

Coordination Compounds

Date / /
Page No.

① Coordination Numbers and Geometries

- a) Isomerism in Transition Metal Atom Compounds
- b) Crystal field Theory
- c) Energy level diagram for Transition Metal ion
- d) magnetic properties.

Metal \rightarrow (metal cation) \rightarrow electron deficient species

(or) Lewis acid

(or) electrophile

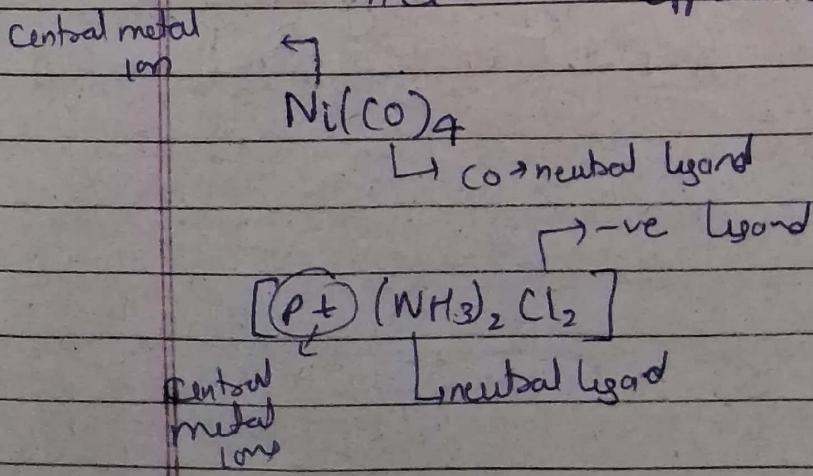
Tons/molecule \rightarrow having lone pair of e⁻ (ligands)

or e⁻ rich species (or) Lewis base

(or) Nucleophile

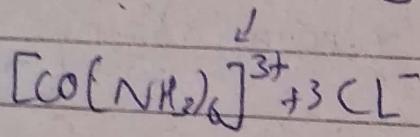
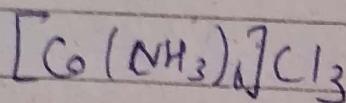
M : L \rightarrow metal cation is attached to group of ligands
by coordinate bonds \rightarrow complex (or) coordination compounds

Coordination Compounds \rightarrow is one which contains a central metal atom (or) ion surrounded by a number of oppositely charged (or) neutral molecules.



Ionic coordination Compounds: coordination compounds retain their identity on dissociation.

Complex coordination cation/ anion



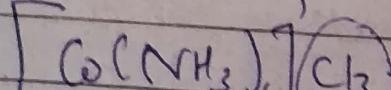
→ Inside [] → square bracket

→ coordination sphere

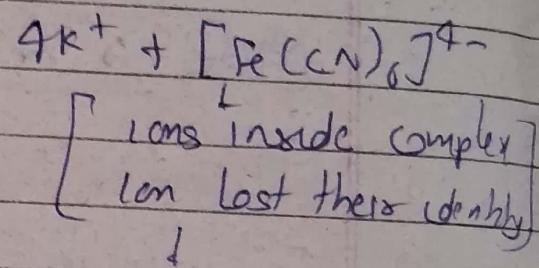
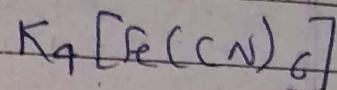
→ no. of attached ligands

↓ Coordination number

→ coordination sphere



↓ Coordination number



CN^- will not show test
because it's not freely available

The branch of inorganic chemistry dealing with the study of coordination compounds → coordination chemistry

Weiner Theory

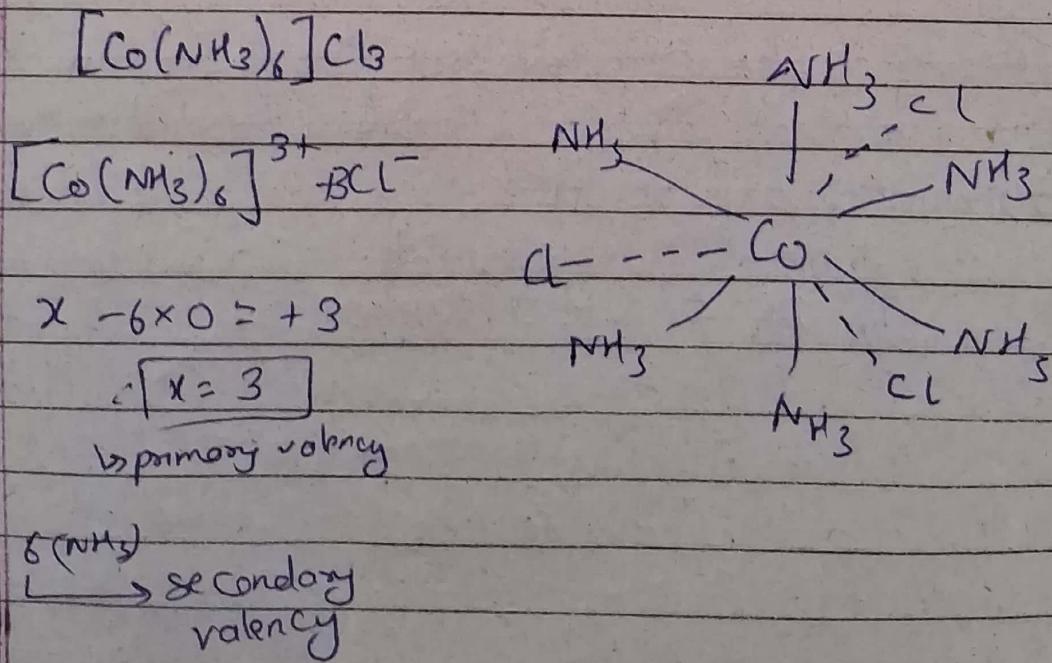
1893 → [Weiner] produced a theory of coordination compounds
 JSt Inorganic chemist
 ↓
 1913 → noble prize
 to explain structure and formation of Compounds.

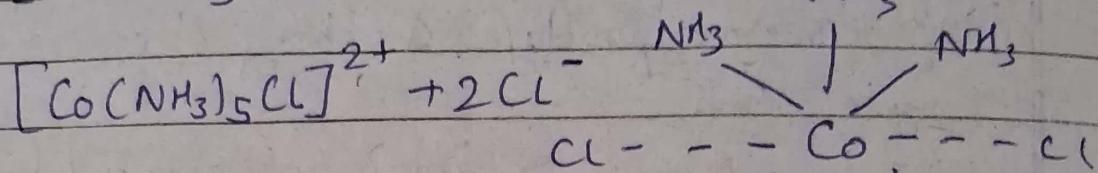
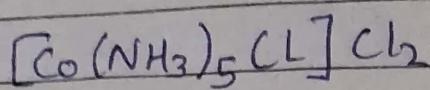
Postulates -

- ① Metal consist of two types of valencies
 - a) primary
 - b) secondary

Primary : → Ionisable . . . dotted , responsible for charge on central metal atom.

Secondary : non-ionisable . — solid line , It determines (co-ordination number) the number of ligand attached to central metal atom.

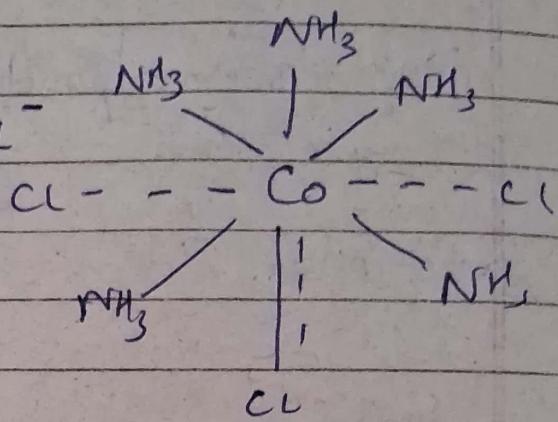




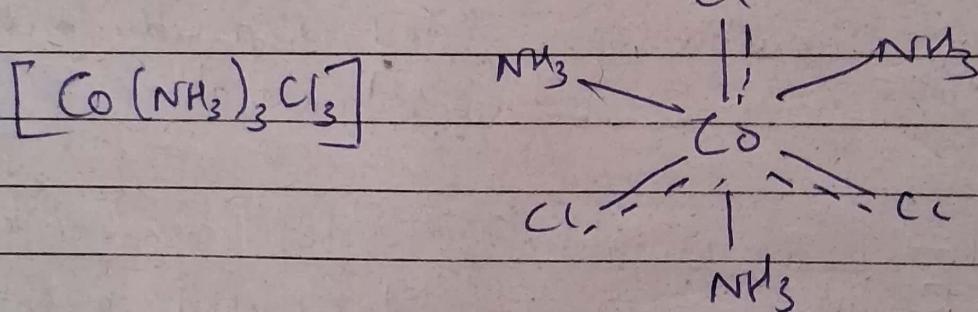
$$x + 5(0) - 1 = 12$$

$$\boxed{x=3}$$

formal valency



$\left. \begin{matrix} 5 & \text{NH}_3 \\ 1 & \text{Cl} \end{matrix} \right\} 6 \rightarrow \text{Coordination no} \rightarrow \text{secondary valency,}$



