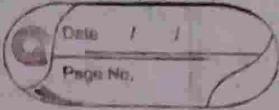


Coordination Compounds



① Coordination Numbers and Geometries

- a) Isomerism in Transition Metal cation 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

Ions/molecule \rightarrow having lone pairs of e⁻ (ligands)

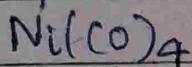
or e⁻ rich species (or) Lewis base

(or) Nucleophile

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

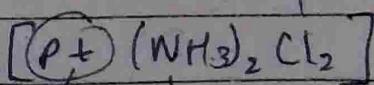
Coordination Compounds \rightarrow is one which contains a central metal atom (or) ion surrounded by a number of oppositely charged (or) neutral molecules.

Central metal ion



co-neutral ligand

-ve ligand



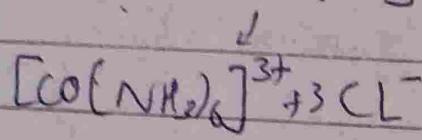
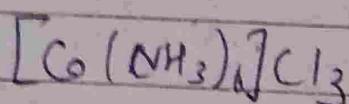
Central metal ion

Neutral ligand



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

Complex coordination cation / anion



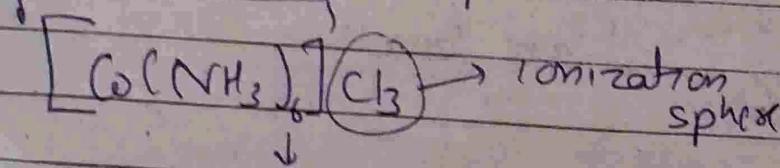
→ Inside [] → square bracket

→ coordination sphere

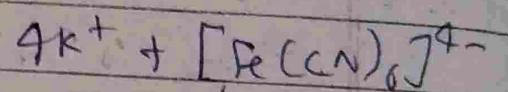
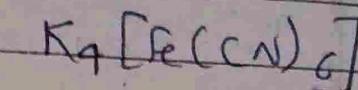
→ no. of attached ligands

→ coordination number

→ coordination sphere



↓
Coordination number



[Ions inside complex
Ion lost their identity]

CN⁻ will not show test
because its not freely available

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



Weiner Theory

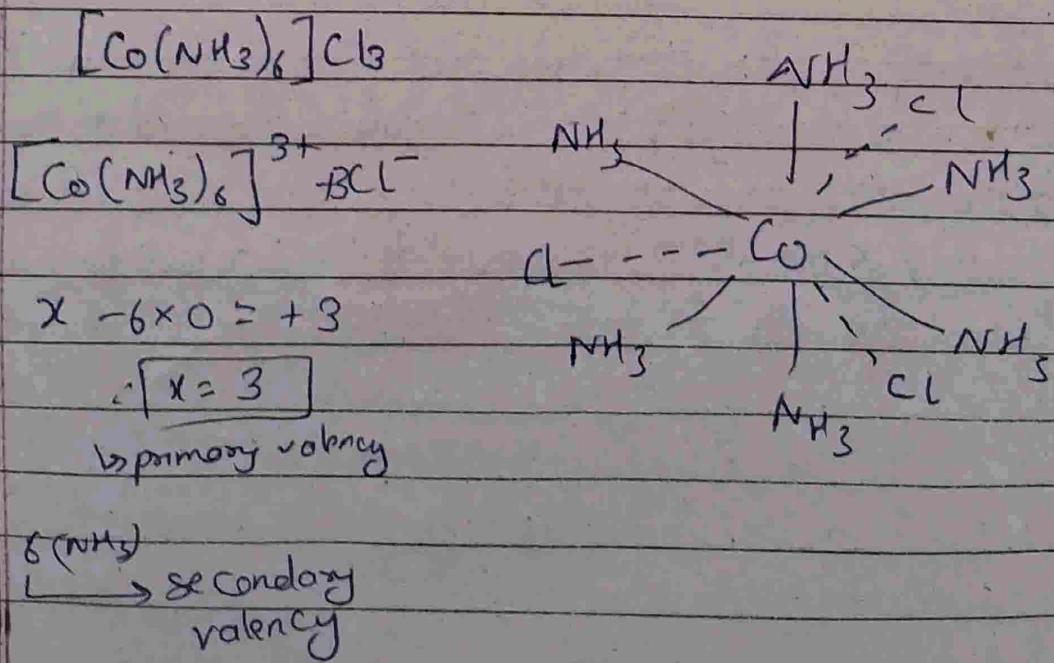
1893 → [Weiner] produced a theory of coordination compounds
 I S¹ Inorganic chemist
 ↘
 1913 → noble prize
 d
 to explain structure and formation of Compounds.

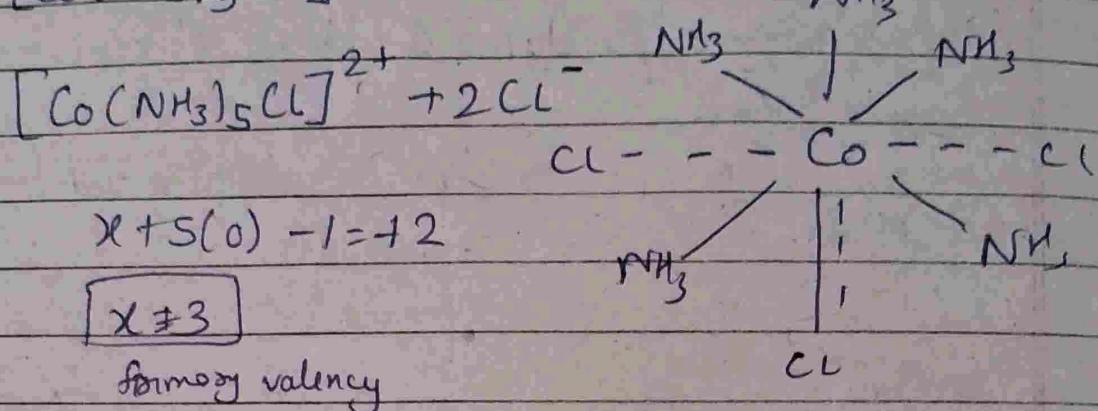
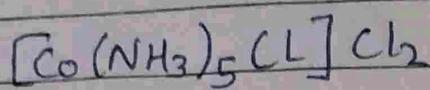
Postulates-

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

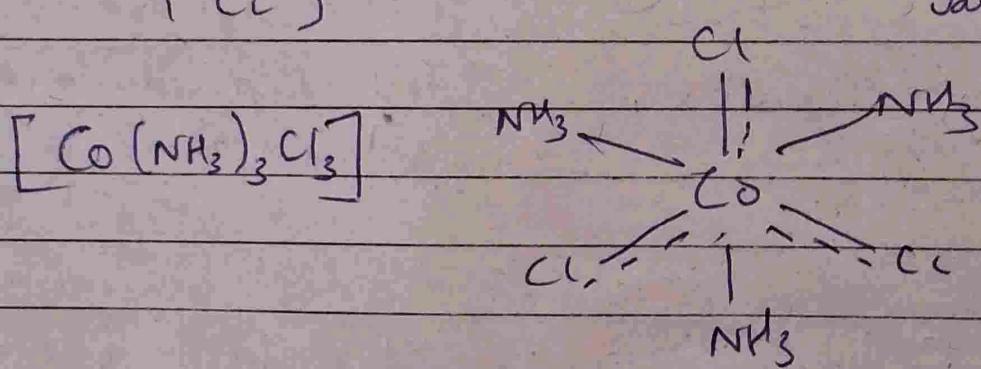
Primary: → Ionisable. --- dotted, responsible for charge on central metal atom.

