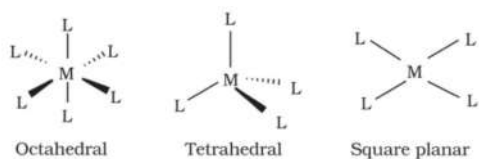


Flow Chart Of Complete Chapter (NCERT)

IUPAC Nomenclature



Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Purple

Addition Comp.

Double comp.

Complex Comp.

Terminology related to coordination Compounds

Coordination Compounds

Isomerism

Structural Isomerism

Stereoisomerism

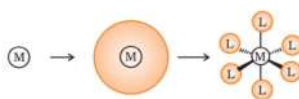
Geometrical

Optical

Bonding in Coordination compounds

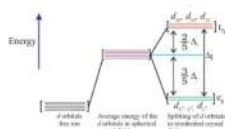
Werner's Theory

Valence Bond Theory



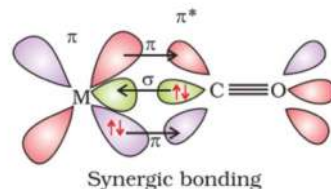
Crystal Field Theory

Octahedral Complex



Tetrahedral Complex

Bonding in Metal Carbonyl



Co-ordination Compounds

Addition Compound —: They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Addition Compounds

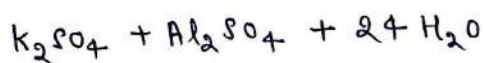
Double Salts

[CBSE 2019] (1M)

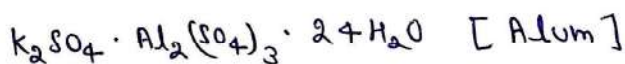
Coordination Compounds

[Complexes]

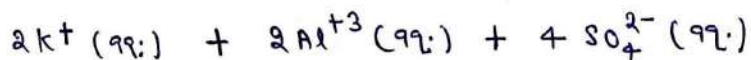
→ Compounds which lose their identity in solution are called double salts.



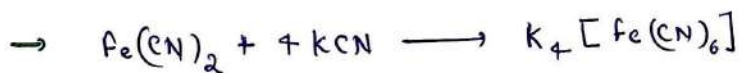
↓



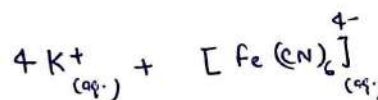
↓
H₂O (Aqueous)



→ Compounds which does not lose their identity in solution are called coordination compound.



↓
Aq.



Terminology related to Co-ordination Compounds :-

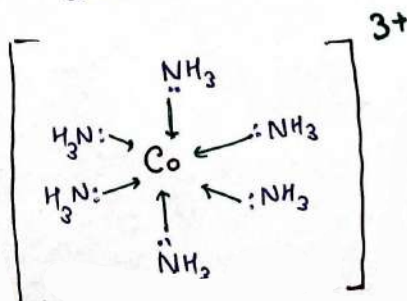
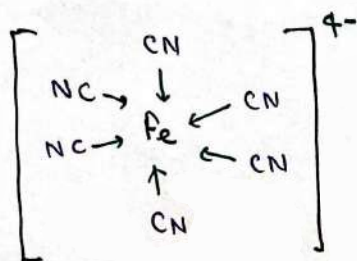
1. > Co-ordination Entity —: The central atom/ion and the ligands attached to it are enclosed in square brackets are collectively known as co-ordination entity or co-ordination sphere.

Ligand —: The donor atoms, ions or molecules which donate a pair of electrons to the central metal atom/ion are called ligands.

For example → $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$

Here Fe is a central metal and CN⁻ is a ligand.

Here Co is central metal and NH₃ is a ligand.

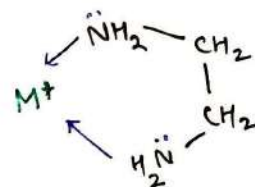


b. > Denticity :- The no. of donor atoms present in a ligand, is called denticity of ligand.

→ Unidentate :- Only one donor atom [Cl^- | NH_3 | H_2O etc.]

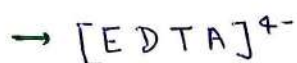
→ Bidentate / didentate - : When a ligand can bind through two donor atoms

For example → Ethane-1,2-diamine [$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$]
or
Ethylenediamine [en]

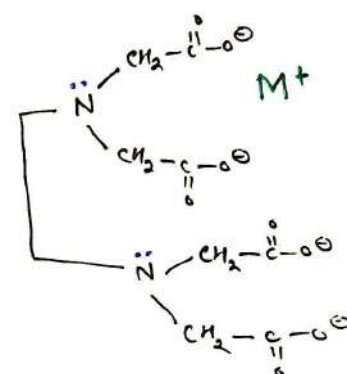


→ Polydentate : More than two donor atoms.

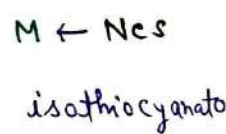
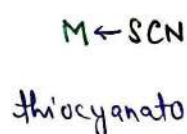
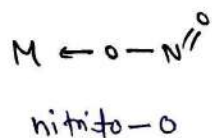
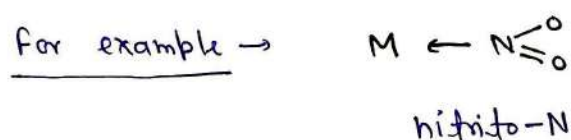
For example → Ethylene diamine tetra-acetate ion



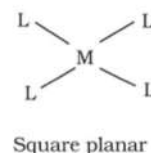
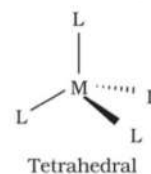
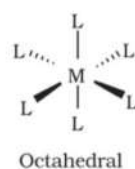
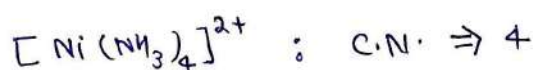
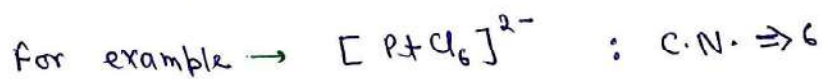
→ It can bind through two nitrogen and four oxygen atoms to a central metal ion.



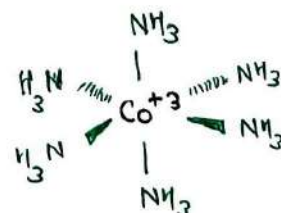
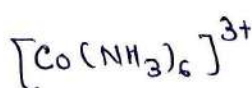
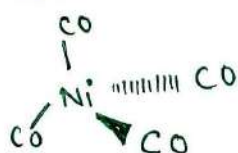
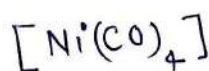
c. > Ambidentate ligand - : Unidentate ligands containing more than one co-ordinating atoms are ambidentate ligands.



d. > Co-ordination Number - : The no. of ligand donor atoms to which the metal is directly bonded.



e. > Co-ordination Polyhedron - : The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a co-ordination polyhedron about the central atom.