Limitations

- a) why complex compounds are formed by few metals?
- b) directional properties of bonds in coordination compounds?
- c) magnetic properties
 optical
 color etc } cannot explain

Terms used in coordination compounds :-

a) Ligands: charged (ox) neutral group (or) molecule that coordinate to central atom (ox) ion in a coordination compound.

monodentate ligand

(-ve r charged)

F⁻ - fluoro

I⁻ → Iodo

Cl⁻ → chloro

OH⁻ → hydroxo
etc

Neutral

:NH₃

Amonia

CO

carbonyl

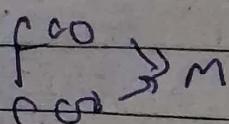
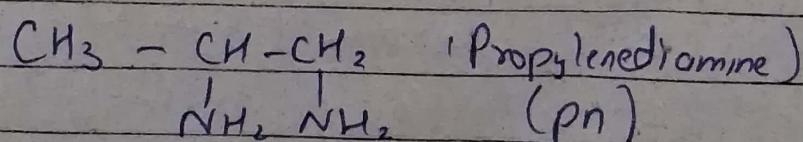
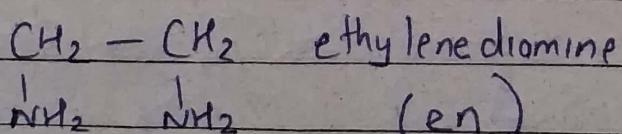
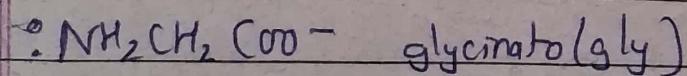
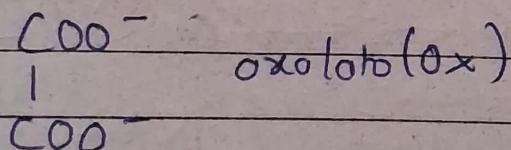
H₂O

Aqua

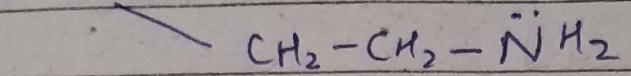
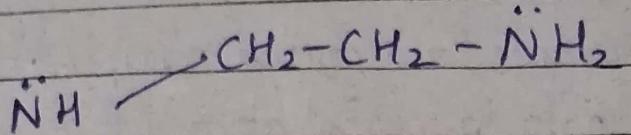
C₅H₅N

Py (Pyridine)

Bidentate ligands



Tetridentate ligands



(diethylene triamine) (dien)

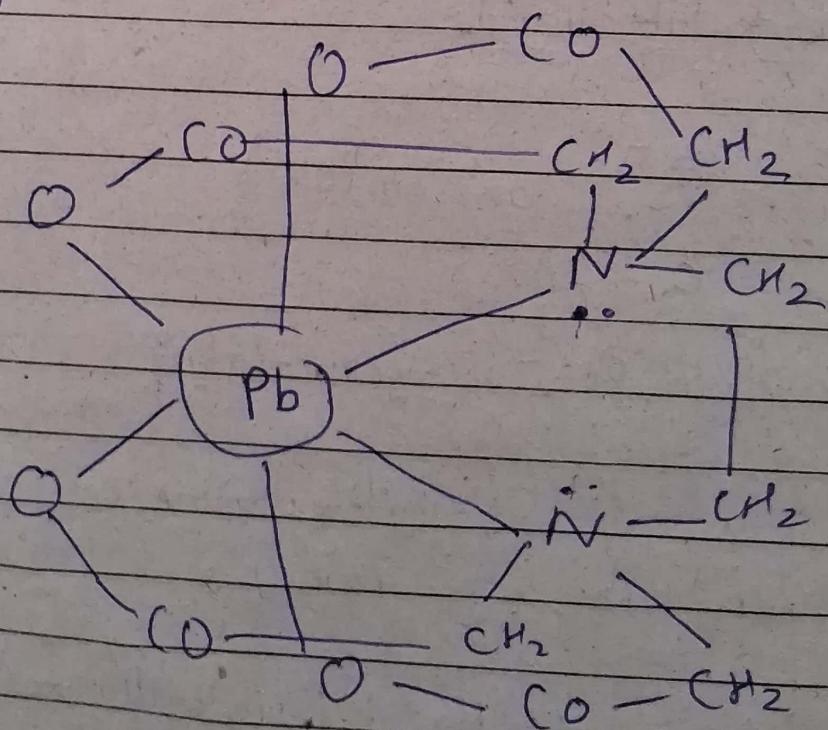
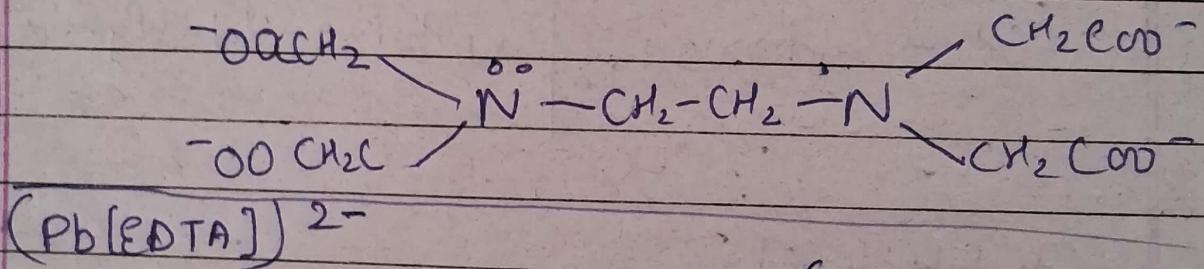
Tetradentate

Penta dentate

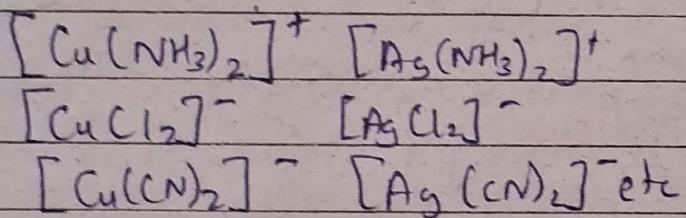
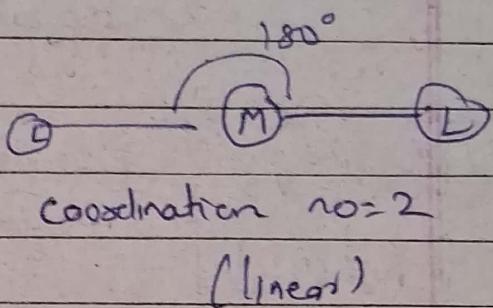
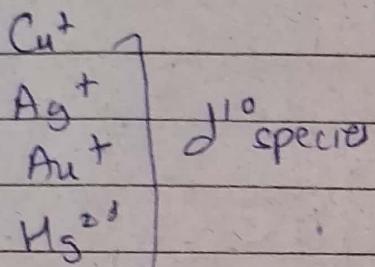
Hexadentate