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





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



Limitations

- a) Why complex compounds are formed by few metals?
- b) Directional properties of bonds in coordination compounds?
- c) Magnetic properties

optical
Cbr etc

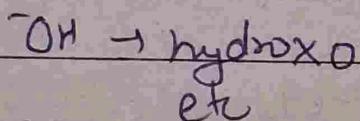
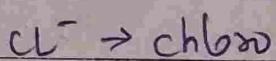
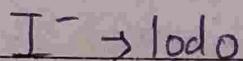
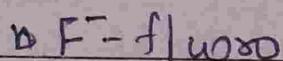
cannot
explain

Terms used in coordination compounds

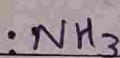
a) Ligands: charged (ox) neutral group (or) molecule that coordinate to central atom (ox) ion in a coordination compound.

monodentate ligand

(-ve or charged)



Neutral



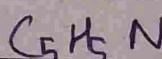
Amonia



Carbonyl

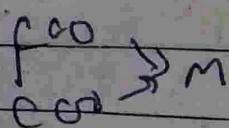
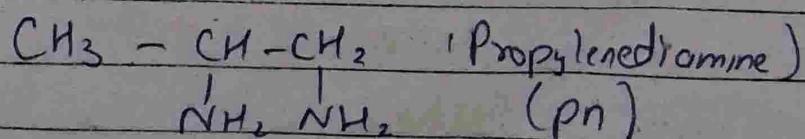
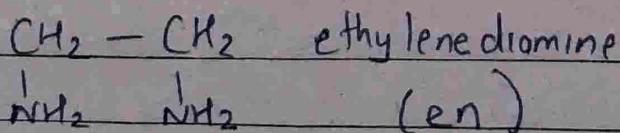
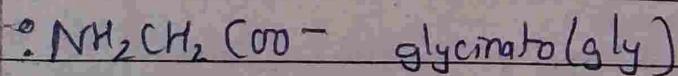
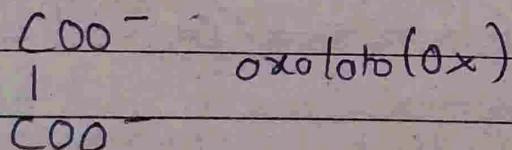


Aqua

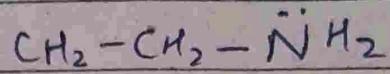
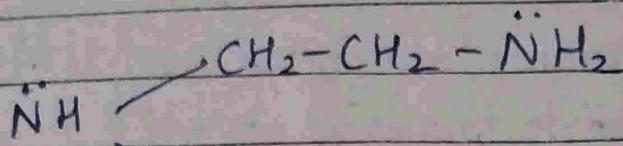


Py (Pyridine)

Bidentate ligands



Tetridentate ligands



(diethylene triamine) (dien)

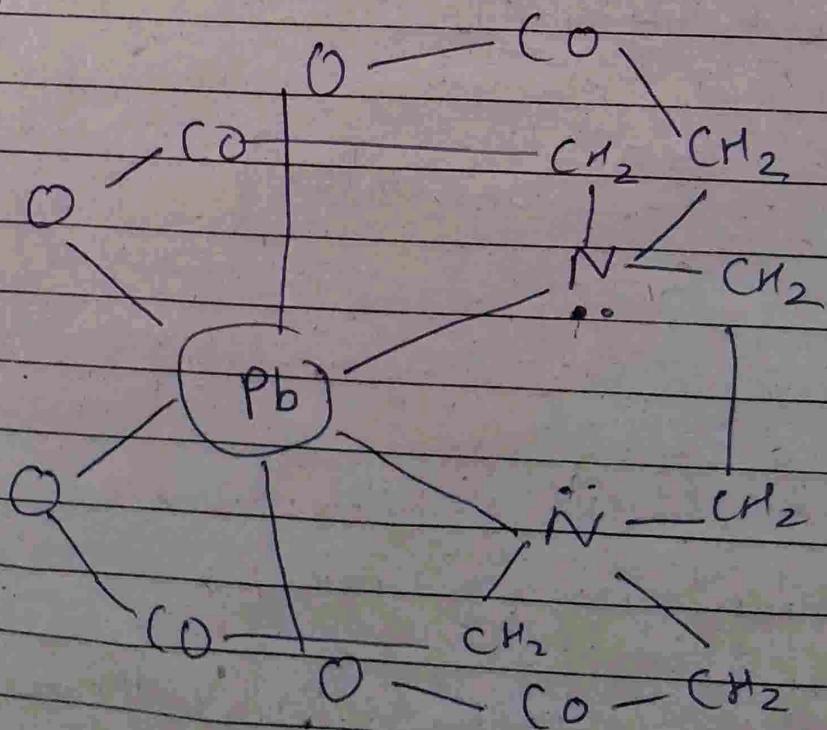
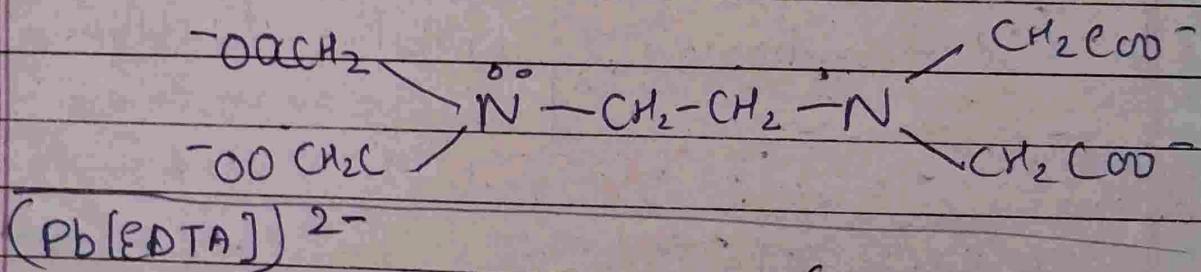
Tetradentate

Penta dentate

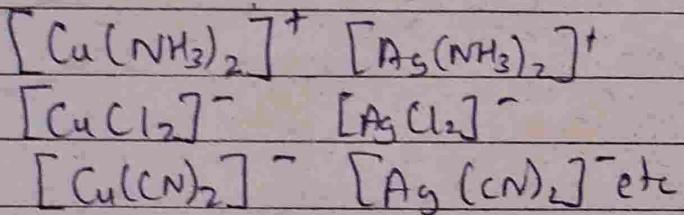
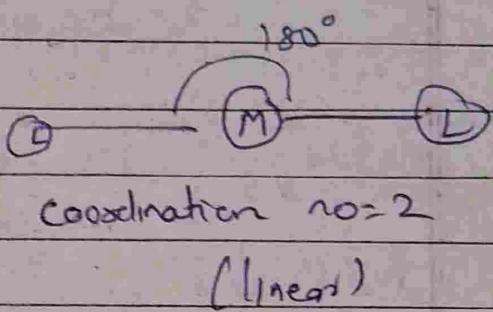
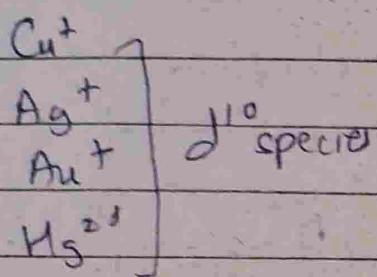
Flexadentate

EDTA

ethylene diamine tetraacetatol

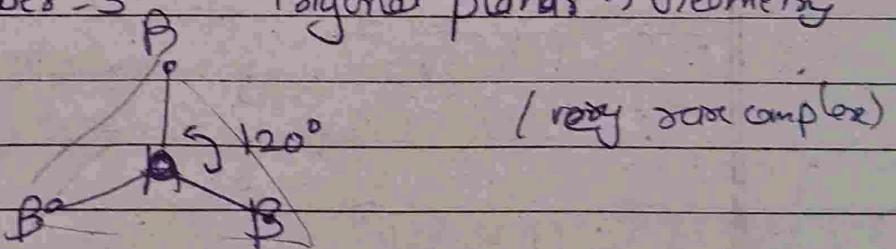


b) Coordination number: Number of ligands attached directly to central metal atom (ox) ion by coordinate bonds in given complex.

