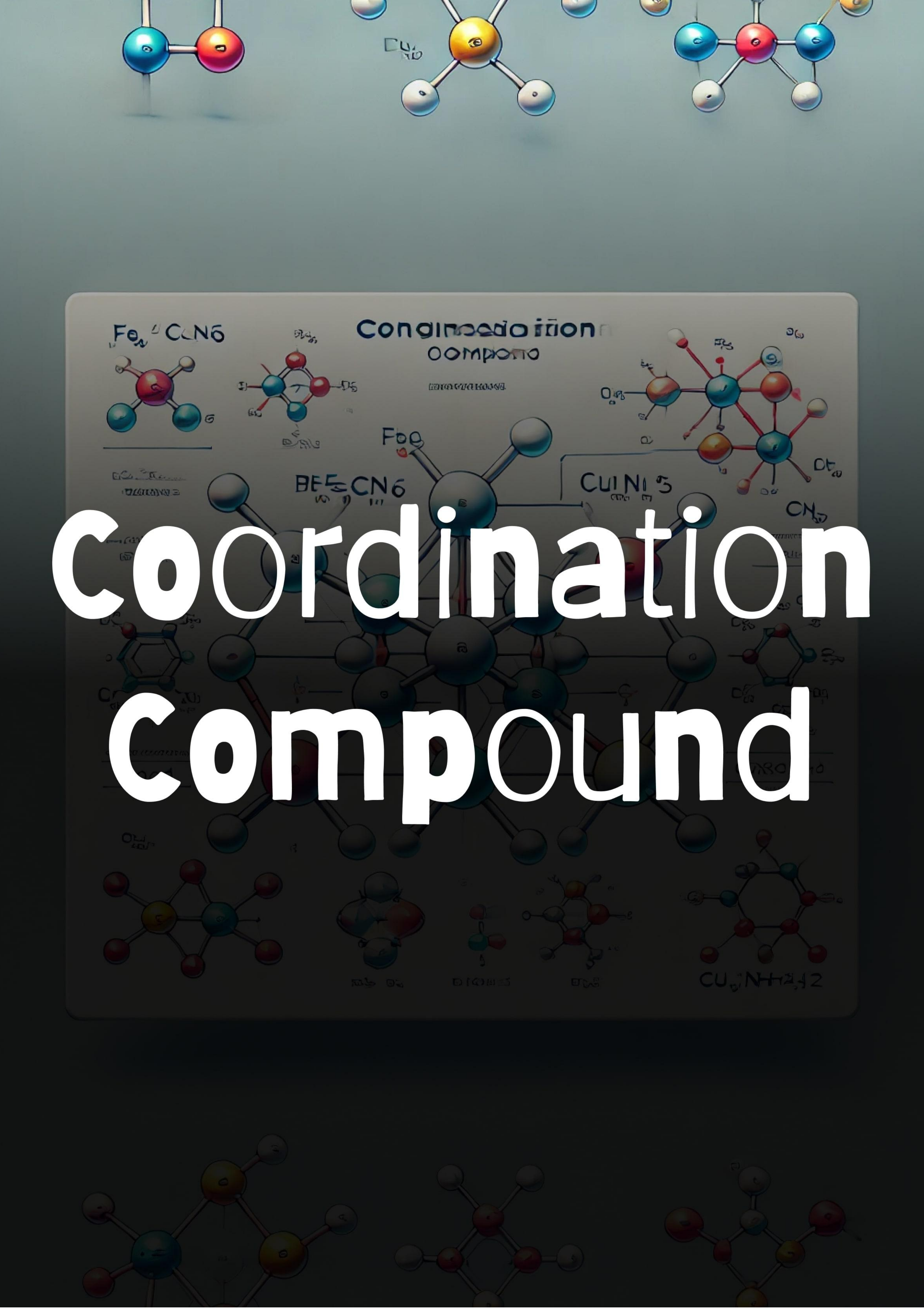


Coordination Compound

* Coordination Compounds. *

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

→ comp. in which metal atom (central metal atom) is bonded to anion / neutral (Ligand) molecule by coordinate bond is cordinate comp.

Chlorophyll - Mg
Haemoglobin - Fe
Vitamin B12 - Co

* Werner's Theory.