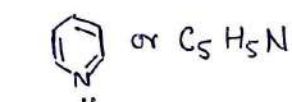
f. > Homoleptic and Heteroleptic Complexes :-

→ Complexes in which a metal is bound to only one kind of donor groups, are known as homoleptic.
For example → $[\text{Co}(\text{NH}_3)_6]^{3+}$

→ Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complex.

For example → $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

→ Formula IUPAC Name



Pyridine

NO

Nitrosyl



Ammine

NO_2^-

Nitro



Aqua

ONO^-

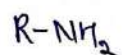
Nitrito-o



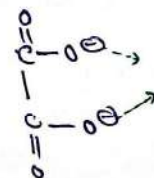
Carbonyl

NH_2^-

Amido



Alkylamine



oxalato [ox]



chlorido



bromido



Hydroxo.



Cyanido / Cyano



Carbonato

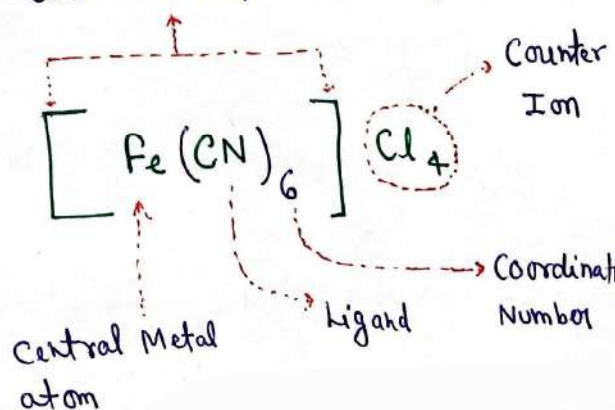


thiocyanato



isothiocyanato

Coordination sphere / entity



g. > Oxidation No. of central atom :-

oxidation no. of CA + sum of charge on total ligands = charge on co-ordination sphere

→ $[Cu(NH_3)_4]^{2+}$: Oxidation no. of Cu ??

$$x + 4(\text{charge on } NH_3) = 2$$

$$x + 4 \times 0 = 2 \quad \text{then } x = +2$$

Nomenclature of Co-ordination Compounds

→ Rules for writing formula of mononuclear co-ordination complexes :-

a.→ Formula of Cation [simple or complex] is written first.

b.→ Co-ordination entity is enclosed in square bracket.

c.→ In coordination sphere, metal atom is written first, followed by ligands in alphabetical order of their names.

d.→ In abbreviated ligands [like en, ox] → first letter of abbreviation is considered.

e.→ When ligands are polyatomic, their formulas are enclosed in parenthesis.

For example → (SCN), (PPh₃) etc.

f.→ There should be no space between the ligands and the metal.

g.→ For charged coordination entity :- charge is indicated outside the square brackets as a right superscript with the no. before the sign.

For example → $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$ etc.

h.→ The charge of the cation is balanced by the charge of anion.

For example:- $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

Alphabetical :
Order Aqua > Chloro

Rules for naming of mononuclear co-ordination compounds →

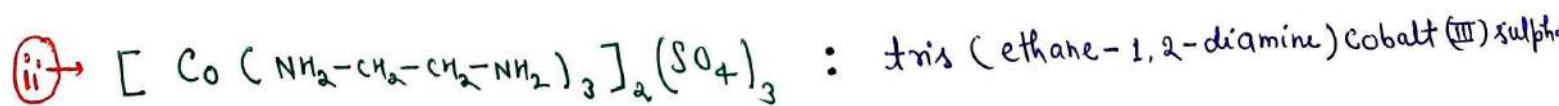
- a.) Complex cation is named first followed by anion (if present).
- b.) The ligands are named in alphabetical order before the name of metal atom/ion.
- c.) Names of anionic ligands end in -o. [For example → Cyano | chlorido].
Neutral ligands have no special ending [H_2O → Aqua, NH_3 → ammine].
Positive ligands end in -ium. [NO^+ : Nitrosonium]
- d.) Prefixes mono, di, tri... are used to indicate the number of the individual ligands.
→ When the names of ligands include a numerical prefix, then terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parenthesis.
- e.) Oxidation state of metal is indicated by Roman numerical in parenthesis.
- f.) If complex ion is a cation, the metal is named same as the element.
→ If complex ion is an anion, the name of the metal ends with suffix -ate.
→ The neutral complex molecule is named similar to that of the complex cation.



$$\text{Oxidation no. of Cr} + 3(\text{charge on } NH_3) + 3(\text{charge on } H_2O) + 3(\text{charge on chlorine}) = 0$$

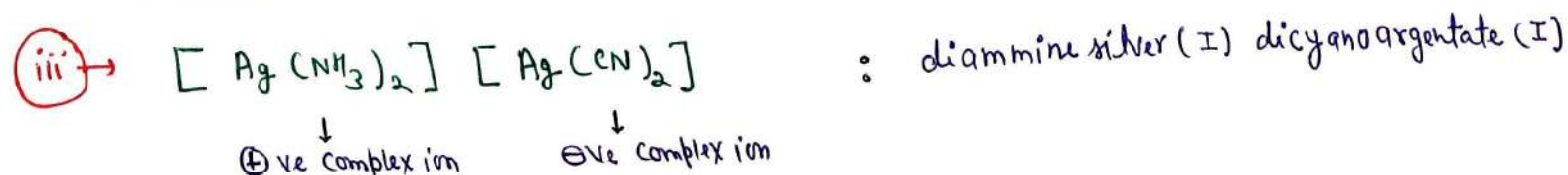
$$\rightarrow \text{Oxidation no. of Cr} + 3 \times 0 + 3 \times 0 + 3 \times -1 = 0$$

$$\rightarrow \text{Oxidation no. of Cr} = +3$$



$$\rightarrow 2(x + 3 \times 0) + 3(-2) = 0$$

$$\rightarrow \boxed{x = +3}$$



(iv) $\text{Ni}(\text{CO})_4$: TetraCarbonyl nickel (0) (v) $\text{K}_4[\text{Fe}(\text{CN})_6]$

$\rightarrow x + 4(0) = 0$ then $x = 0$ Potassium hexacyanidoferrate (II).

chloro / chlorido $\rightarrow \text{Cl}$

[CBSE 2015] (1M)

$$4(+1) + x + 6(-1) = 0$$

then $x = +2$

(vi) $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$: dichlorobis(ethane-1,2-diamine) platinum (IV) ion

(vii) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$: hexaammine nickel (II) chloride [Delhi 2015C] (1M) [Delhi 2011C]

(viii) $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$: diamminechlorido methylamine platinum (II) chloride