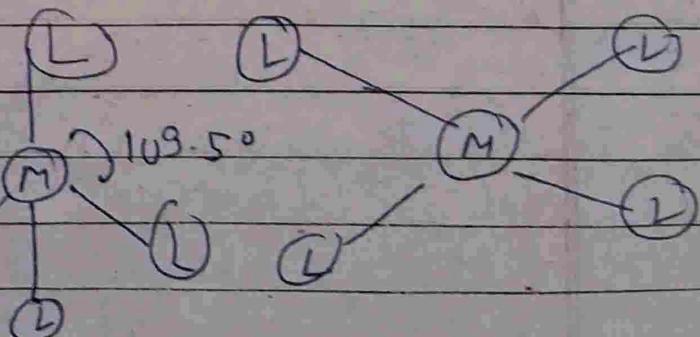
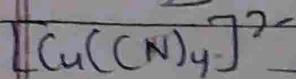
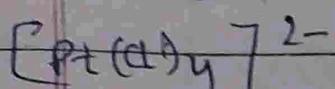
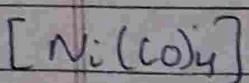
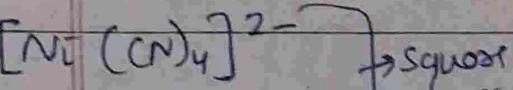
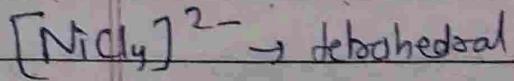


i) Coordination number = 3

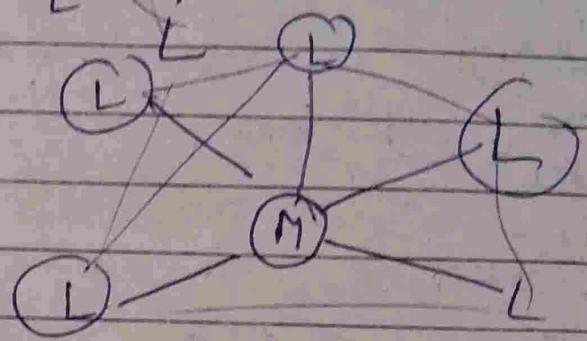
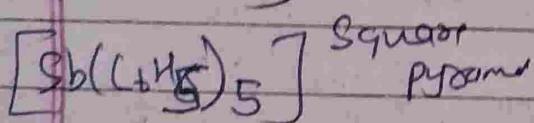
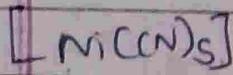
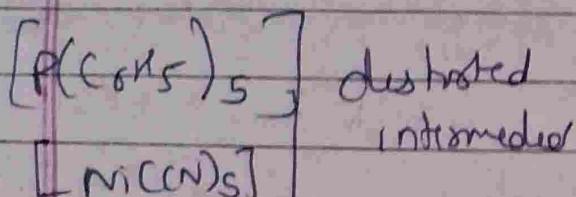
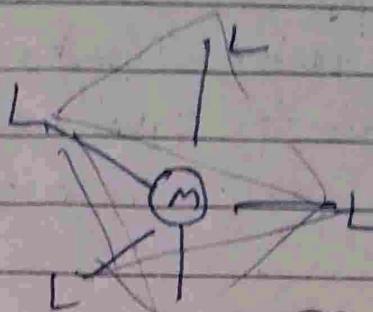
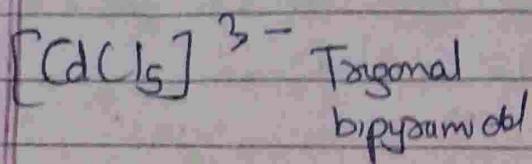
Tetrahedral planar \rightarrow Geometry



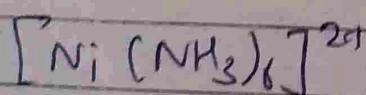
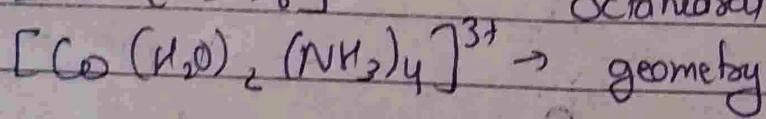
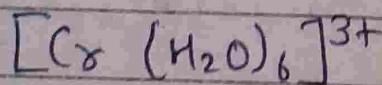
ii) Coordination number = 4 (Tetrahedral or square plane)