First scientist to study about the structure

Postulates of werner theory

1) metals have 2 types of valency

i) Primary valency

→ (Oxidation no, ionizable, satisfied by -ve ligand. non-directional)

→ $CrCl_3 \rightarrow 3$
$CoCl_2 \rightarrow 2$
$PdCl_2 \rightarrow 2$

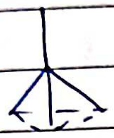
ii) Secondary valency

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

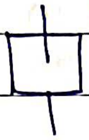
→ $CoCl_3 \cdot 6NH_3$ $[Co(NH_3)_6]Cl_3 \longrightarrow$ 3 mol AgCl Yellow.
$CoCl_3 \cdot 5NH_3$ $[Co(NH_3)_5Cl]Cl_2 \longrightarrow$ 2 mol AgCl Purpl
$CoCl_3 \cdot 4NH_3$ $[Co(NH_3)_4Cl_2]Cl \longrightarrow$ 1 mol AgCl Green
$CoCl_3 \cdot 4NH_3$ $[Co(NH_3)_4Cl_2]Cl \rightarrow$ 1 mol AgCl viole

isom

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



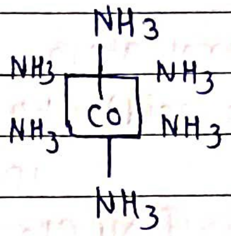
tetrahedral



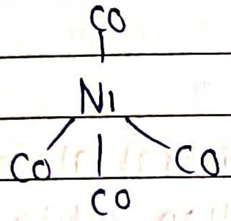
octahedral

sq. planar

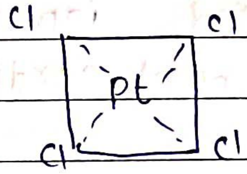
$[Co(NH_3)_6]^{+3}$ → octahedral



$[Ni(CO)_4]$ → tetrahedral



$PtCl_4^{-4}$ → sq. planar



coordination entity → species inside sq. bracket
counter ion → outside the sq. bracket

Difference betn Double salt & coordination comp

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

$KCl \cdot MgCl_2 \cdot 6H_2O$ kernalite.
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ Mohr's salt
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Potash Alum
$KAl(SO_4)_2 \cdot 12H_2O$

coordination comp. which do not dissociate completely into H_2O

$K_4[Fe(CN)_6] \xrightleftharpoons{H_2O} 4K^+ + [Fe(CN)_6]^{-4}$

* Imp definition

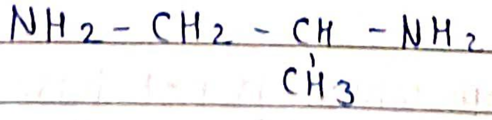
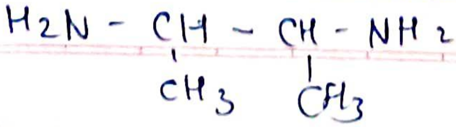
1) Cordination Entity - central metal atom / ion bonded to ligand and enclosed in square bracket
$[Co(NH_3)_3Cl_3]$
$[Ni(CO)_4]$

2) Central atom - atom / ion to which ligands are bonded (lewis acid) by cordinate bond in a definite geometry inside cordination entity
$[NiCl_2(H_2O)_4] \rightarrow Ni^{+2}$
$[Co(Cl)(NH_3)_5] \rightarrow Co^{+3}$

3) Ligand - ion / molecule bonded to central atom through (lewis base) cordinate bond in cordination entity.

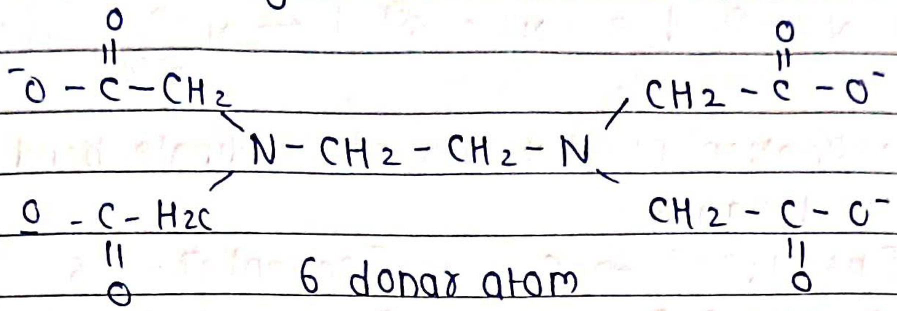
(chloro) chlorido, aqua, ammine, ~~Floro~~ fluorido, Hydrooxido, oxido
Unidentate → Single donor atom - Cl^-, H_2O, NH_3, F^-, OH^-, O^{-2},

O_2^{-2}	O_2^-	NH_2^-	NH^{-2}	N^{-3}	N_3^-
Peroxido	Super oxido	amido	Imido	nitrodo	azido

Didentate - two donor atom
① en - ethylenediammine
(ethane, 1,2 - diammine)
$NH_2 - CH_2 - CH_2 - NH_2$
② Pn - propylene diammine
propane 1,2 - diammine