(ix) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$: tetraaminedichlorido platinum (IV) chloride [CBSE 2011C]

(x) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$: hexaammine chromium (III) hexacyanocobaltate (III)
 $\uparrow$ $\uparrow$
 $\oplus$ ve complex $\ominus$ ve complex [CBSE 2011C]

$[\text{Pt}(\text{NH}_3)_3(\text{NO})\text{Cl}_2]\text{Br}_2$: triaminedichloridonitrosyl platinum (IV) bromide [Delhi 2011C]

$[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{Cl}$: tetraammine dicyano cobalt (III) chloride [Delhi 2011C]

$[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$: pentaammine isothiocyanato chromium (III) tetrachlorido zincate (II)
 $\uparrow$ $\uparrow$
 $\oplus$ ve complex $\ominus$ ve complex [CBSE 2011C]

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$: pentaammine chlorido cobalt (III) chloride [Delhi 2010C]

$[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]\text{Cl}$: diammine dichlorido (ethane-1,2-diamine) chromium (III) chloride [Delhi 2015]

$\text{K}_3[\text{Fe}(\text{CN})_6]$: Potassium hexacyanoferrate (III) [CBSE 2015]

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$: hexaammine cobalt (III) chloride [CBSE 2015]

$[\text{Co}(\text{en})_3]^{3+}$: tris (ethane-1,2-diamine) cobalt (III) ion. [CBSE 2010C]

$[\text{NiCl}_4]^{2-}$: Tetrachloridonickelate (II) ion. [CBSE 2015 / Delhi 2014C] (1M)

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$: Pentaammine nitrito-N cobalt (III) ion.

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$: Diammine dichloridoplatinum (II).

→ co-ordination No → 4

→ oxidation state → +2

$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$: Trioxalatocobaltate (III) ion.

$[\text{Cr}(\text{CO})_6]$: Hexacarbonylchromium (0).

$[\text{PtCl}_3(\text{C}_2\text{H}_4)]$: Trichlorido ethene platinum (IV)

→ [CBSE 2014] (3M)

$[\text{CoBr}_2(\text{en})_2]^+$: Dibromido bis (ethane -1,2-diamine) Cobalt (III) ion. [Delhi 2013]

$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$: Potassium trioxalato ferrate (III) ion. [Delhi 2013C]

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$: Hexamine platinum (IV) chloride. [Delhi 2013C]

$[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$: Trioxalatochromate (III) ion

$[\text{Co}(\text{en})_2\text{Cl}_2]^+$: Dichlorido bis (ethane -1,2-diamine) Cobalt (III) ion

→ Hexamine cobalt (III) sulphate : $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ [Delhi 2019]

Potassium trioxalatochromate (III) : $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ (2M)

Potassium trioxalatoaluminate (III) : $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$

Dichlorido bis (ethane -1,2-diamine) cobalt (III) ion : $[\text{CoCl}_2(\text{en})_2]^+$ [CBSE 2017]

(2M)

→ Pentamminenitrito-o-cobalt (III) ion : $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

Delhi 2015

(1M)

→ Sodiumdicyanidoaurate(I): $\text{Na}[\text{Au}(\text{CN})_2]$

Delhi 2017

2M

→ Tetraamminechloridonitrito-N-platinum (IV) sulphate : $[\text{Pt}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{SO}_4$

→ Mercury tetrathiocyanatocobaltate (III) : $\text{Hg}[\text{Co}(\text{SCN})_4]$

→ Potassium trioxalato aluminate (III) : $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$

Apni kaksha

→ Potassium tetrahydroxozincate (II) : $\text{K}_2[\text{Zn}(\text{OH})_4]$

Bonding in Co-ordination Compounds

Werner's Theory

Valence Bond Theory

Crystal Field Theory

Werner's Theory :- Werner was the first to formulate his idea about the structures of Co-ordination compounds. The main postulates are →

(i) In coordination compounds metals show two types of valency → Primary and secondary

(ii) The primary valences are normally ionisable and are satisfied by negative ions.

(iii) The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions.

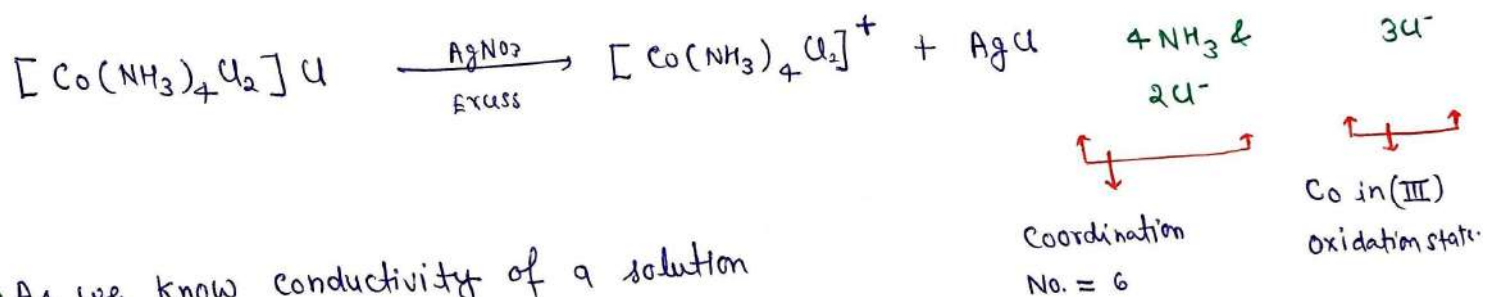
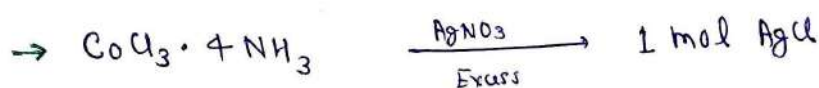
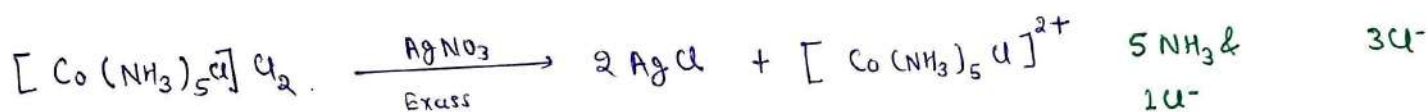
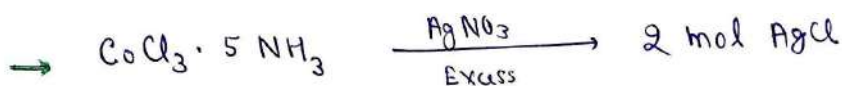
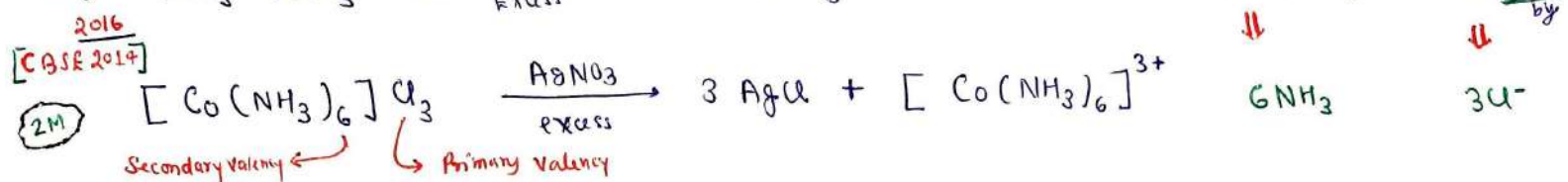
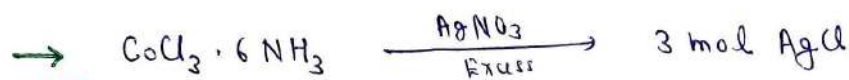
(iv) The ions/groups bound by secondary valency to metal have spatial arrangements corresponding to different coordination numbers.