EDTA

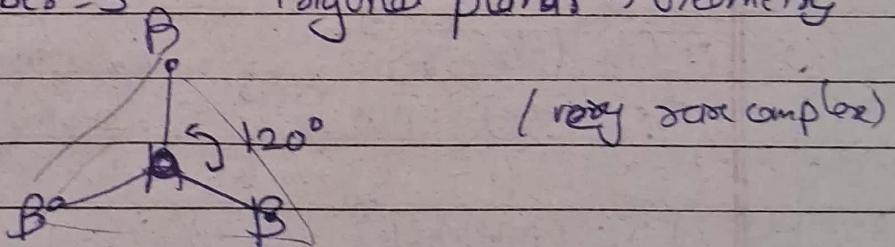
ethylene diamine tetraacetatol



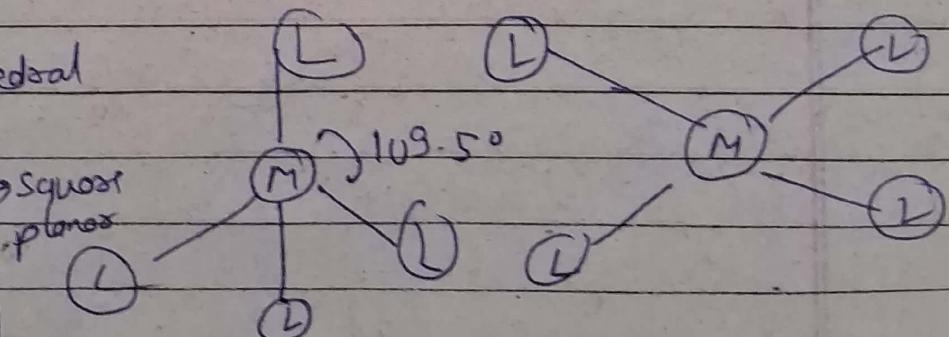
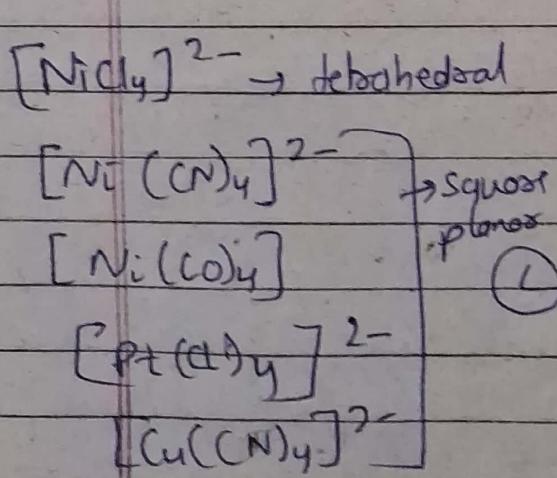
b) Coordination number: Number of ligands attached directly to central metal atom (ox) ion by coordinate bonds in given complex.



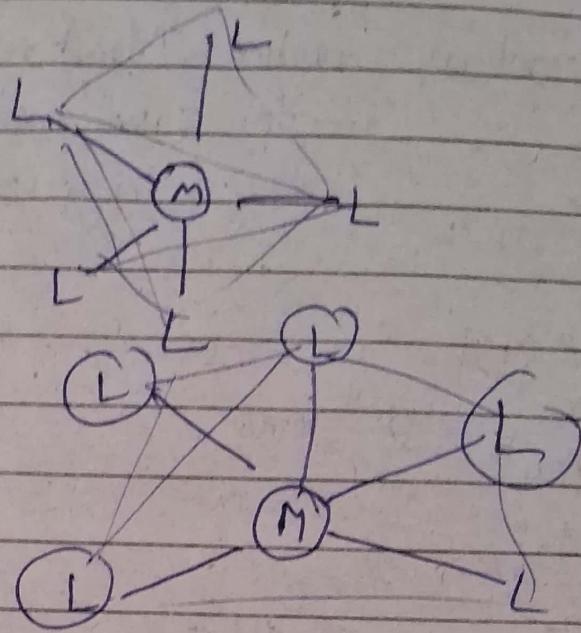
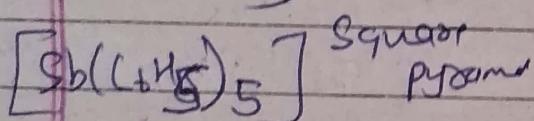
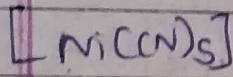
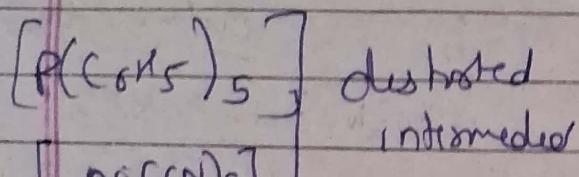
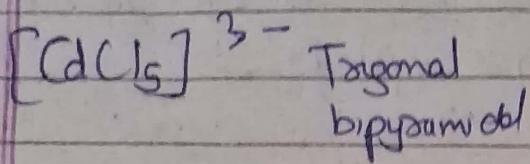
i) Coordination number = 3 Trigonal planar \rightarrow Geometry



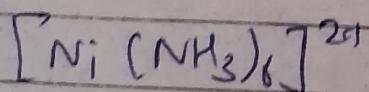
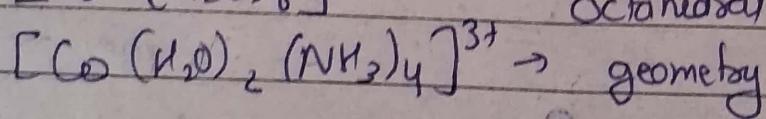
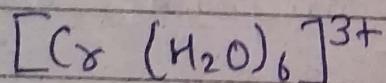
ii) Coordination number = 4 (Tetrahedral or square plane)