$NH_2 - CH_2 - CH(CH_3) - NH_2$
③ bn - butylenediammine
Butane 2,3 - diammine

$H_2N - CH(CH_3) - CH(CH_3) - NH_2$

polydentate - Several donar atom

$(EDTA)^{-4}$ ethylenediamminetetraacetate



6 donar atom

Hexadentate

-4 Charge

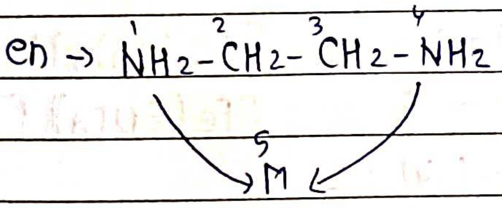
dien - diethylenetriammine

$\underline{NH_2}-CH_2-CH_2-\underline{NH}-CH_2-CH_2-\underline{NH_2}$

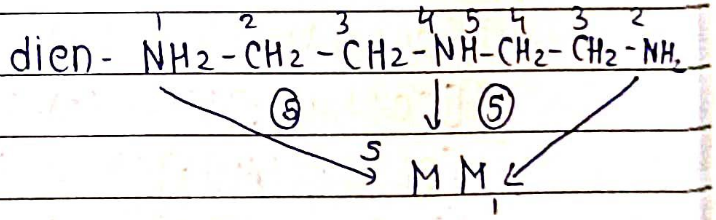
Tridentate

trien- $NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$

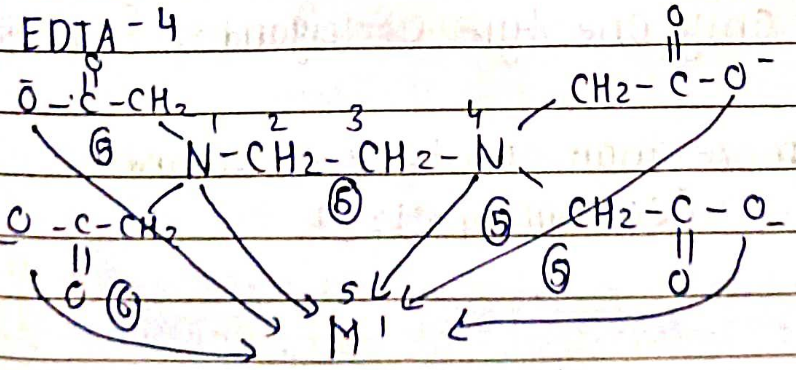
Chelate ligand → didentate / polydentate which forms 5-6 member ring after donation (stable)



5 member ring



5 member ring



5 member Ring → $\boxed{5}$

Ambidentate Ligand. which can donate through 2 diff atom

$\leftarrow {}^{\ominus}C \equiv N$	$\leftarrow {}^{\ominus}S-C \equiv N$	$\leftarrow \bar{O}-N=O$	$\leftarrow \dot{O}-C \equiv N$
$\leftarrow N \equiv C^{\ominus}$	$\leftarrow N \equiv C-S^{\ominus}$	$\leftarrow N^{=O}_{-O}$	$\leftarrow N \equiv C-O^-$

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

$[Pt\,Cl_6]^{-2} \rightarrow 6$ $\quad$ $[Co\,(en)_3] \rightarrow 6$

$[Fe\,(C_2O_4)_3] \rightarrow 6$ $\quad$ $[Ni\,(NH_3)_4] \rightarrow 4$

↓
didentate

Cordination sphere
vs
ionization Sphere.

$K_4\,[Fe\,(CN)_6]$

↓ ionization Sphere

→ cordination entity or cordination Sphere

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

$[Cu(CN)_4]^{-3} \rightarrow (-3)-(-4)=+1$

$[Co(NH_3)_6]^{+3} \rightarrow (3)-(6\times0) = 3$

$[Pt\,Cl_4\,(NH_3)_2]^{-2} \rightarrow (-2)-(-4)=2$

$[Fe\,(C_2O_4)_3]^{-3} \rightarrow (-3)-(-6) = +3$

$[Co\,(en)_3]^{+3} = 3$

$[Fe\,(EDTA)]^{-1} = (-1)-(-$

$= 3$

Homoleptic- only one type of Ligand → $[Co\,(NH_3)_6]^{+3}$

Heteroleptic- more than one type of Ligand
$[Co\,(NH_3)_4\,Cl_2]^{+}$

Effective Atomic number (EAN)

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

$$\boxed{EAN = Z - O.S + 2 \times CN}$$

$K_4[Fe(CN)_6] \rightarrow 26 - 2 + 2\times6 = 36$

$K_3[Fe(CN)_6] \rightarrow 26 - 3 + 2\times6 = 35$

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

$[Mn(CO)_5] \rightarrow 25 - 0 + 2\times5 = 35$

$[Mn(CO)_5]^- \rightarrow 25 - (-1) + 2\times5 = 36 \rightarrow$ stable

$Mn(CO)_6 \rightarrow$ EAN $\rightarrow 25 - 0 + 2\times6 = 37 \rightarrow e^- \rightarrow 35$