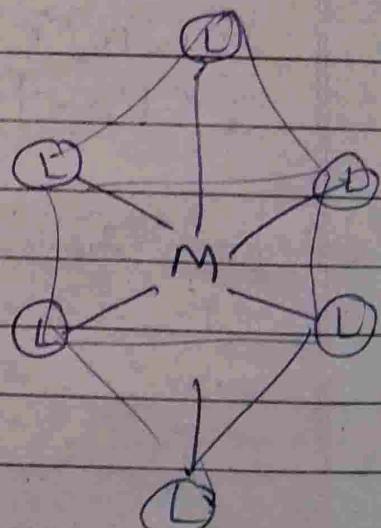
Coordination no = 5



Coordination no = 6

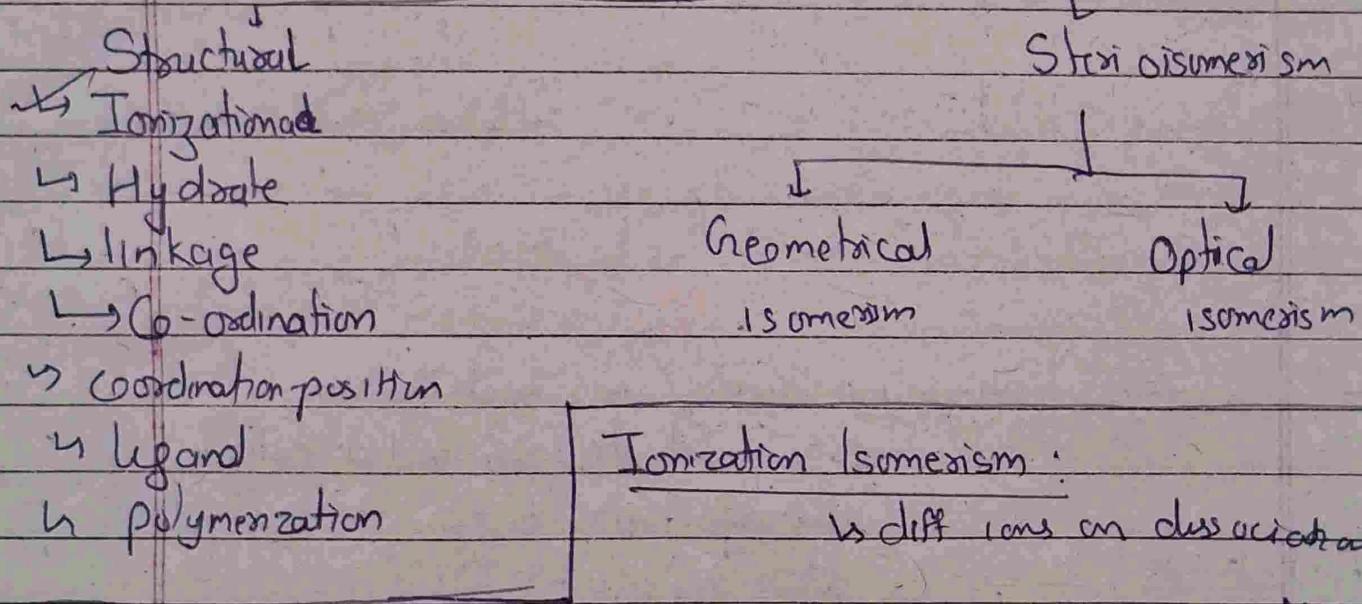


etc



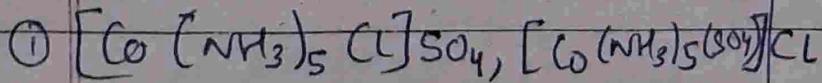
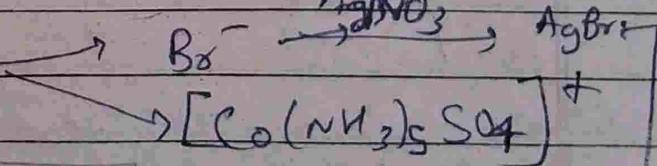
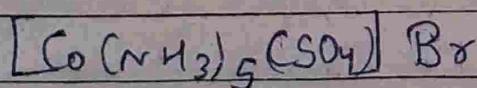
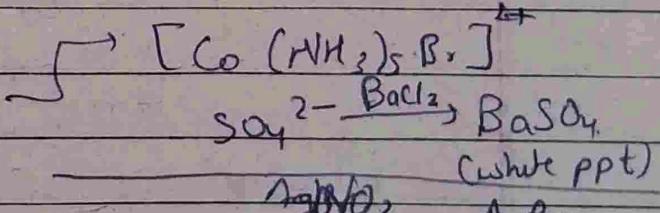
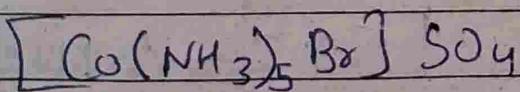
- ① Explain Ionization isomerism & linkage isomerism for transition metal complex with an example for each? (6)
- ② Explain geometrical isomerism & optical isomerism.

Isomerism → same chemical composition but different arrangement

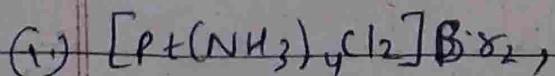


Ionization Isomerism:

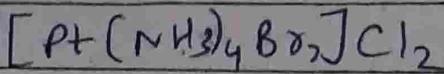
→ diff ions on dissociation



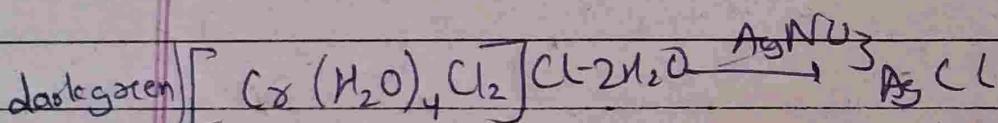
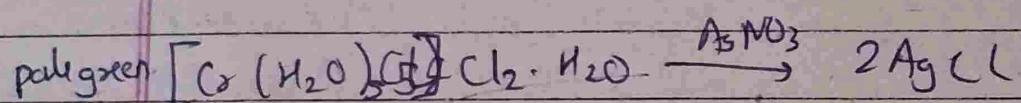
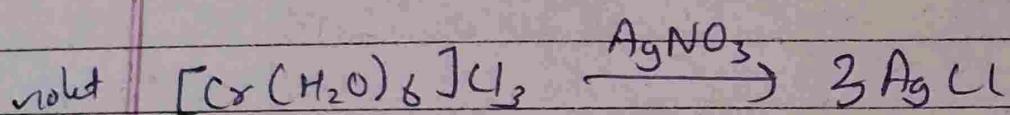
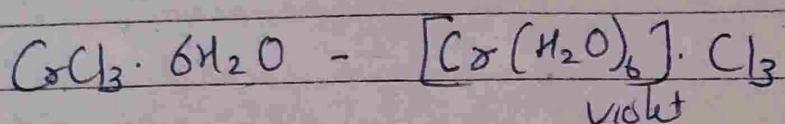
(cream color precipitate)



indicate presence of Br^-

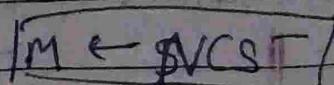
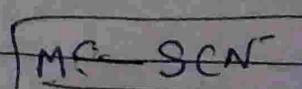
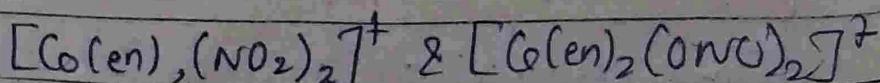
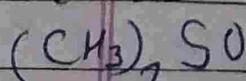
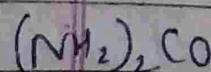
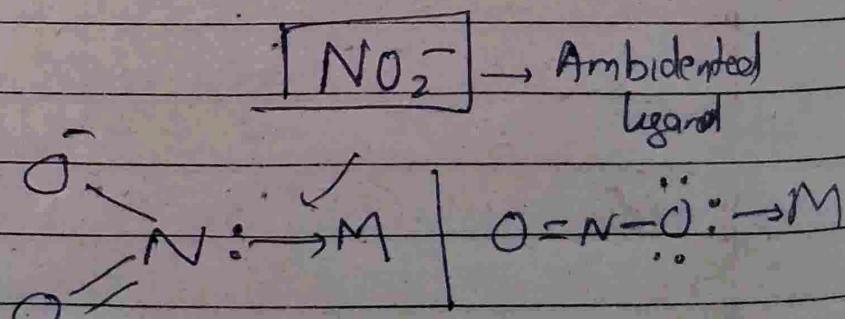
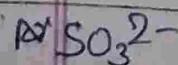
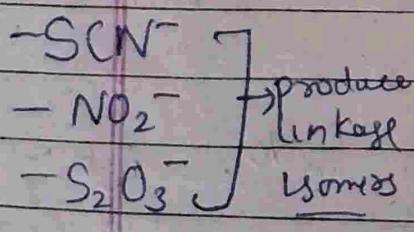


Hydrate Isomerism: water molecules are exchanged between coordination sphere & ionization sphere

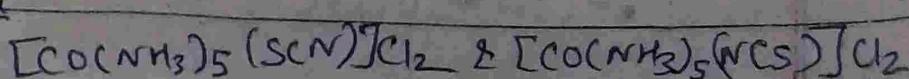


Linkage Isomerism: arise when ambidentate ligand can coordinate to metal cation through either of two different donor atoms.