NOTE :- In modern formulation :- Primary valency corresponds to oxidation state of metal.

→ Secondary valency corresponds to coordination No. of central metal.

→ Spatial arrangements are called coordination polyhedra.

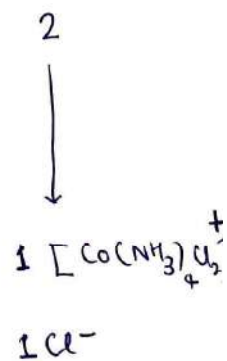
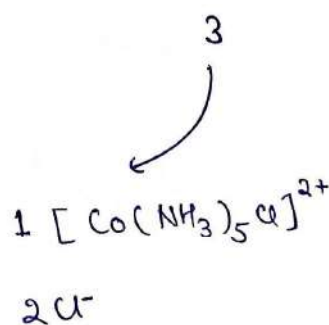
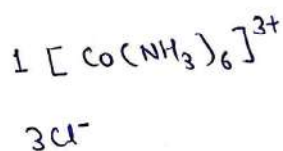
Experiments -: ① In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of chloride ions could be precipitated as AgCl on adding excess AgNO₃ solution but some remained in solution.



② → As we know conductivity of a solution depends on no. of ions present in solution.

Experimental order of conductivity: $\text{CoCl}_3 \cdot 6\text{NH}_3 > \text{CoCl}_3 \cdot 5\text{NH}_3 > \text{CoCl}_3 \cdot 4\text{NH}_3$

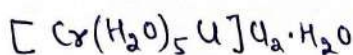
No. of ions in their solution: 4
(per mole of electrolyte)



→ When a coordination compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is mixed with AgNO₃, 2 moles of AgCl are precipitated per mole of compound.

(i) → Write structural formula -: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{AgNO}_3} 2 \text{ AgCl} \downarrow$: means that 2Cl⁻ is ionisable.

[Delhi 2014 | 2016]
CBSE 2019 (1M)



ii) → IUPAC Name of complex :- Pentaquachloridochromium(III) chloride [Delhi 2014] 1M

Valence Bond Theory

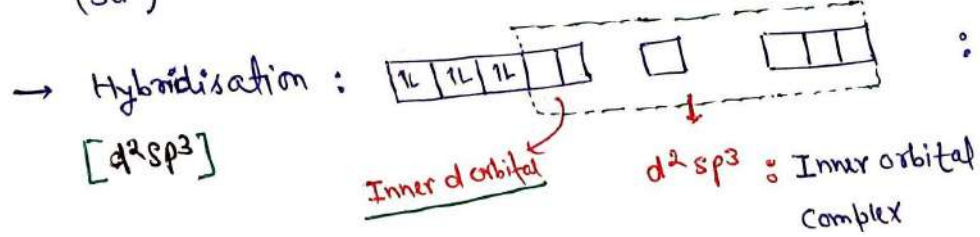
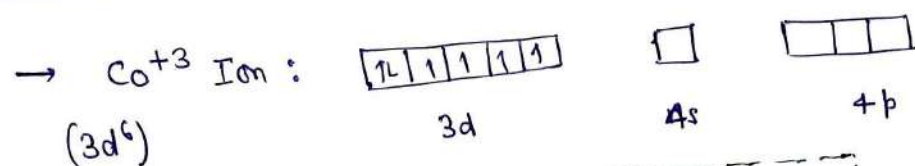
- According to this theory, the metal ion or atom under the influence of ligand can use its $(n-1)d, ns, np$ / ns, np, nd orbitals for hybridisation to give a set of equivalent orbitals of definite geometry.
- These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

<u>Coordination Number</u>	<u>Type of hybridisation</u>	<u>Geometry</u>
# 4	$\swarrow$ sp^3 $\searrow$ dsp^2	$\longrightarrow$ $\longrightarrow$ Tetrahedral Square Planar
# 6	$\swarrow$ $sp^3 d^2$ $\searrow$ $d^2 sp^3$	$\longrightarrow$ $\longrightarrow$ Octahedral Octahedral

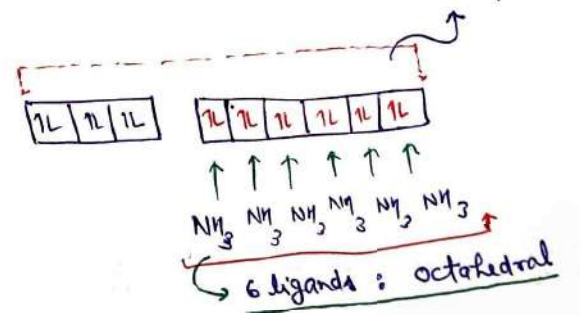
- It is possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of VBT.
- Magnetic moment of a complex depends on no. of unpaired electrons.

Magnetic moment $\mu = \sqrt{n(n+2)}$
 $n = \text{No. of unpaired electron.}$

Example - : (i) $[Co(NH_3)_6]^{3+}$: Diamagnetic in nature.