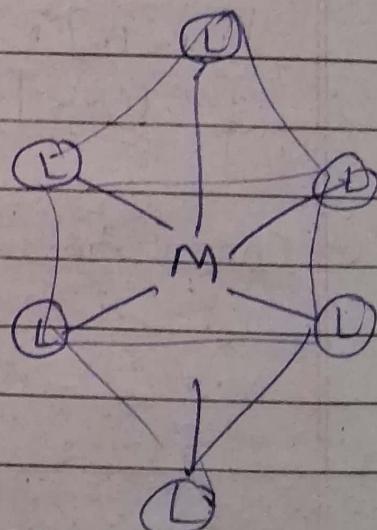
Coordination no = 5



Coordination no = 6

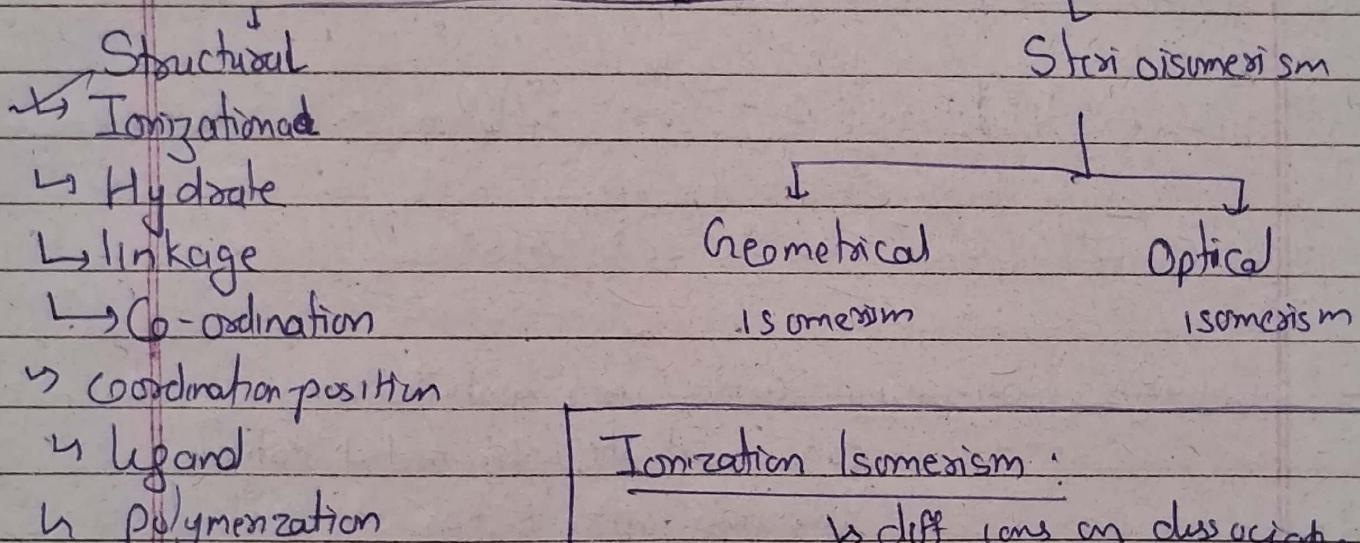


etc



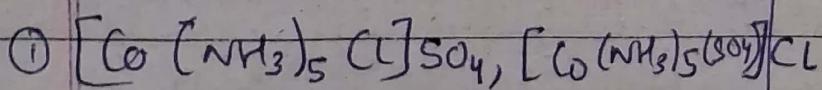
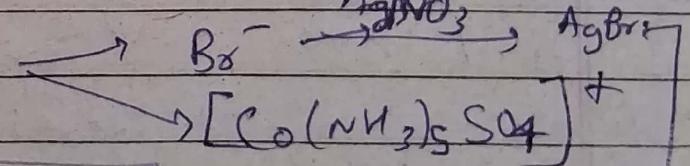
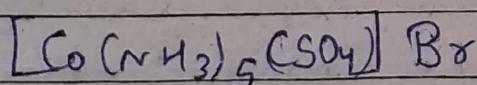
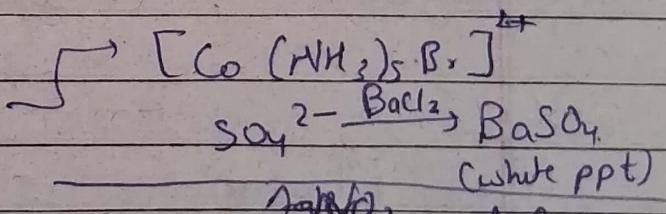
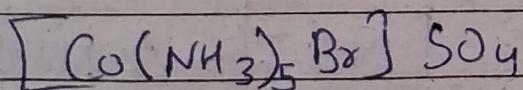
- ① Explain Ionization isomerism & linkage isomerism for transition metal complex with an example for each? (6)
 ② Explain geometrical isomerism & optical isomerism.

Isomerism → same chemical composition but different arrangement

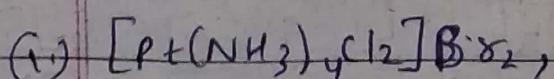


Ionization Isomerism:

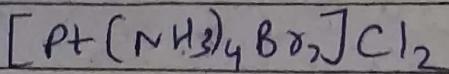
→ diff ions on dissociation



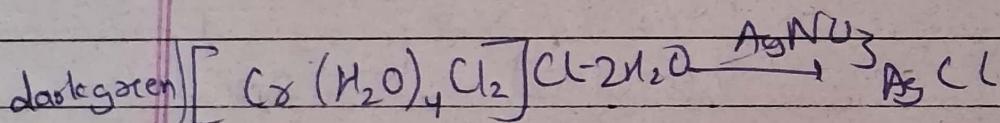
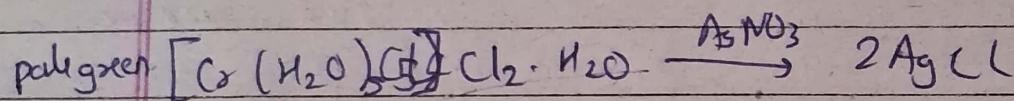
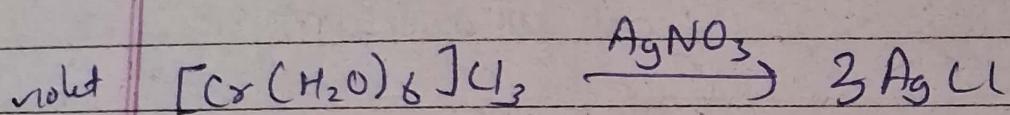
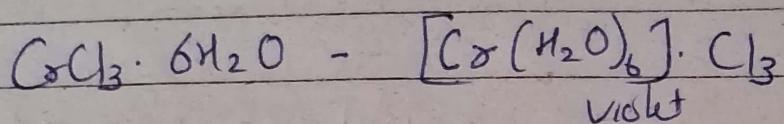
(cream color precipitate)



indicate presence of Br^-

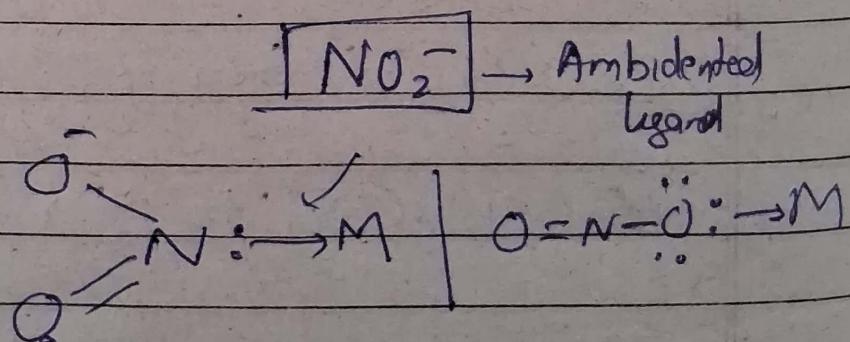
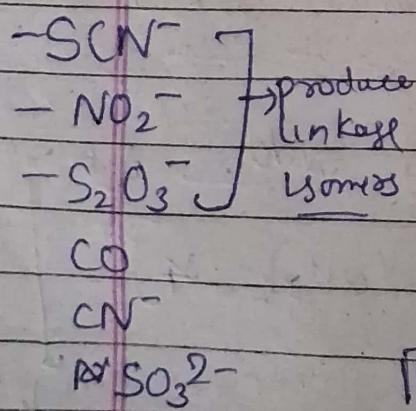


Hydrate Isomerism: water molecules are exchanged between coordination sphere & ionization sphere

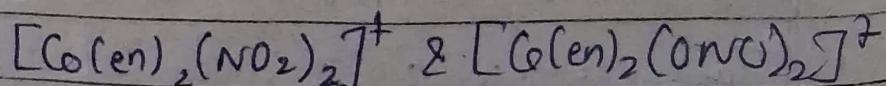
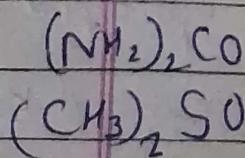


Linkage Isomerism: arise when ambidentate ligand can coordinate to metal cation through either of two different donor atoms.

Ambidentate Ligands



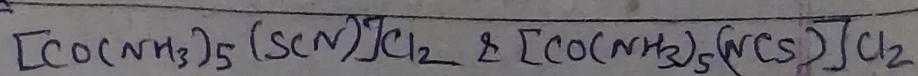
Ex



M + SCN⁻

[M ← SCN⁻]

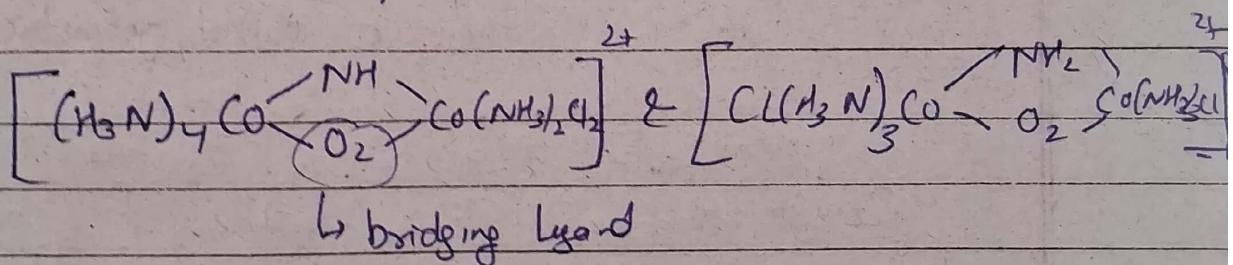
Ex



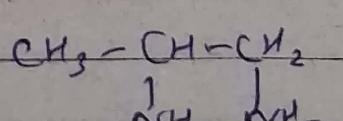
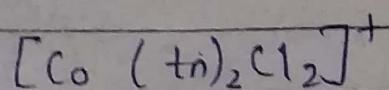
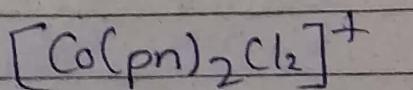
Coordination Isomerism: In complex: when cation and anion both are complex ions, these may be exchanged of ligands between two complex ions resulting in coordination isomers.

- i) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ & $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- ii) $[\text{Cu}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_4]$ & $[\text{Pt}(\text{NH}_3)_4][\text{Cu}(\text{Cl})_4]$

Coordination Position Isomerism: In bridging complexes an ligand between two metal cations give rise to coordination position isomerism.

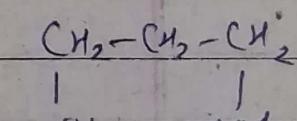


Ligand Isomerism: If ligand itself exist in two/more isomeric forms, then complexes containing such ligands exists in isomeric forms.