Ambidentate Ligands



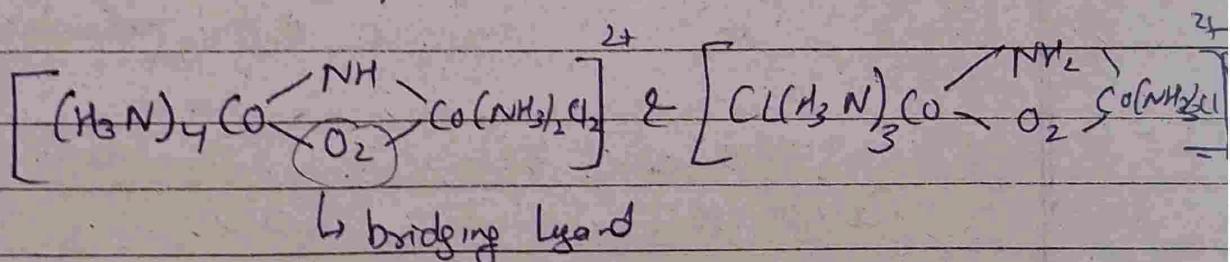
Ex



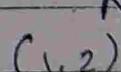
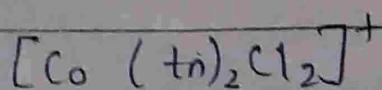
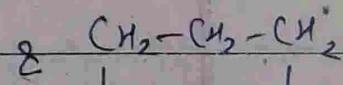
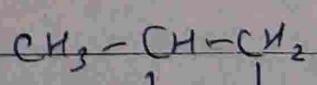
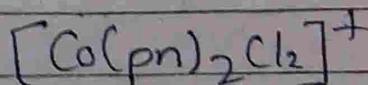
Coordination Isomerism: In complex: when cation and anion both are complex ions, these may be exchanged of ligands between two complex ions resulting in coordination isomers.

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

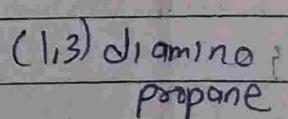
Coordination Position Isomerism: In bridging complexes an ligand between two metal cations give rise to coordination position isomerism.

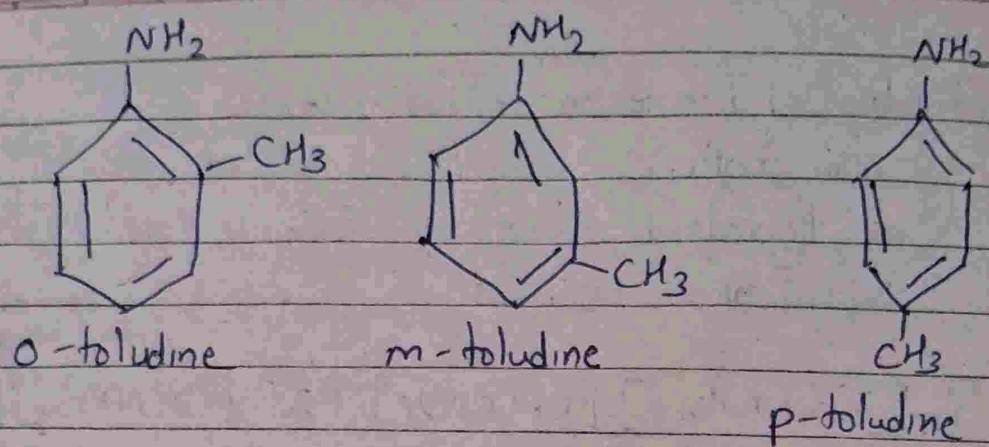


Ligand Isomerism: If ligand itself exist in two/more isomeric forms, then complexes containing such ligands exists in isomeric forms.



di amino propane





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

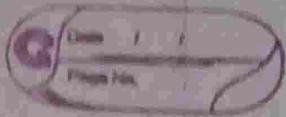
[G.I]

bent shape

Cannot inter-converted without
breaking Metal-ligand M-L

bond # Bond angle will change

Coordination Comp



Coordination no = 4

octahedral



angle

sys $109^{\circ}28'$

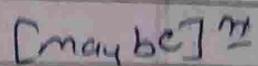
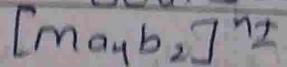
Square
planar

CIS 2 bonds

1 isomer

Coordination no = 6

octahedral



a)

CIS

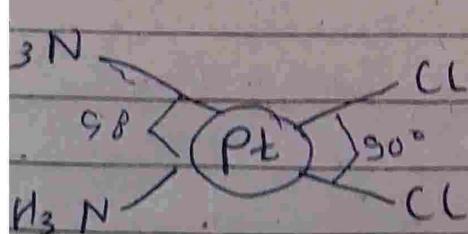
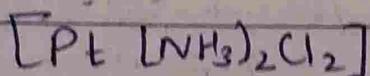
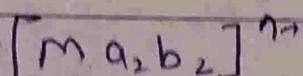
same ligand

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

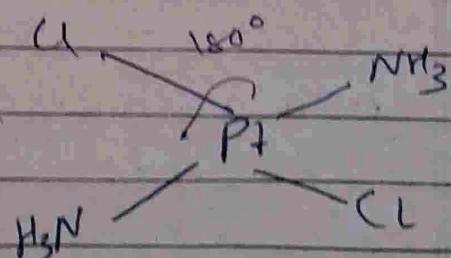
TRANS

same ligands

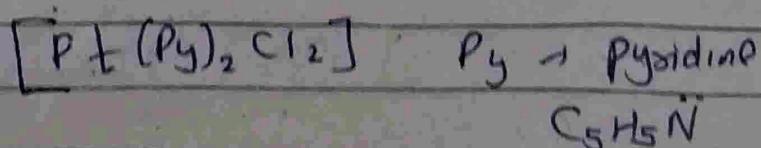
$A-B=180^{\circ}$



CIS - Isomer

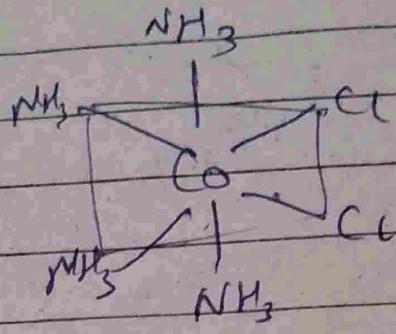
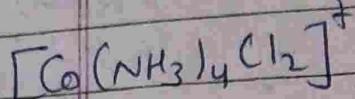


TRANS - Isomer

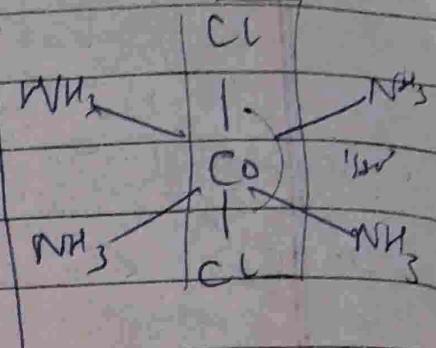


Octahedral

$[\text{M}(\text{a}_4\text{b}_4)]^{n+}$ complex



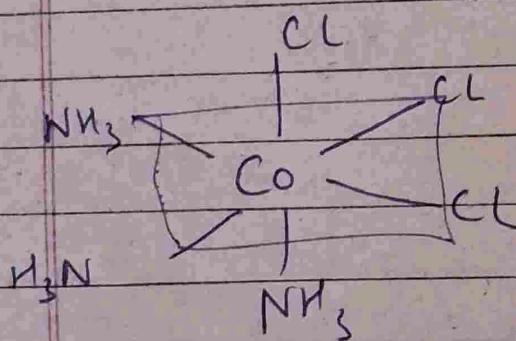
cis-isomer



trans-isomers

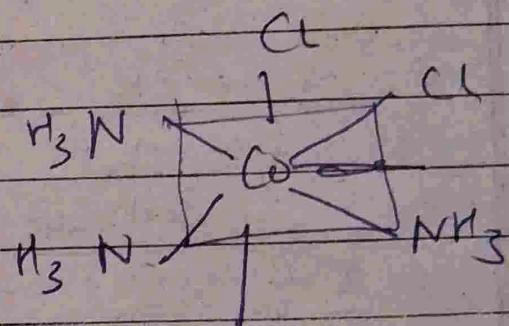
(b)