[CBSE 2010] 2M



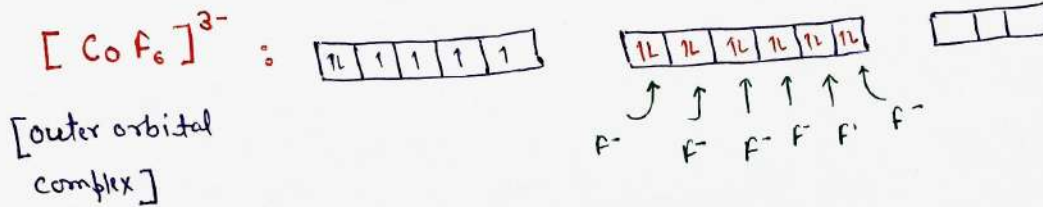
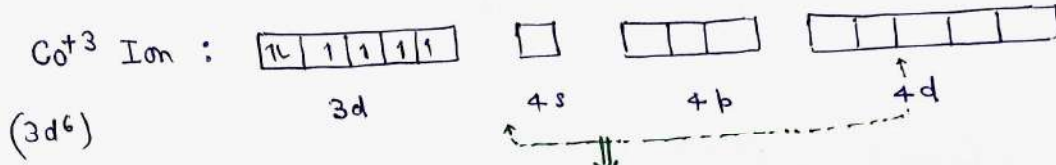
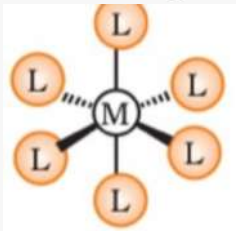
→ Inner Orbital complex : d^2sp^3 : Low spin complex : spin paired complex.

→ Outer orbital complex : sp^3d^2 : High spin complex : spin free complex.

(ii) → $[CoF_6]^{3-}$: Paramagnetic Octahedral complex.

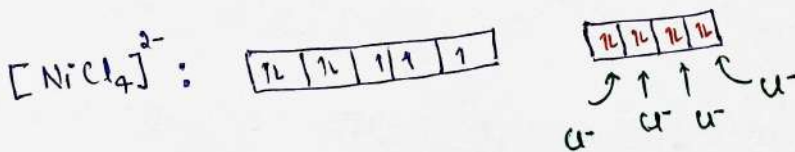
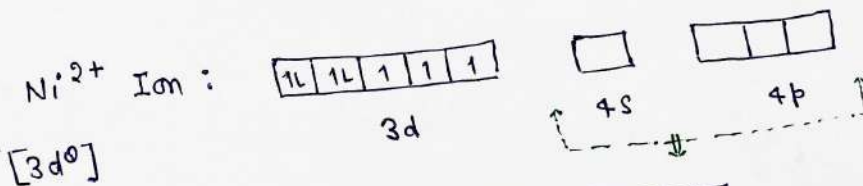
CBSE 2018
[CBSE 2014C]
[Delhi 2010]

↳ Presence of unpaired electrons.



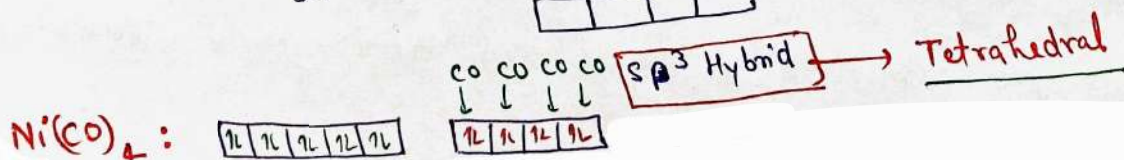
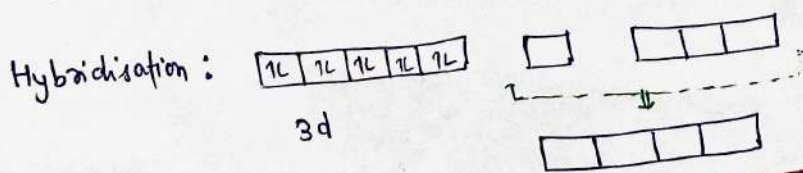
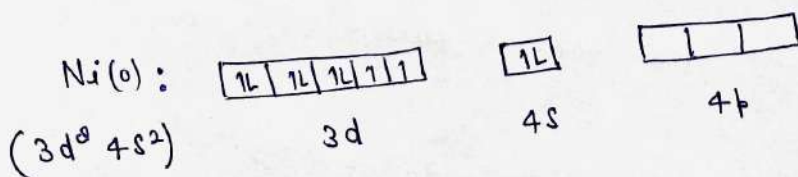
(iii) → $[NiCl_4]^{2-}$: Paramagnetic in nature.

← [CBSE 2017]



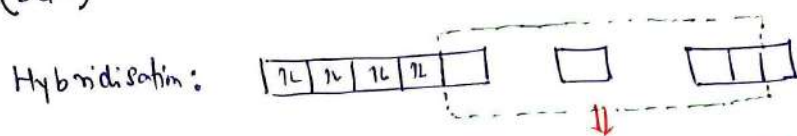
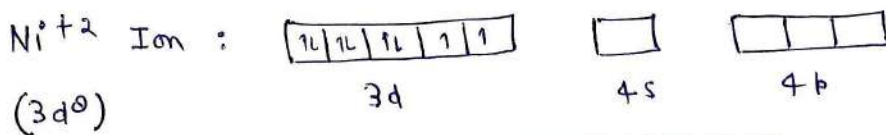
(iv) → $Ni(CO)_4$: Diamagnetic in nature.

[Delhi 2012]

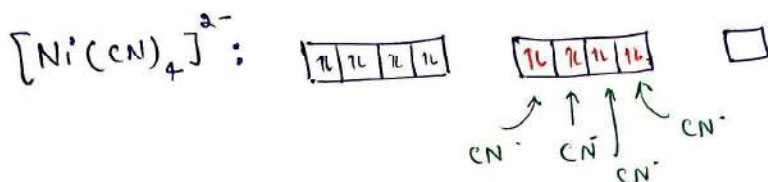


Delhi 2010
C.BSE 2019
2011

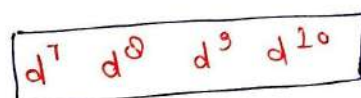
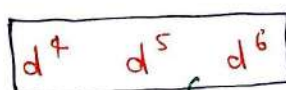
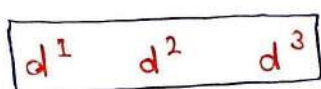
Q → $[Ni(CN)_4]^{2-}$: Square Planar Complex : Diamagnetic.



d^2sp^2 : Square Planar



NOTE - :



For Octahedral
Complex :

Always d^2sp^3
2 Inner d orbitals are
always available for hybridisation.

d^2sp^3 | sp^3d^2
both are possible. It
can be determined by
value of magnetic moment.

Always sp^3d^2
Because inner d
orbitals are not
available.

⇒ $[Mn(CN)_6]^{3-}$: Magnetic moment of 2 electrons : d^2sp^3 : Paramagnetic [C.BSE 2014]

$[MnCl_6]^{3-}$: Magnetic moment of 4 electrons : sp^3d^2

→ $[Fe(CN)_6]^{3-}$: $M = \sqrt{n(n+2)} = \sqrt{1(1+2)}$: 1 unpaired electron : d^2sp^3

$[FeF_6]^{3-}$: $M = \sqrt{5(5+2)}$: 5 unpaired electrons : High spin complex [sp^3d^2]

→ $[Co(C_2O_4)_3]^{3-}$: Diamagnetic : d^2sp^3 : Inner orbital complex. [Delhi 2017]

$[CoF_6]^{3-}$: Paramagnetic with four unpaired electron : sp^3d^2

Limitation of VBT - : (i) It involves no. of assumptions.