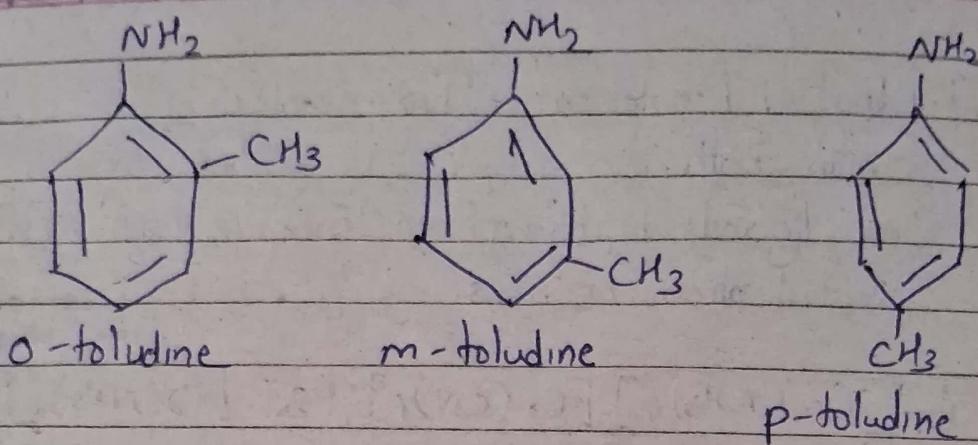


(1,2)

di amino propane



(1,3) di amino propane



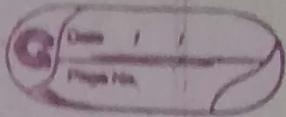
Geometrical Isomerism :- Stereoisomerism in which relative position (or) orientation of ligands (or) more specifically donor atoms around the metal cation is different are called geometrical isomers.

[G.I]

bent in p.

Cannot inter-converted without
breaking Metal-legand M-L
bond # Bond angle will change

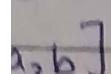
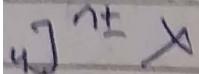
Coordination Comp



Coordination no = 4

Coordination no = 6

Octahedral



angle

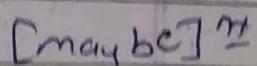
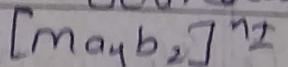
ys $105^\circ 38'$

Square planar

Cis 2 bonds

Isomers

Octahedral



a)

Cis

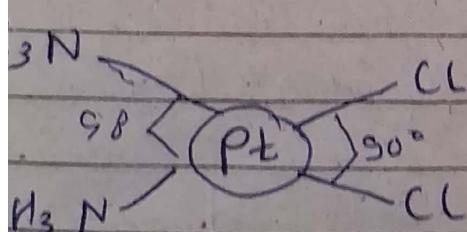
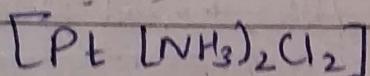
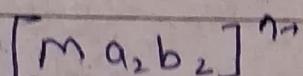
same ligand

$$B-A=90^\circ$$

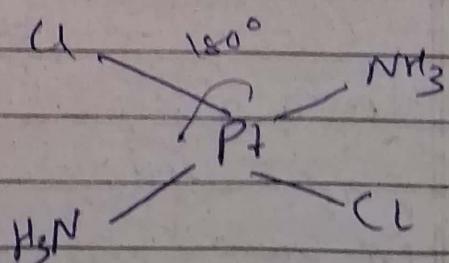
trans

same ligands

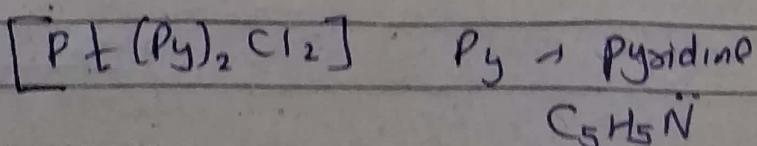
$$\text{angle} = 180^\circ$$



Cis - Isomer

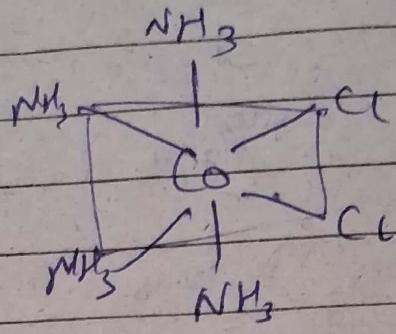
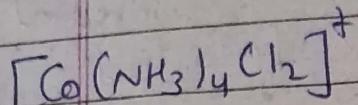


trans - Isomer

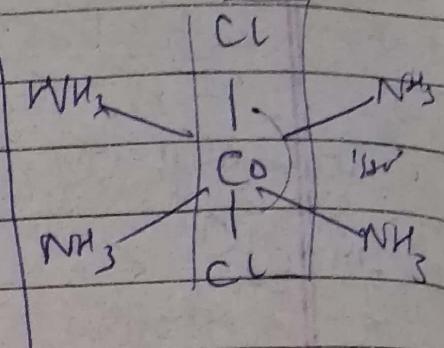


Octahedral

$[\text{Mayby}]^{n+}$ complex



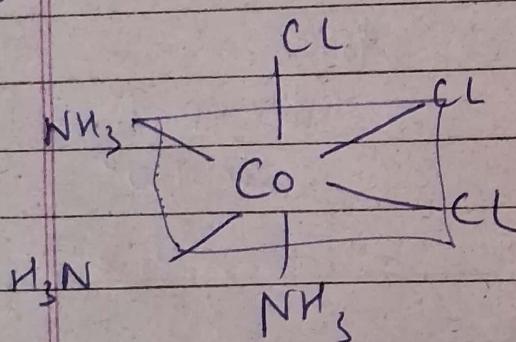
cis-isomer



trans-isomer

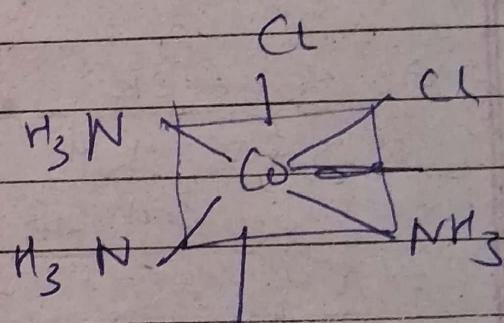
(b)

$(\text{m}_3\text{b}_3)^{n+}$ complexes

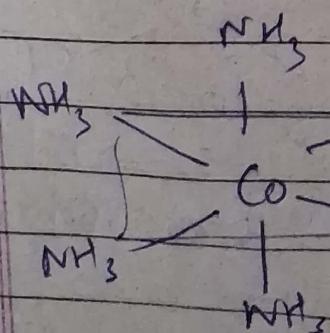
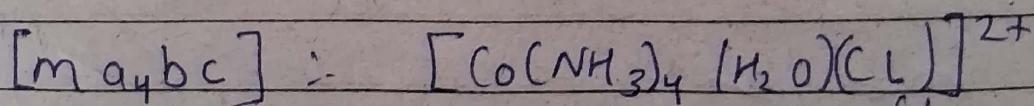


facial

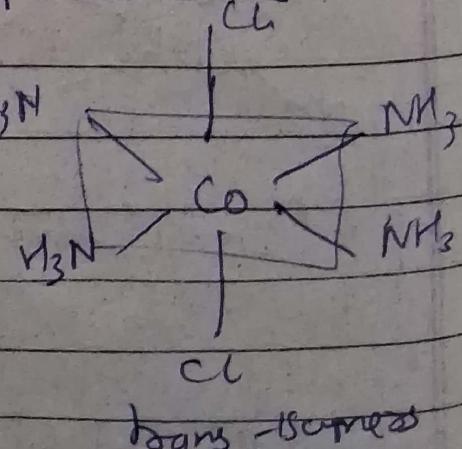
1 isomer



Meridional-1 isomers



cis-isomer



trans-isomer

Optical Isomerism (or) mirror image isomerism → Compounds

optical isomers (enantiomers)