$[Mn(CO)_6]^+ \rightarrow$ EAN $\rightarrow 25 - 1 + 2\times6 = 36 \rightarrow$ stable

Q.) $V(CO)_6 \rightarrow 23 - 0 + 12 = 35 + e^- \rightarrow 36$

$[V(CO)_6]^- \rightarrow 23 - (-1) + 12 = 36 \rightarrow$ stable

if EAN < atomic no. of inert gas → oxidizing agent.

EAN > atomic no. of inert gas → Reducing agent

* Nomenclature

Rules for writing formula.

→ identify central atom.

→ write ligands in alphabatical order.

→ abbreviated ligand → consider first letter for alphabatical order

→ write formula in sq. bracket

→ no space betn ligand & metal.

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

Triammine triaqua chromium (III) chloride

$[Cr(NH_3)_3(H_2O)_3]^{+3}Cl_3$

tris (ethane-1,2-diammine) cobalt (III) Sulphate

Co

$Co(en)_3$

$[Co(en)_3]^{+3}$ SO_4^{-2}

$[Co(en)_3]_2(SO_4)_3$

Naming of cordination compound

→ cation is named first than anion. then LCO Rule

→ Ligands are named first (alphabatical order) then central atom is named & then oxd^n no. is written in Roman

naming of ligand-
anionic ligand ends in O.

Cl^- → chlorido
$C_2O_4^{-2}$ → oxalato
O^{-2} → oxido
OH^- → Hydroxido

neutral ligand. NH_3 - ammine
H_2O - aqua
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

$[NiCl_2(PPh_3)_2]$

dichloro (triphenylphosphine) nickel (II)

complex - cationic → central atom has same name
complex - anionic → central atom add 'ate' in en

$[Co(SCN)_4]^{-2}$ → Cobaltate

$[Fe(CN)_6]^{-4}$ → Ferrate

$[Pt(NH_3)_6]^{+2}$ → Platinum

$[Cr(NH_3)_3(H_2O)_3]^{+3}$ → triamminetriaquachromium (III) chloride

$[Co(en)_3]_2(SO_4)_3$ →

$[Co(en)_3]^{+3}\ SO_4^{-2}$ → tris (ethylenediammine) cobalt sulphat
(ethane 1,2, diammine)

$[Ag(NH_3)_2]^+\ [Ag(CN)_2]^-$
diammine silver (I) dicyanoargentate (I)

* Isomerism

* structural isomerism

i) ionization
→ comp. which give diff. ions
$[Co(NH_3)_5SO_4]Br$
$[Co(NH_3)_5Br]SO_4$

ii) Solvate
→ no. of water molecules inside & outside cordination sphere is different
$[Cr(H_2O)_6]Cl_3$
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

iii) Linkage
→ ambidentate ligand
$[Co(NH_3)_5NO_2]Cl_2$
$[Co(NH_3)_5ONO]Cl_2$

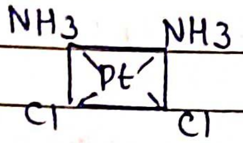
iv) cordination
→ cation & anion both are complex
$[Co(NH_3)_6][Cr(CN)_6]$
$[Co(CN)_6][Cr(NH_3)_6]$

* Stereo isomer
i) Geometrical isomer:
Tetrahedral ✗
sq. planar ✓
octahedral ✓

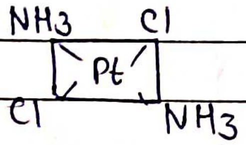
Cordination no. = 4

Ma_4 - 0
Ma_3b - 0
Ma_2b_2 - 2 < cis trans
Ma_2bc - 2 < cis trans
Mabcd - 3 < 2 cis trans

$[Pt(NH_3)_2Cl_2]$
$Ma_2b_2 \rightarrow 2$ GI < cis trans

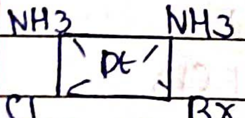


cis.