(ii) It does not explain colour of coordination compounds.

(iii) It does not give explanation of kinetic and thermodynamic stabilities of complex

(iv) → It does not distinguish between weak and strong ligands.

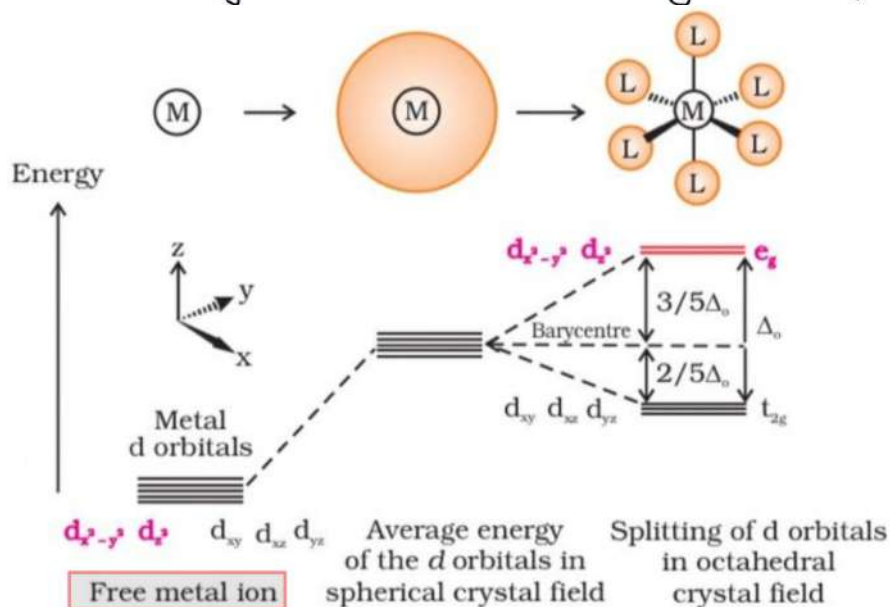
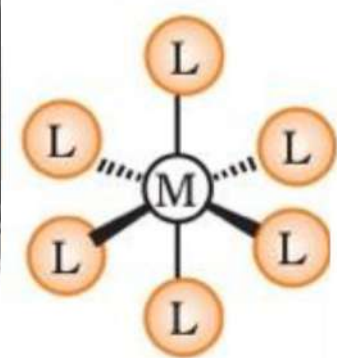
Crystal Field Theory

- CFT is an electrostatic model which considers the metal-ligand bond to be ionic, arising purely from electrostatic interactions between the metal ion and ligand.
- Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. (H_2O , NH_3 etc.)
↓
[Cl^- , Br^- , OH^- etc.]

Crystal Field Splitting in Octahedral complexes :-

- Under the influence of 6 ligands field, degeneracy of d orbitals has been removed due to ligand-metal electron repulsions in octahedral complex.
- Removal of degeneracy gives three orbitals [d_{xy} , d_{yz} , d_{zx}] of lower energy (t_{2g}) and two orbitals of higher energy [d_{z^2} , $d_{x^2-y^2} = e_g$ set].
- $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the axis along the direction of the ligand, will experience more repulsion and will be raised in energy.
- d_{xy} , d_{yz} , d_{zx} orbitals are directed between axes, will be lowered in energy relative to average energy (in the spherical crystal field).
- Splitting of degenerate levels due to the presence of ligands in a definite geometry is called crystal field splitting and the energy separation is denoted by Δ_o [crystal field splitting energy].

[Delhi 2011C/1M]

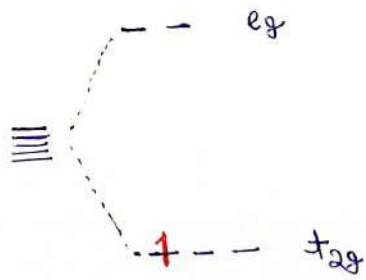


d orbital splitting in an octahedral crystal field

→ The extent of splitting depends upon the field produced by ligand and charge on metal ion.

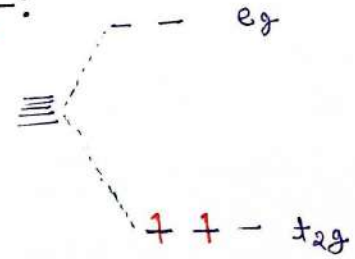
→ d^1 :-

→ $t_{2g}^1 e_g^0$



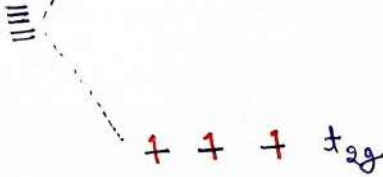
d^2 :-

→ $t_{2g}^2 e_g^0$



d^3 :-

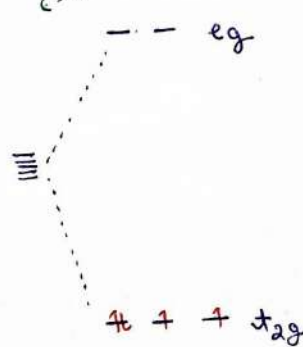
$t_{2g}^3 e_g^0$



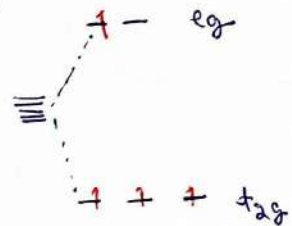
[CBSE 2013] (3M)

d^4

(i)



(ii)



Spectrochemical Series :-

→ If ligands are arranged in a series in the order of increasing field strength, then that series is called spectrochemical series.

→ halogen donors < oxygen donors

< Nitrogen donors < Carbon donors

(i) If $\Delta_o > P$

Now 4th electron enters into t_{2g} orbital and configuration = $t_{2g}^4 e_g^0$

→ Ligands for which $\Delta_o > P$ are known as strong field ligand. [SFL]

(ii) If $\Delta_o < P$

Here, 4th electron enters one of e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

→ Ligands for which $\Delta_o < P$, are known as weak field ligand. [WFL]

→ $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

→ Generally, CN^- & CO are SFL with M^{+2} and rest ligands are WFL.

→ CN^- , CO , en , NH_3 & H_2O are SFL with M^{+3} .

Question :- (i) $[CoF_6]^{3-}$

(ii)

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

(iii) $[Co(NH_3)_6]^{3+}$

→ F^- as WFL.