pair of → non-superimposable

mirror image of each other

other

a) centre of symmetry should be absent

b) plane of symmetry also should be absent



optically active compound

optical isomerism

Tetrahedral

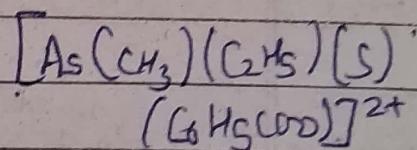
$[ma_4]^{n\pm}$ } do not show

$[ma_3b]^{n\pm}$ optical isomerism

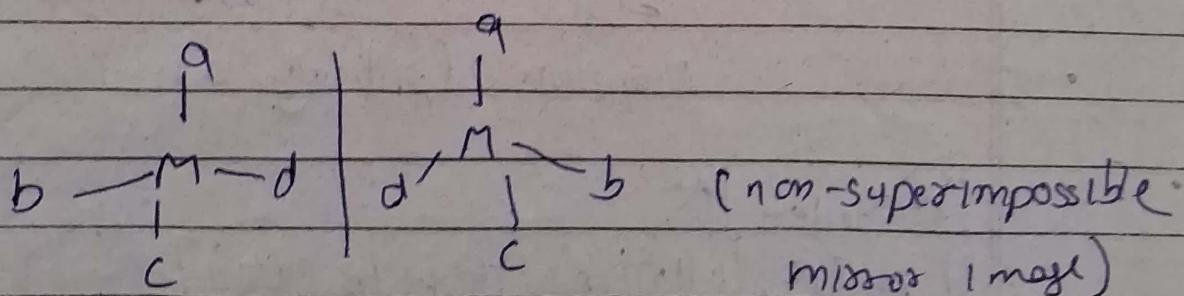
$[ma_2b_2]^{n\pm}$ } (P.S. present)

Ex:

$[mabcd]$ → all four ligands diff
optically active

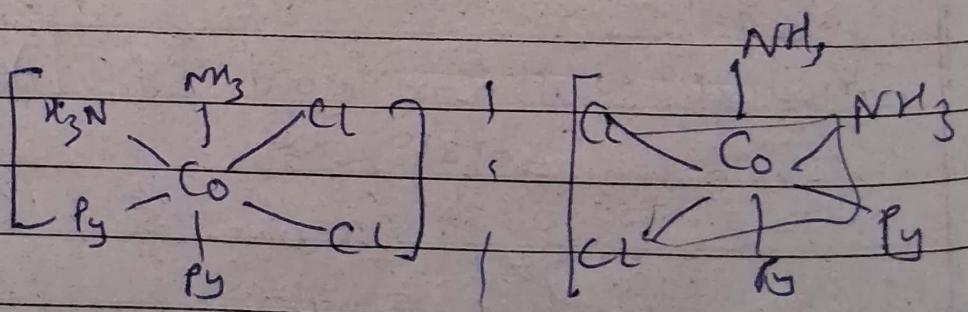
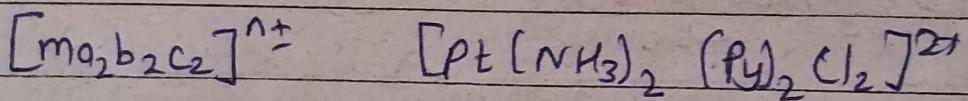
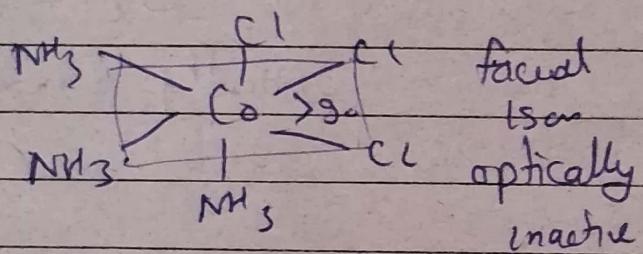
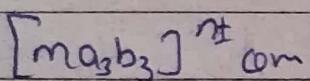
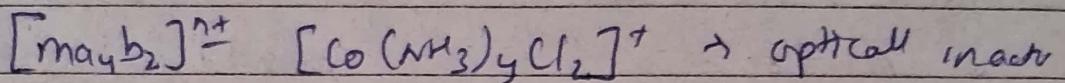
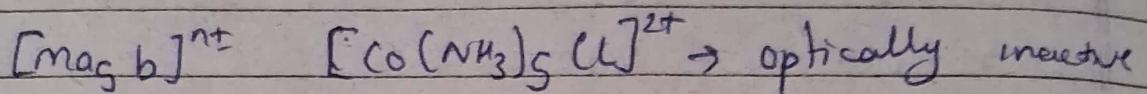
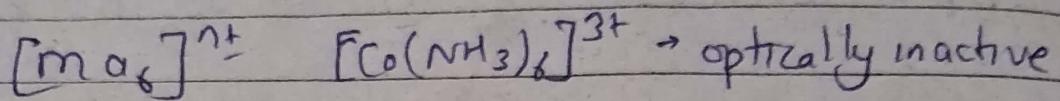


absence of P.S.

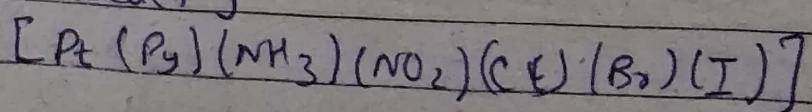
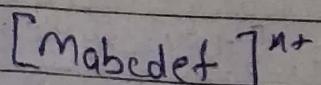


↓
optical isomers

Octahedral complexes

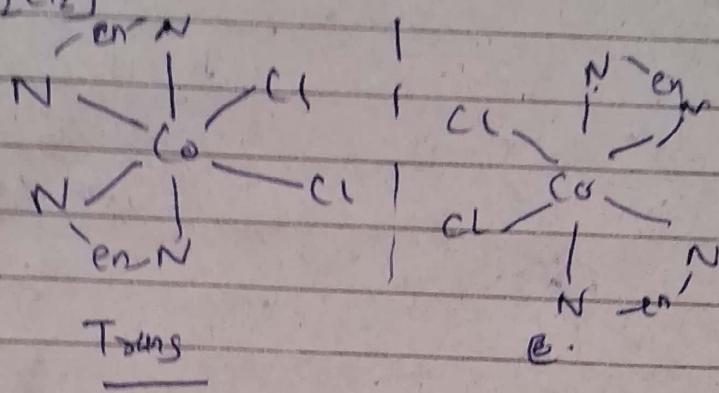
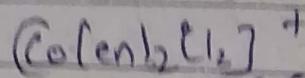


Enantiomers (optically active)

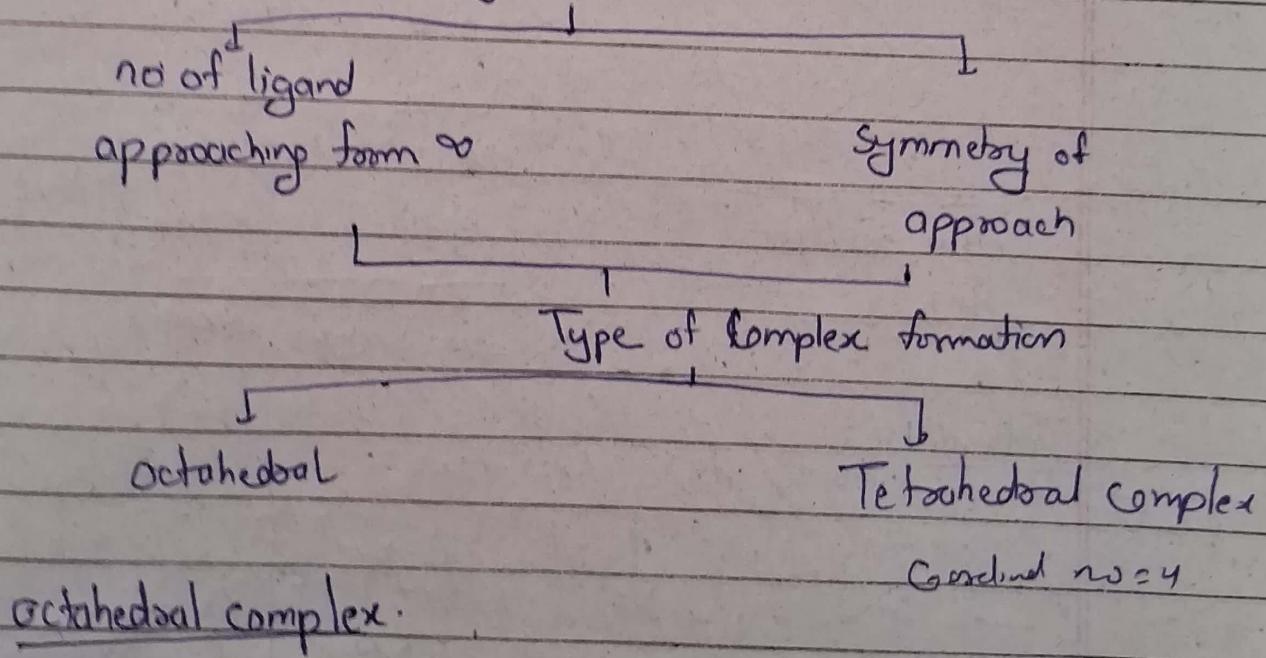


optically active

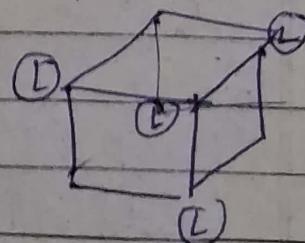
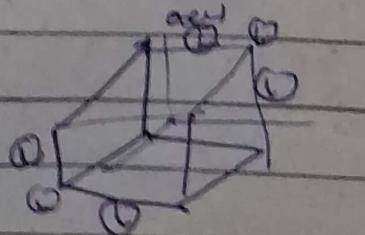
Bidentate ligands → out of plan optically act.