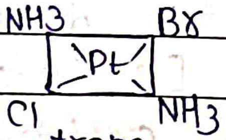


Trans

$Pt(NH_3)_2ClBr$
Ma_2bc - 2 GI < cis trans

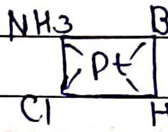


cis

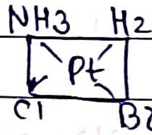


trans

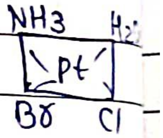
& $Pt(NH_3)(H_2O)(Cl)(Br)$
Mabcd → 3 GI < 2 cis 1 trans



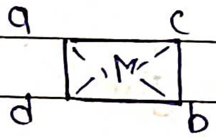
(ab cd)



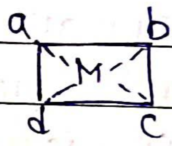
(ac bd)



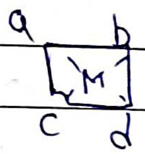
(ad bc)



Trans



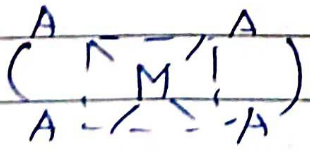
cis



cis

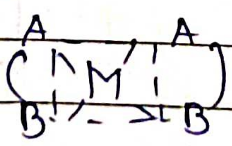
Bidentate

$[Pt(en)_2]^{+2}$
$[M(AA)_2]^{+2}$
2 donar atom of bidentate ligand never lie at 180°

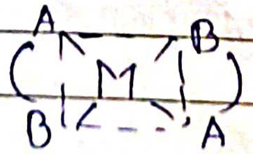


no GI

$[Pt(gly)_2]$
$[M(AB)_2]$

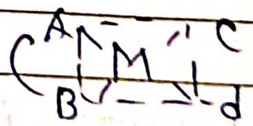


cis

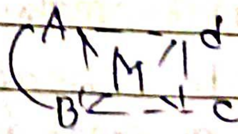


trans

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



cis



Tran

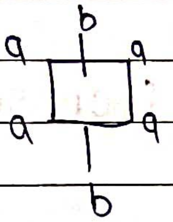
Geometrical & optical isomer in octahedral

	GI	Pair of enantiomer	no. of Stereoisomer (GI + OI)
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
$Mabcde$	9	6	15
$Mabcdef$	15	15	30

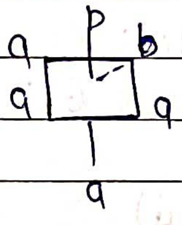
$[Pt(NH_3)_4Cl_2]$ or $[Co(NH_3)_4Cl_2]^+$

Ma_4b_2

GI = 2 < cis, Trans



Trans

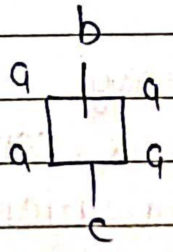


Cis

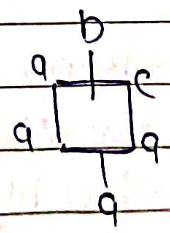
$[Pt(NH_3)_4ClBr]$

Ma_4bc

GI = 2 < cis, Trans



Trans



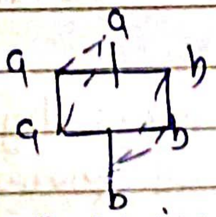
cis

Ma_3b_3

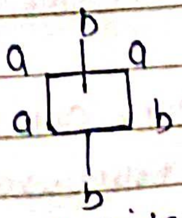
$[Co(NH_3)_3Cl_3]$

$[Co(NH_3)_3(NO_2)_3]$

2 GI – fac, mer



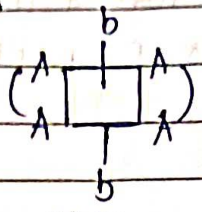
facial isomer (fac)



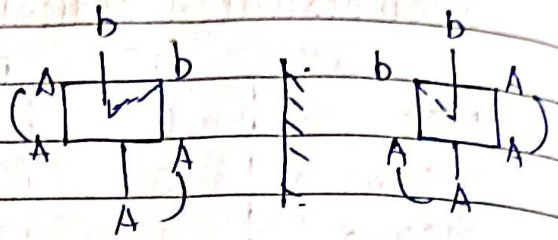
meridonal isomer (mer)

Bidentate ligand

$[Co\,Cl_2\,(en)_2]$
$[M\,(AA)_2\,b_2]$

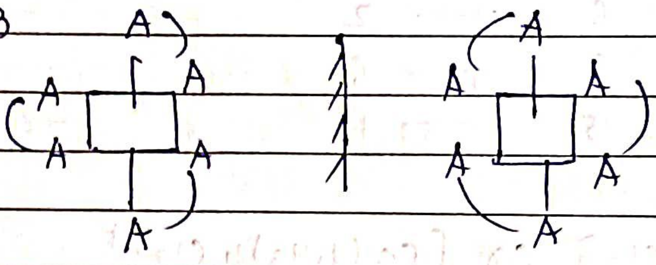


Trans



cis
(chiral molecule)
shows O.I
non superimposable mirror im

$M(AA)_3$



Chiral
shows G.I (non superimposable mirror image

(d) dextrorotatory
PPL { (+ve) rotation

(l) leavorotatory
PPL { (-ve) rotation

* Valence - Bond Theory.