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

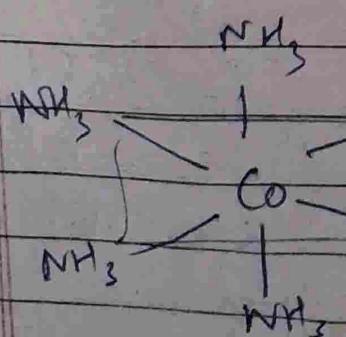
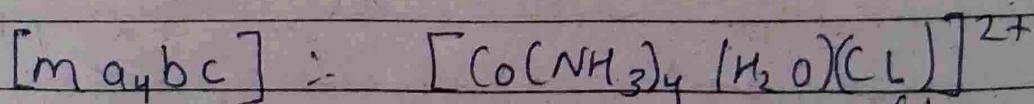


facial

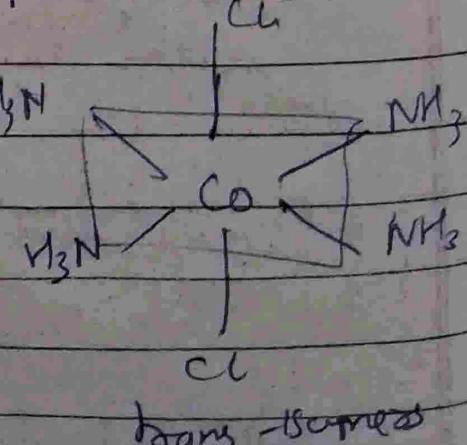
1 isomers



Meridional-1 isomers



cis-isomer



trans-isomers

Optical Isomerism (or) mirror image isomerism → Compounds

optical isomers (enantiomers)

parent → 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

optically isomers

Tetrahedral

$[m_4]^{n\pm}$

$[ma_3b]^{n\pm}$

$[ma_2b_2]^{n\pm}$

do not show

optical isomerism

→ (P.S. present)

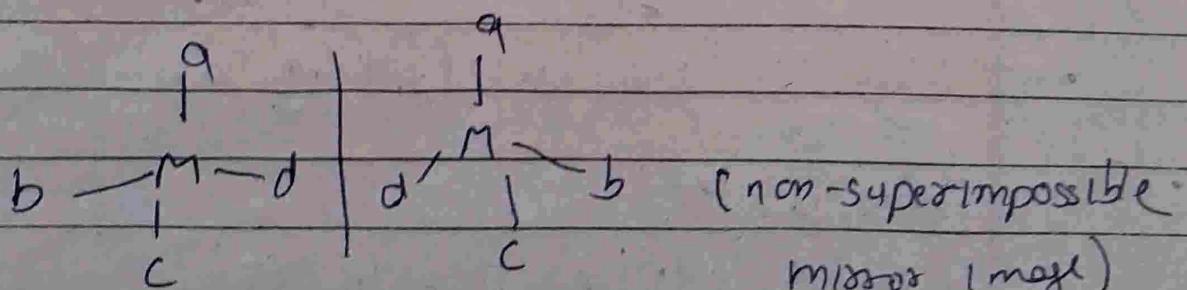
Ex:

$[mab_3d] \rightarrow$ all four ligands diff

optically active

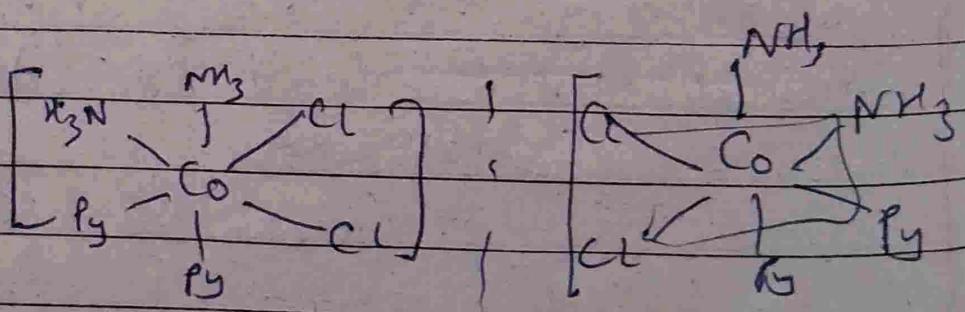
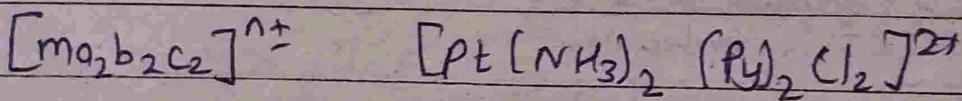
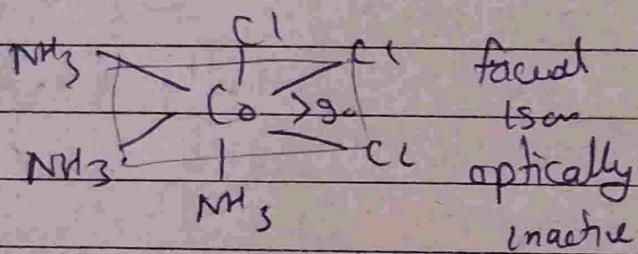
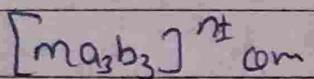
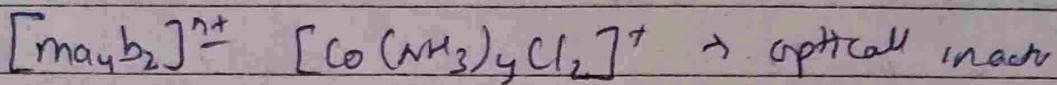
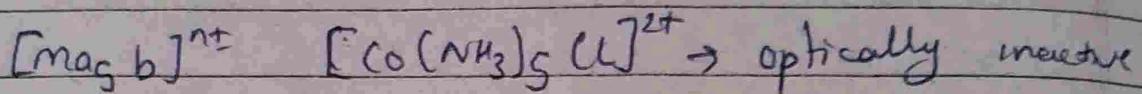
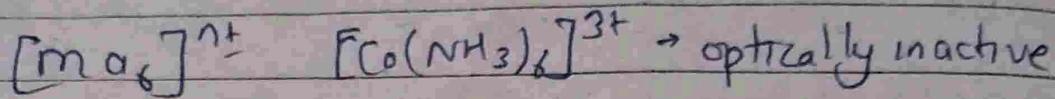
$[As(CH_3)(C_2H_5)(S)]$
 $(C_6H_5COO)]^{2+}$

↓
 absence of P.S.