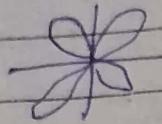
Crystal field Theory (CFT)



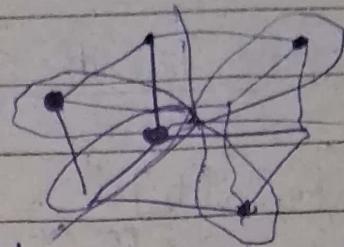
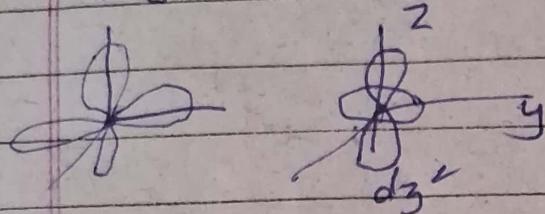
Octahedral complex:



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

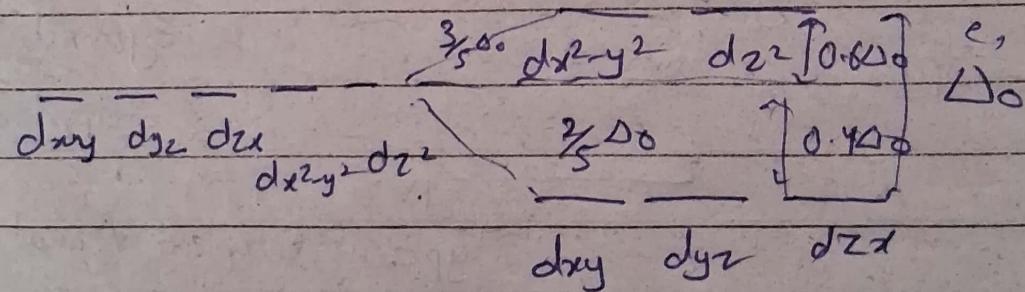


$d(x^2-y^2)$ d_{z^2} alone can

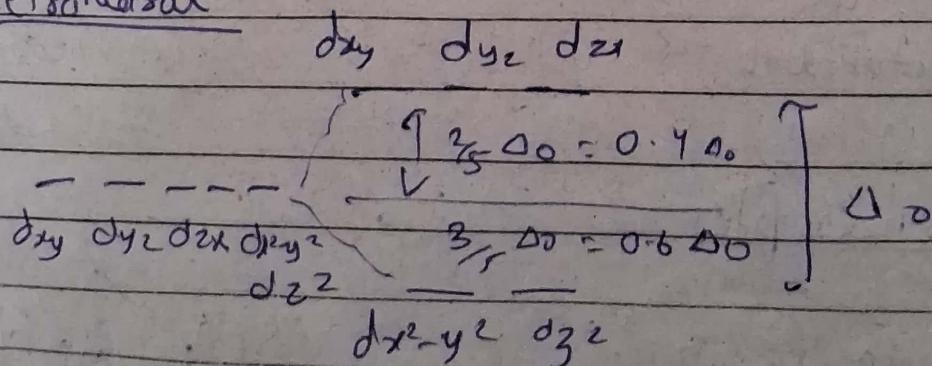


d_{xy}, d_{yz}, d_{zx} orbitals present b/w areas exert more repulsion.

- ① metal m^+ attract ligand (L^-) (primary attraction)
- ② orbital / lone e^- repelled ligands (secondary attract)



Tetrahedral



$$\Delta_{eff} = \left(\frac{2}{3}, \frac{2}{3} \right) \Delta_o$$

$$= \frac{1}{9} \Delta_o$$

Factors affecting magnitude of Δ :

① Oxidation state of metal cation.

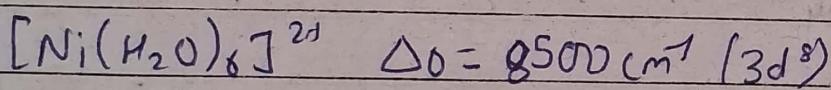
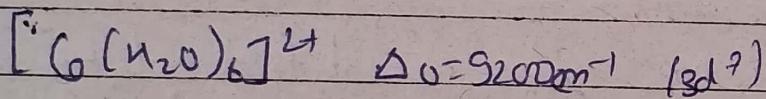
metal cation \rightarrow more the charge on metal
 ↓ more value of Δ (splitting energy)

$$\Delta_0 [\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9200 \text{ cm}^{-1}$$

$$\Delta_0 [\text{Co}(\text{H}_2\text{O})_6]^{3+} = 20760 \text{ cm}^{-1}$$

$$[\text{Co}^{3+}] > [\text{Co}^{2+}]$$

② Same oxidation state of metal cation but no of d-electrons d_{10}

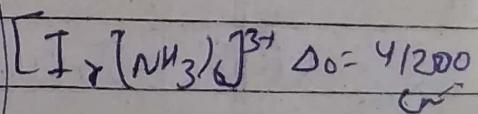
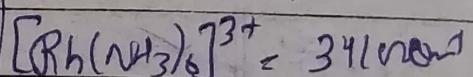
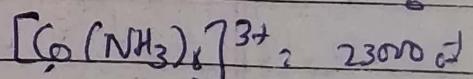


e^+ in d-orbital upcoming repelled and cannot approach more.
 ↓
splitting decreases

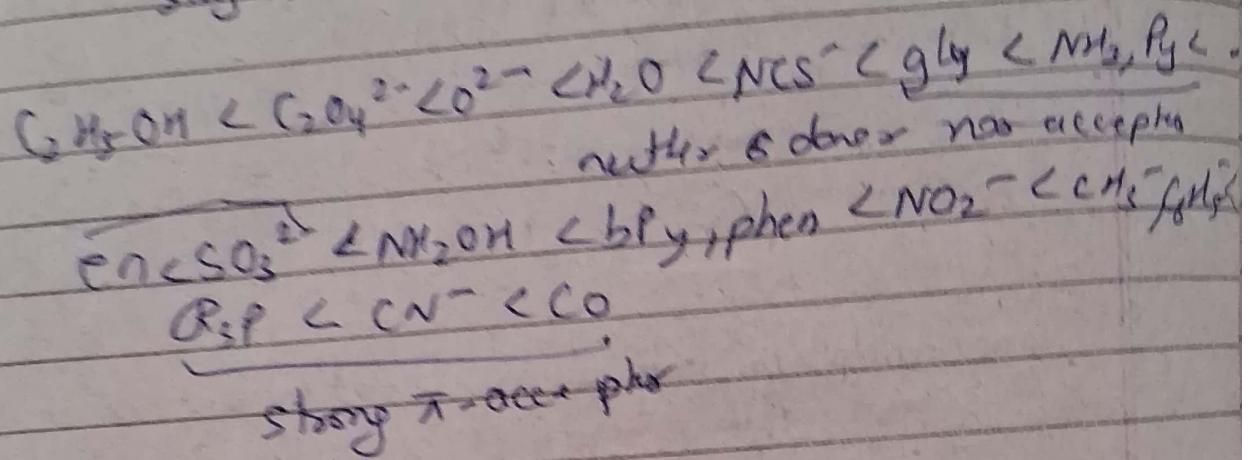
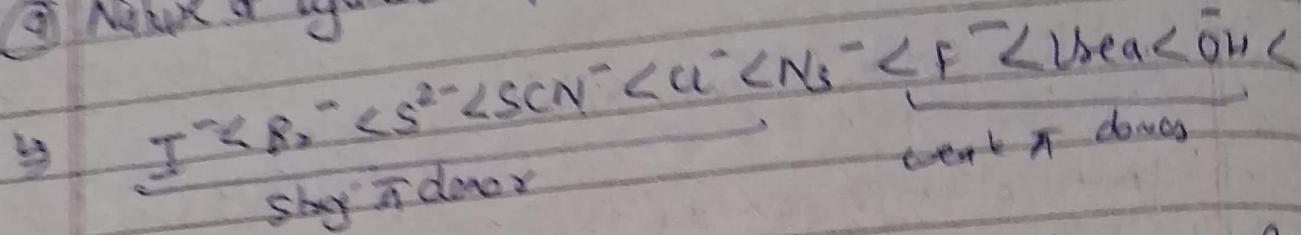
③ Among 3d, 4d & 5d series