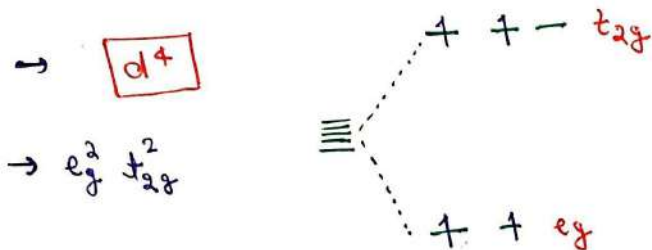
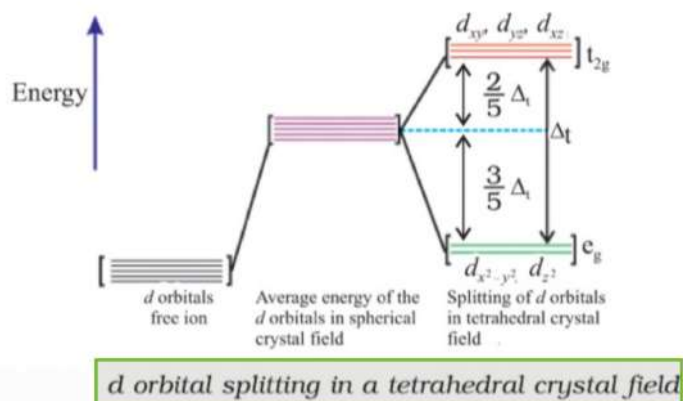
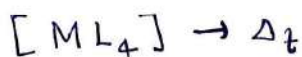
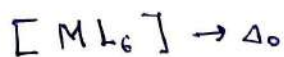
→ en as SFL

→ NH_3 as SFL.

Crystal Field Splitting in tetrahedral complexes:-

→ In tetrahedral coordination entity formation the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

→ For same metal and ligand : $\Delta_t = \frac{4}{9} \Delta_o$



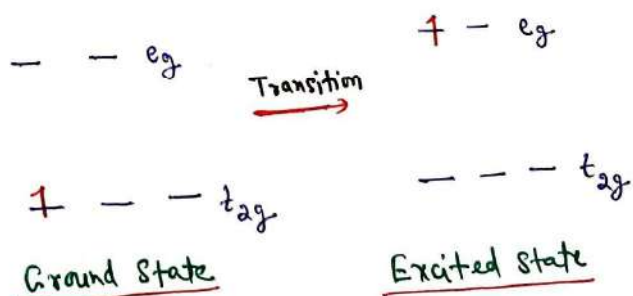
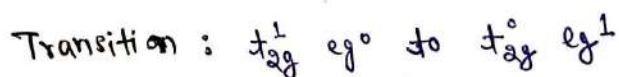
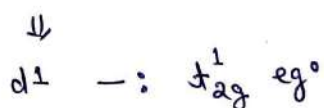
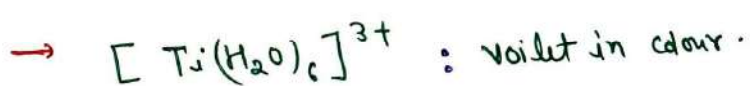
⇌ For tetrahedral complex : $\Delta_t < P$

Always

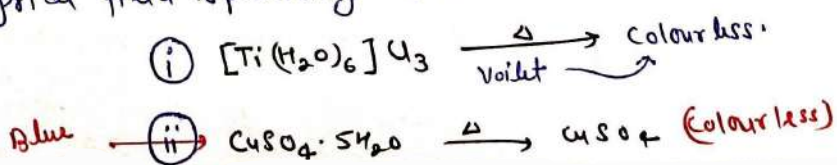
Colour in Coordination Compounds

→ When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electrons from lower d-energy level to higher d-energy level. This transition is called d-d transition of electron.

→ Colour of the compound is the complementary colour of absorbed light. For example if green is absorbed by the complex, it appears red.

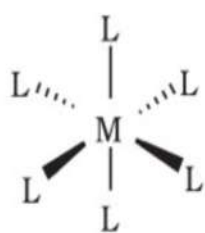


→ In absence of ligand crystal field splitting does not occur and hence the substance is colourless.

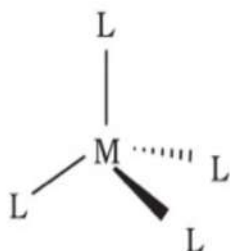


Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

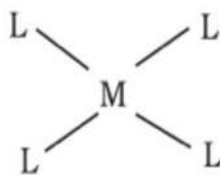
Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Purple



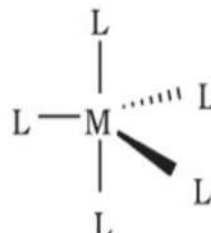
Octahedral



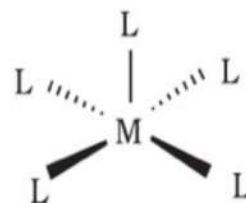
Tetrahedral



Square planar

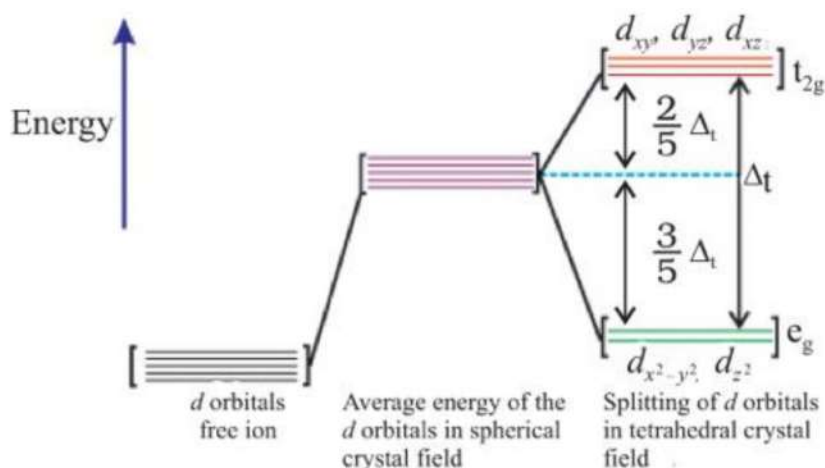


Trigonal bipyramidal



Square pyramidal

Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.



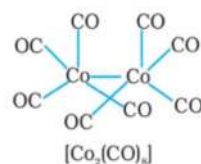
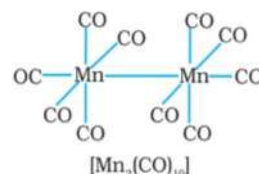
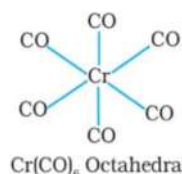
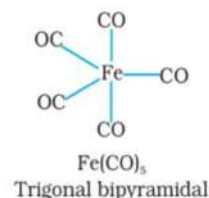
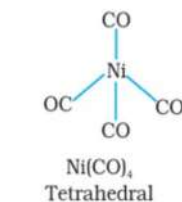
d orbital splitting in a tetrahedral crystal field.