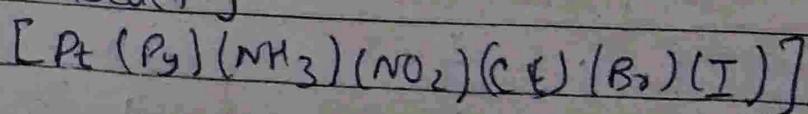
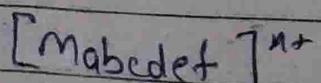


↓
 Optical isomers

Octahedral complexes

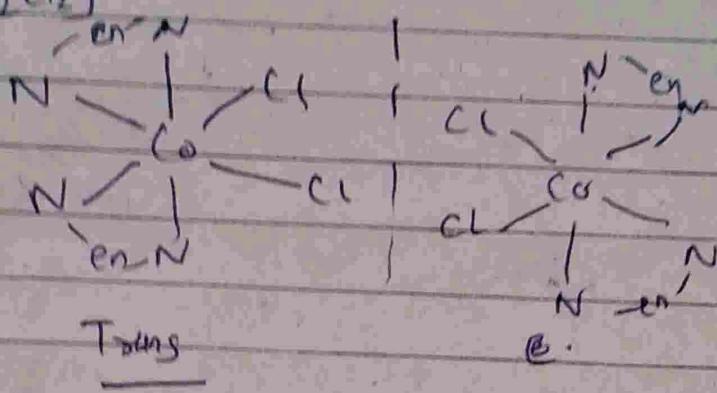
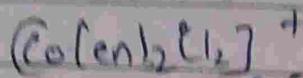


Enantiomers (optically active)



optically active

Bidentate ligands → out of plan optically act.



e.

Crystal field Theory (CFT)

no of ligand

approaching form ∞

Symmetry of approach

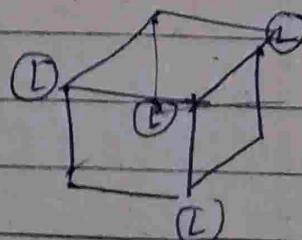
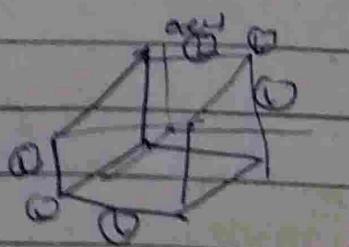
Type of complex formation

Octahedral

Tetrahedral complex

Octahedral complex

Coordination no = 6

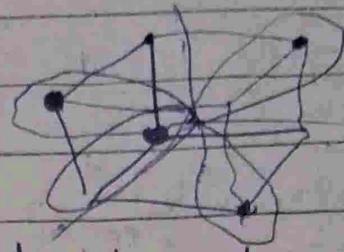
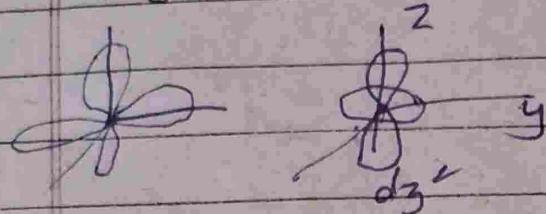


Coordination no = 6

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

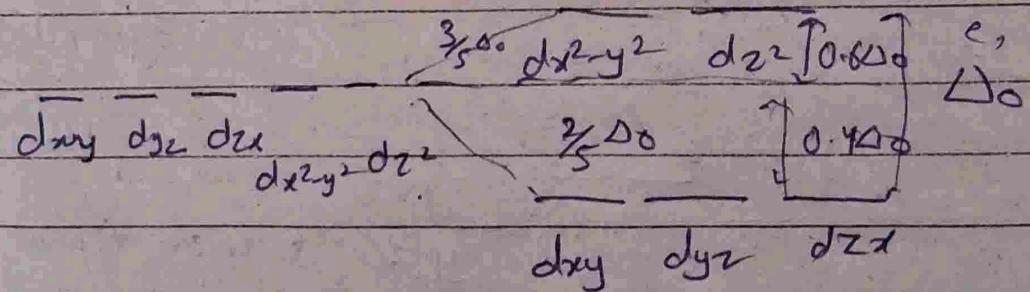


$d(x^2-y^2)$ d_3^2 alone can

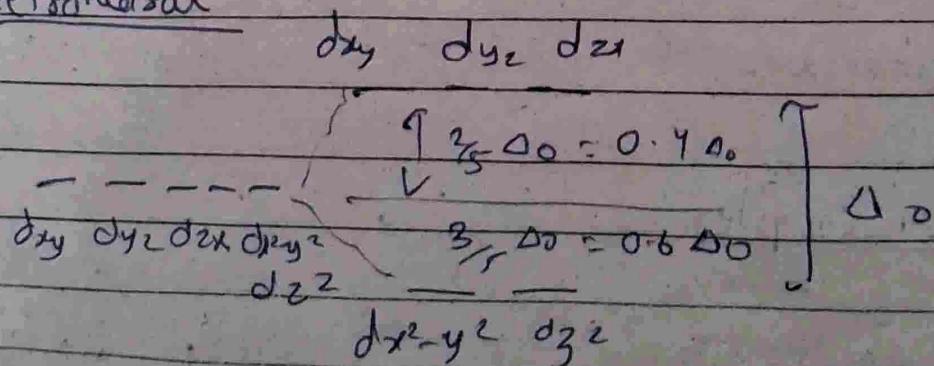


d_{xy}, d_{yz}, d_{zx} orbitals present the atoms experience more repulsion.

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



Tetrahedral



$$\Delta_{\text{tet}} = \left(\frac{2}{3} \cdot \frac{2}{3} \right) \Delta_0$$

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

Factors affecting magnitude of Δ :

① Oxidation state of metal cation

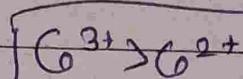
metal cation

more the charge on metal

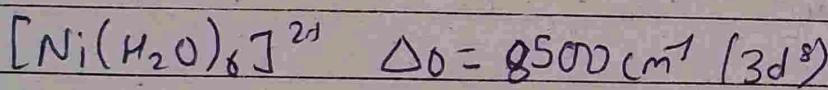
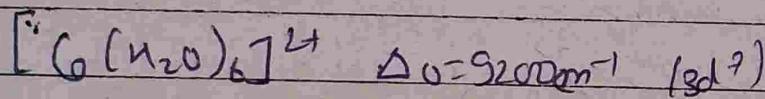
↳ more value of Δ
(splitting energy)

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

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



② Same oxidation state of metal cation but no δ -electrons d₁₋₁₀



e⁺ in d-orbital
upcoming repelled
and cannot approach
more.

splitting decreases

③ Among 3d, 4d & 5d series

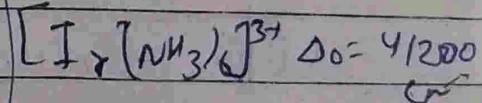
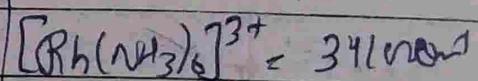
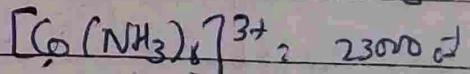
3d