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

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

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

CN=4 (sp^3 - Tetrahedral
(dsp^2 - Sq. planar

CN=6 (d^2sp^3 - Octahedral
(sp^3d^2 - Octahedral

SFL → Pairing occurs
WFL → pairing do not occurs

Spectrochemical series

$I^- < Br^- < SCN^- < Cl^- < S^{-2} < F^- < OH^- < C_2O_4^{-2} < H_2O < NCS^-$
$< EDTA < NH_3 < en < NO_2^- < CN^- < CO$

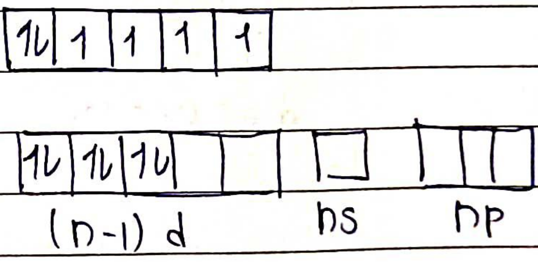
carbon / nitrogen donar - SFL
oxygen / halogen donar - WFL

Imp point

- → All ligand act as SFL with 4d / 5d metal ions
- → F^- act as SFL with Ni^{+4}
- → H_2O & $C_2O_4^{-2}$ act as SFL Co^{+3}
- → NH_3 → WFL → Fe^{+2} & Mn^{+2}
- → H_2O → SFL → Cu^{+2} (CN=4)

Co - $3d^1 4s^2$

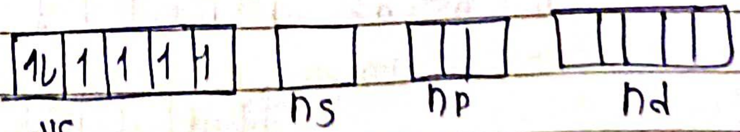
$[Co(NH_3)_6]^{+3}$ $Co^{+3} \rightarrow 3d^6$



↓ CN=6
SFL
↓
Pairing ✓

d_2sp^3
inner orbital complex
low spin / spin paired
diamagnetic

$[CoF_6]^{-3} \rightarrow Co^{+3} \rightarrow 3d^6$

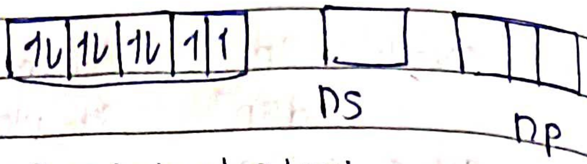


↳ WFL
↓
pairing ✗

paramagnetic

sp^3d^2
outer orbital complex / high spin /
spin free complex

$[NiCl_4]^{-2}$ $Ni^{+2} \rightarrow 3d^8$



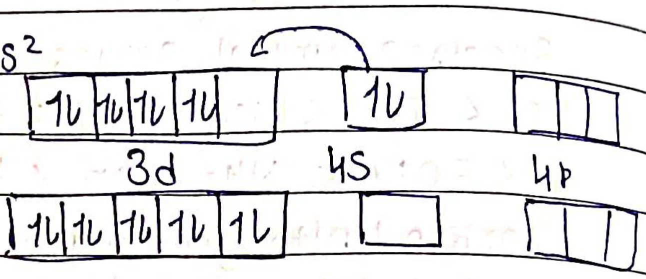
↳ WFL

Pairing ×

sp3 tetrahedral

paramagnetic

$[Ni(CO)_4]$ $Ni \rightarrow 3d^8\ 4s^2$



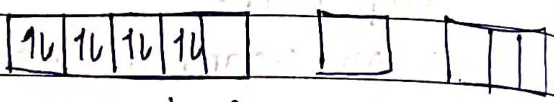
↳SFL

Pairing ✓

∴ sp3 Tetrahedral

diamagnetic

$[Ni(CN)_4]^{-2} \rightarrow Ni^{+2} \rightarrow 3d^8$



SFL

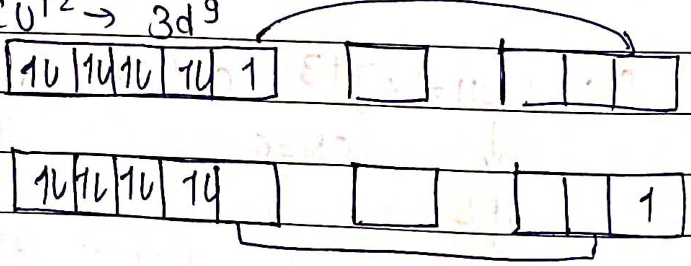
Pairing ✓

dsp^2

Sq. planar

diamagnetic

$[Cu(NH_3)_4]^{+2} \rightarrow Cu^{+2} \rightarrow 3d^9$



SFL

d e⁻ excites

dsp^2

Sq. planar paramagnetic

Magnetic property of C.C

Octahedral case

d^1, d^2, d^3

SFL/WFL → always d^2sp^3 inner orbital complex

↓

no pairing is needed

d^8 d^9 d^{10} [↑↓][↑↓][↑↓][↑][↑] SFL / WFL → always sp^3d^2 outer orbital complex