3d
 4d ↓ d-orbital increases
 5d ↓ electron density decreases in them

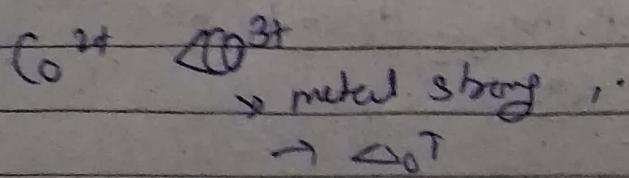
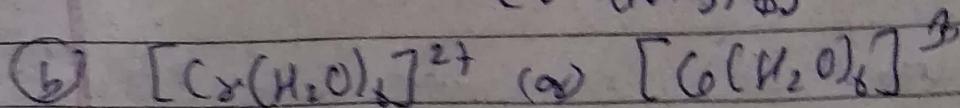
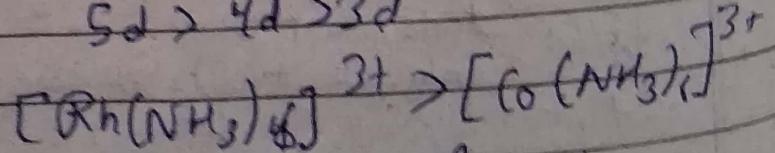
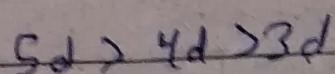
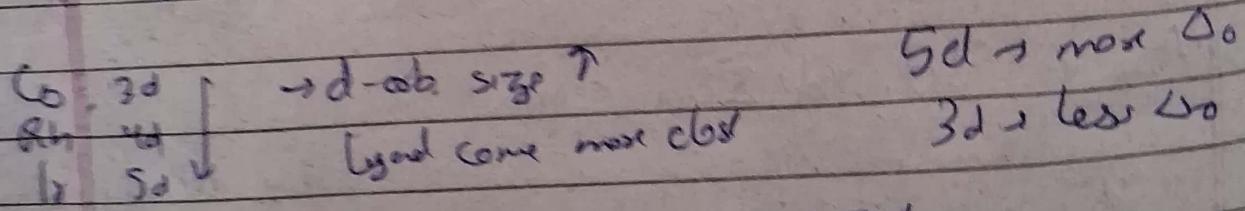
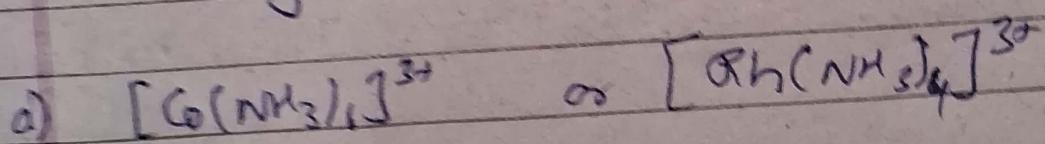
Ligands can approach more with large d-orbital more closely.



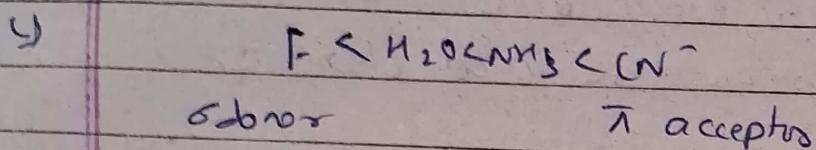
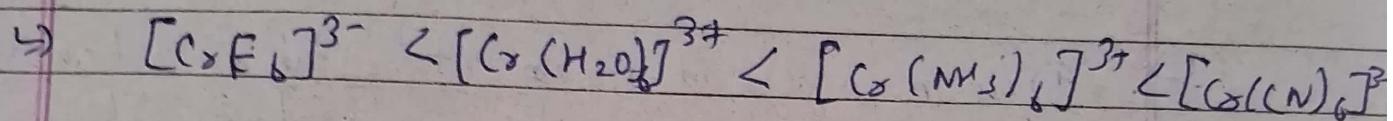
Q) Nature of ligands (spectrochemical series)



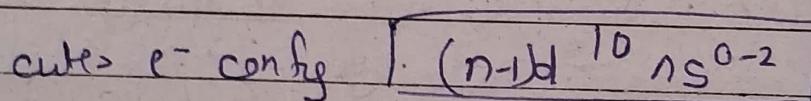
Q) Which complex has larger crystal field splitting and why?



Q) Arrange octahedral complexes in increasing order of their crystal field splitting?



② Transition element: Any element whose atom or at least one of its ions has incomplete d-orbitals



② Why copper consider a transition metal, although it has completely filled d-orbital (3d¹⁰)?

\hookrightarrow Cu²⁺ ions (3d⁹) have incomplete 3d orbital

③ melting point of transition metal are high?

→ This is due to presence of strong covalent bonds b/w atoms, due to d-d overlapping.

④ Why ionic radius of Cu²⁺ less than Co³⁺, where as atom no. of Cu is greater than Co?

→ due to presence of 5 e⁻ in Cu²⁺ (3d⁹) as compared to Co³⁺ (3d⁴), which cause greater attractive force b/w nucleus of copper & e⁻.

① Why are ionization energy of 5d-elements greater than those of 3d-elements?

→ Due to presence of inner 5f-orbital in 5d-elements, the effective nuclear charge in 5d-elements is greater than those in 3d-elements.

② Why is copper (I) diamagnetic; while copper (II) is paramagnetic?

→ Cu^+ ($3d^{10}$) diamagnetic → due to absence of unpaired d-e⁻; whereas Cu^{2+} ($3d^9$) is paramagnetic due to presence of unpaired d-e⁻

③ $\text{Cu}^{2+} \& \text{Cs}^{3+} \rightarrow$ stable?
 $\text{Cs}^{3+} (3d^1)$

④ Cu^+ is colorless but Cu^{2+} is colored. Why?

→ Cu^+ ($3d^{10}$) completely filled d-orbital, colorless
 Cu^{2+} ($3d^9$) 1 unpaired e⁻ → colored

⑤ $\text{Cs}^+ \text{ Cu}^+$
 $\text{Cs}^+ (3d^5) \quad (\text{Cu}^+ (3d^{10}))$
 ↓
 Colored b. colored

180) Zn^{2+} salts are white; while Cu^{2+} salts are blue. Reason

↳ $Cu^{2+} (3d^9) \rightarrow$ colored, 3d-orbital 1 unpaired e⁻ & d-d transition within 3d subshell. Zn^{2+} salt ($3d^{10}$) or colorless (white), due to abs of d-d transition in fully-filled 3d-subshell.

Q) Why do transition metal and metal ions show paramagnetic behavior?

↳ one or more unpaired d-e⁻ presence

20) $Mn^{(II)}$ ion shows max paramagnetic charact among bivalent ions of 1st transition series.

↳ Mn^{2+} ion ($3d^5$) posses max no (=5) of unpaired e⁻ among bivalent ions of 1st transition series.

21) Why does zinc show oxidation state of two only?

Ans: $Zn = [Ar] 3d^{10} 4s^2$ - so by lossy 4s-e⁻, it exhibits +2 oxidant st. 3d-filled & completely stable - so 3d-e⁻ are not available for chemical formation. Zn does not show an oxidation state higher than two.

22) Why is Fe^{3+} more paramagnetic than Fe^{2+}
 $3d^5$ $3d^6$

G_0	Mn^0
$3d^5 4s^1 \rightarrow$ 6 upone	Mn^+
$3d^5 4s^2$	