4d

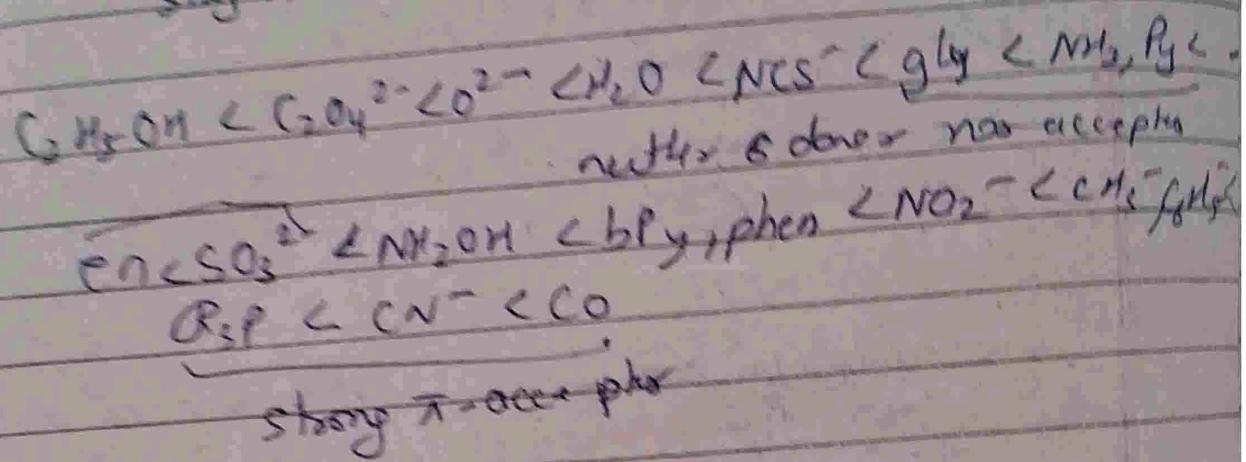
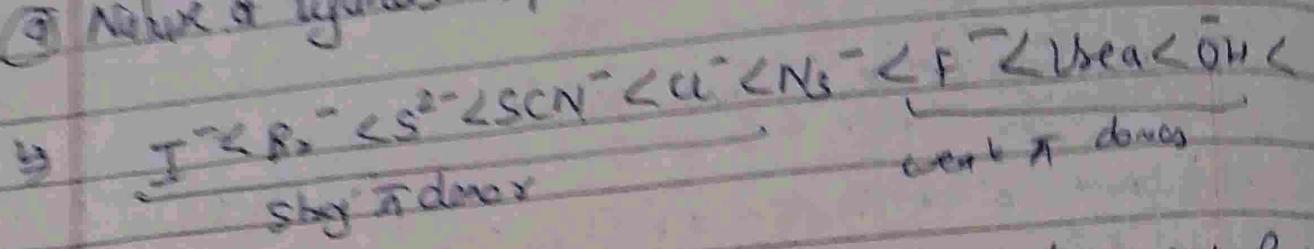
5d

d-orbital increases
electron density decreases in them

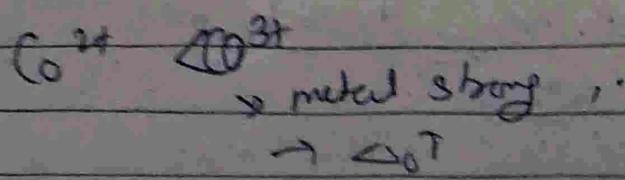
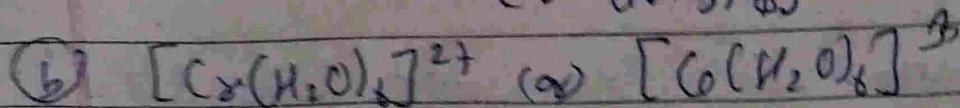
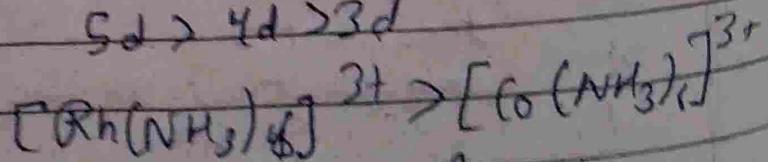
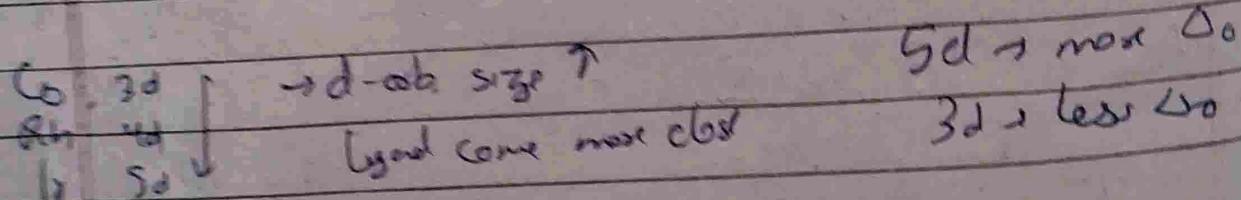
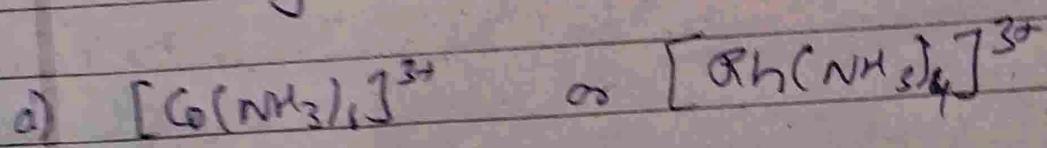
Ligands can approach more
with large d-orbital more
closely.



② Nature of ligands (spectrochemical series)

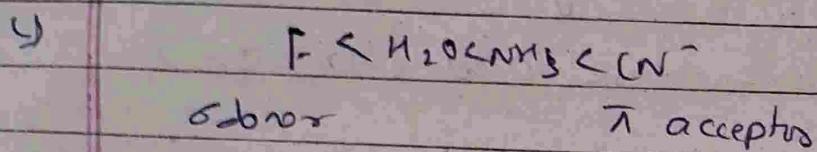
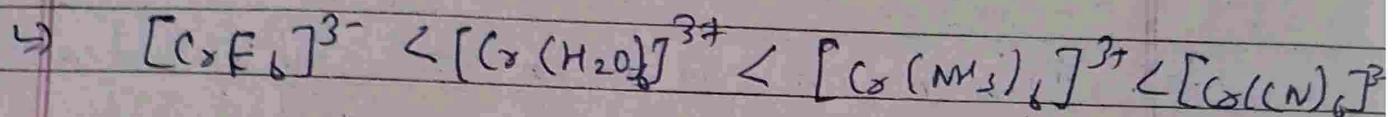


③ Which complex has larger crystal field splitting and why?





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



③ Transition element: Any element whose atom or at least one of its ions has incomplete d-orbitals

cute > e- config \vdash $(n-1)d^{10} ns^{0-2}$

② Why copper consider a transition metal, although it has completely filled d-orbital ($3d^{10}$)?

\hookrightarrow Cu^{2+} ions ($3d^9$) have incomplete $3d$ orbital

⑤ melting point of transition metal are high?

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

⑥ Why is ionic radius of Cu^{2+} less than Cr^{3+} , whereas atomic no. of Cu is greater than Cr?

4) due to presence of S^{2-} in $Cu^{2+} (3d^9)$ as compared to $Ce^{3+} (3d^4)$, 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 7f-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?

Cs^{3+} ($3d^10$)

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

→ Cu^+ ($3d^{10}$) completely filled d-orb, tail, colorless

Cu^{2+} ($3d^9$) 1 unpaired e- → colored

⑤ $\text{Cs}^+ \text{ Cu}^+$

Cs^+ ($3d^5$) $(\text{Cu}^+ (3d^{10}))$

↓
closed

b. colored

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

↳ $Cu^{2+} (3d^9) \rightarrow$ colored; 3d-orbital has 1 unpaired e^- & d-d transition within 3d subshell. Zn^{2+} salt ($3d^{10}$) or colorless (white), due to absence 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 character among bivalent ions of 1st transition series.

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

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

A) $Zn = [Ar] 3d^{10} 4s^2$ - so by loss of 4s e^- , it becomes +2 oxidant state. 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+}

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