↓ no pairing occurs

[↑↓][↑↓][↑↓][↑↓][↑]

[↑↓][↑↓][↑↓][↑↓][↑↓]

Magnetic moment

$[Mn(CN)_6]^{-3} \rightarrow Mn^{+3} \rightarrow 3d^4$ [↑][↑][↑][↑][ ]

→ Pairing [↑↓][↑][↑][ ][ ]

Unpaired $e^- = 2$

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

$= \sqrt{2 \times 4}$

$= \sqrt{8}$ BM

$[MnCl_6]^{-3} \rightarrow Mn^{+3} \rightarrow 3d^4$

para → WFL – no pairing Unpaired $e^- = 4$

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

$= \sqrt{24}$ BM

$[Fe(CN)_6]^{-3} \rightarrow Fe^{+3} \rightarrow 3d^5$ [↑][↑][↑][↑][↑]

para ↳ Pairing

[↑↓][↑↓][↑][ ][ ]

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

* CFT

→ electrostatic Model

→ central metal → +ve charge } electrostatical

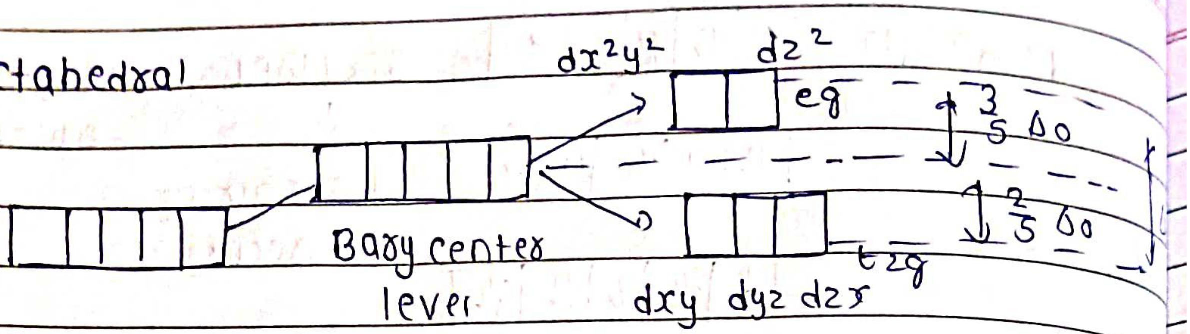
→ Ligand → –ve charge

→ Degeneracy of d orbital breaks when ligand approaches central atom

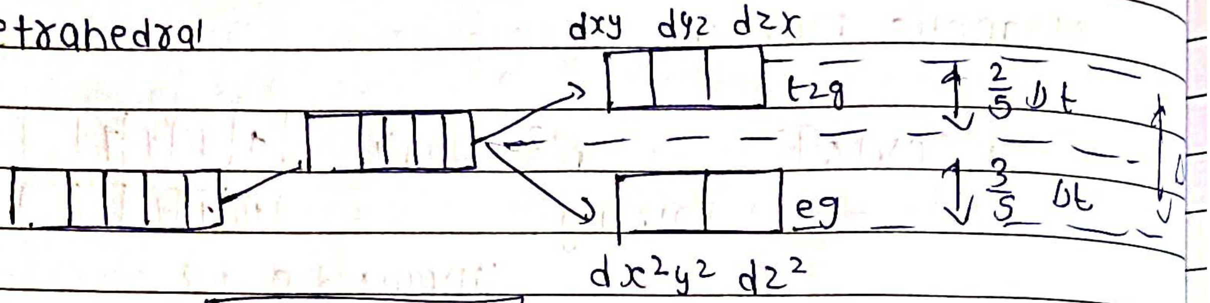
repulsion betn e⁻ of d orbital & lone pair of ligand

so d orbital splitting occurs

Octahedral



Tetrahedral



$$\boxed{\Delta t = \frac{4}{9}\Delta o}$$

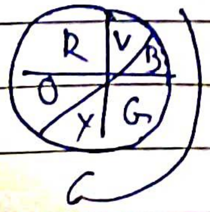
$\Delta o < P$ → WFL → pairing not occur
$\Delta o > P$ → SFL → pairing occur

Factors affecting CFSE
$\Delta o \propto$ charge on CMA
$\Delta o \propto$ zeff of CA
3d < 4d < 5d → CFSE
$\Delta o \propto$ Strength of ligand
Octahedral > tetrahedral $\left(\Delta t = \frac{4}{9}\Delta o\right)$

Color

e⁻ jump (t2g - eg)
(eg - t2g) } d-d transition
↓
color

→ It always shows complimentary colour



λ ↑

eg- $[Ti(H_2O)_6]^{+3} \xrightarrow{\Delta}$ Removal of water
violet
colorless
(ligand is lost)
(attraction is lost)
(spliting is lost)
(no-dd transition)
no colour

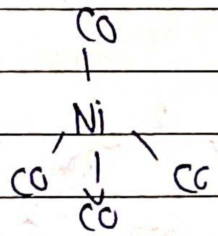
$CuSO_4 \cdot 5H_2O \xrightarrow{\Delta} CuSO_4$
Blue vitrio anhydrous
$4H_2O$ → Ligand colorless
cordinate bond
$1\ H_2O$ → H bond

$[Ni(H_2O)_6]^{+2} + en \longrightarrow [Ni(H_2O)_4(en)]^{+2} \xrightarrow{en} [Ni(H_2O)_2(en)_2]^{+2}$
green blue/ purple
$\downarrow en$
$[Ni(en)_3]^{+2}$
violet

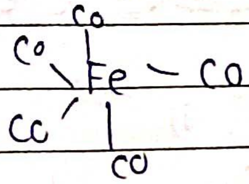
Ans. En → SFL
SFL ↑ CFSE ↑
En ↑ $\lambda \downarrow$

Bonding in metal carbonyl:

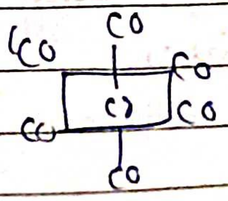
$Ni(CO)_4$ → sp^3 - Tetrahedral



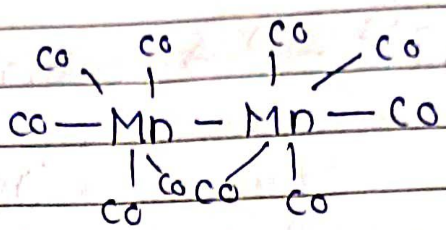
$Fe(CO)_5$ → sp^3d → TBP



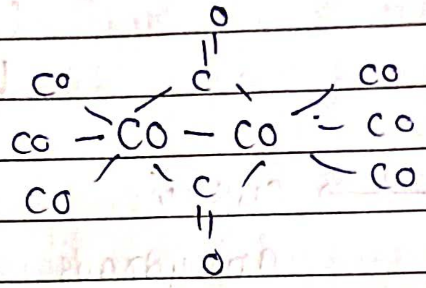
$Cr(CO)_6$ → octahedral



$Mn_2(CO)_{10}$



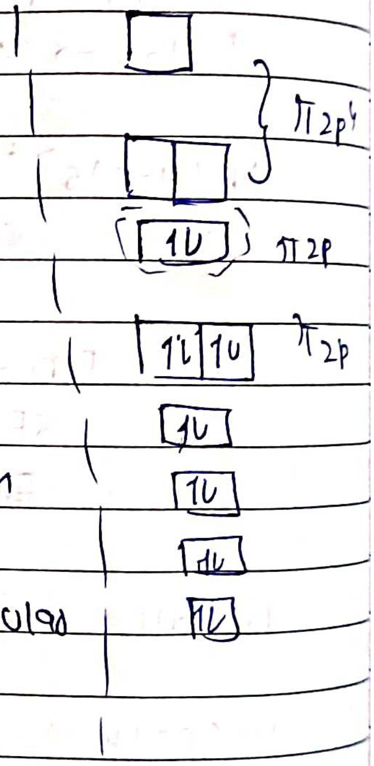
$(Co_2(CO)_8)$

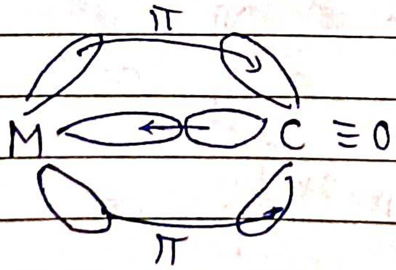


Synergic bond.
metal- carbon bond in metal carbonyl has both σ and π bond.

σ bond in M–C : π 2P orbital CO
↓ donate lp
vacant orbital of metal

π bond in M–C → Filled d orbital of M
↓ donate
π^* (antibonding molecular orbital of CO.





Synergic bond
Strong