Limitations of CFT :- From the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. But it's not true because anionic ligands are found at the low end of spectrochemical series.

Bonding in metal carbonyls

→ Compounds which have at least one metal-carbon bond are called Organometallic compounds.

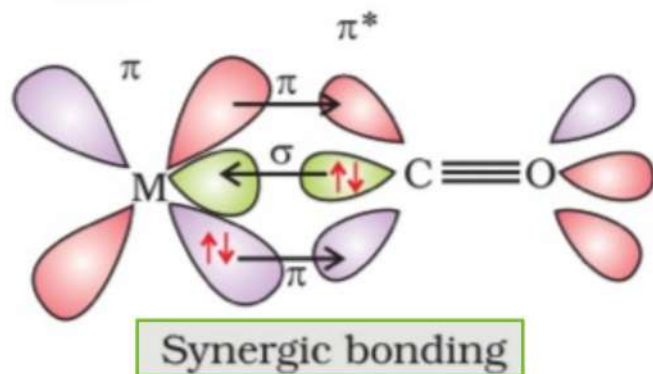
→ The metal carbon bond in metal carbonyls possesses both σ and π character.



→ The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of metal.

→ The M-C π bond is formed by the donation of a pair of electron from a filled d-orbital of metal into vacant π^* orbital of CO.

→ The metal to ligand bonding creates a **Synergic Effect** which strengthens the bond between CO and the metal.



Stability of Co-ordination Compounds

→ The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium.

→ Equilibrium constant for the association expresses the stability.



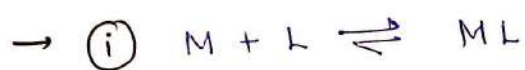
value of equilibrium constant $\uparrow \Rightarrow [\text{ML}_4] \uparrow$

→ Stepwise stability constant -: The equilibrium constant of each step of a complex reaction is called stepwise stability constant. ($K_1, K_2, \dots$) [CBSE 2011C]

2M

→ overall stability constant -: The equilibrium constant for net reaction.

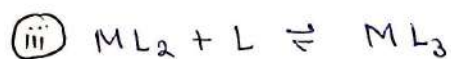
(β_n)



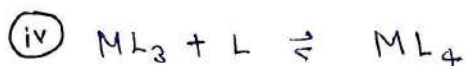
$$K_1 = [ML] / [M][L]$$



$$K_2 = [ML_2] / [ML][L]$$



$$K_3 = [ML_3] / [ML_2][L]$$



$$K_4 = [ML_4] / [ML_3][L]$$



$$\beta_4 = [ML_4] / [M][L]^4$$

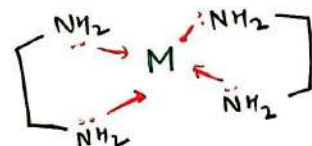
$$\text{Then} \rightarrow \boxed{\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4}$$

Important Previous Year Questions.

$\textcircled{i} \rightarrow$ What is meant by chelate effect? [CBSE 2015] 1M

$\rightarrow$ When a didentate / polydentate ligand containing donor atoms positioned in such a way that, they coordinate with the central metal ion forming a five or six membered ring. The effect is called chelate effect.

$\rightarrow$ As a result of chelate effect, the stability of the complex increases.



$\textcircled{ii} \rightarrow$ Stability of complex : $[CoF_6]^{3-} < [Co(en)_3]^{3+}$

[Delhi 2019]

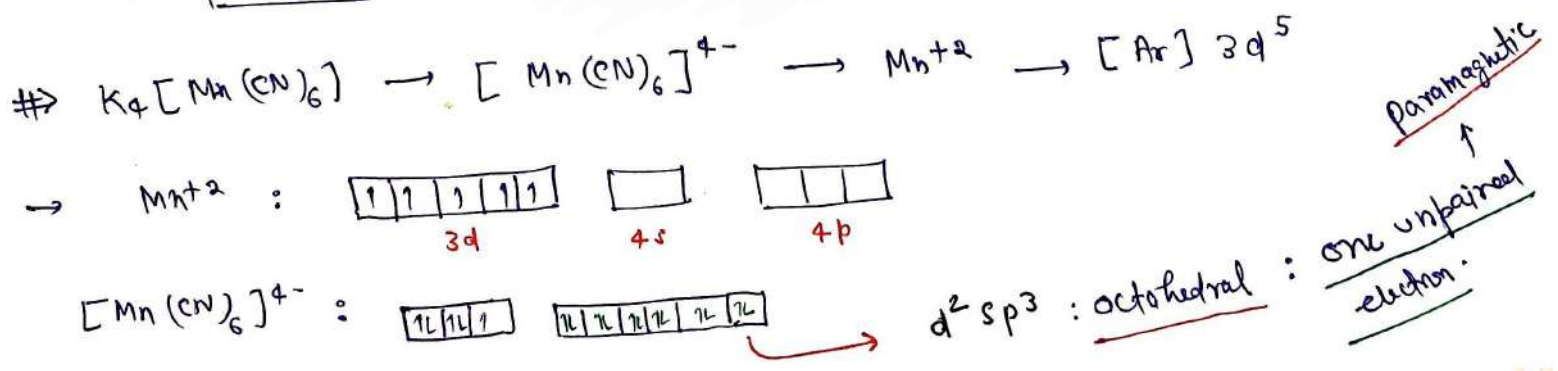
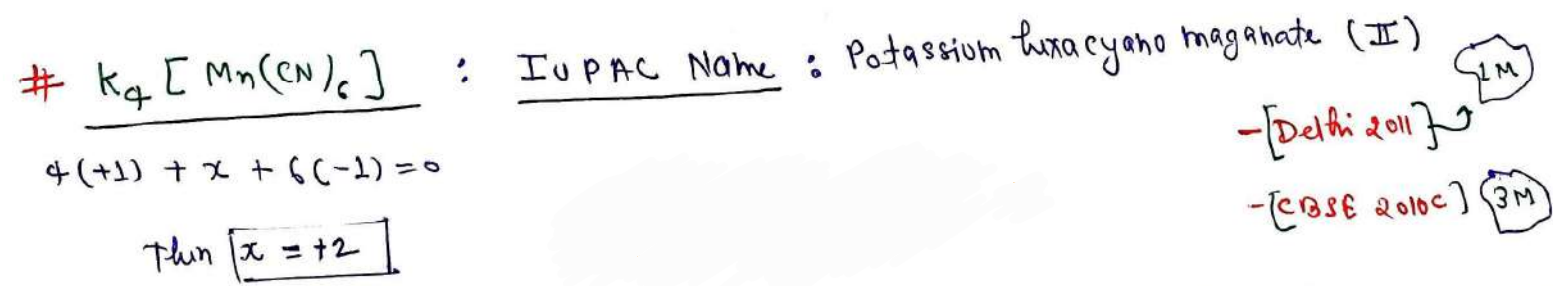
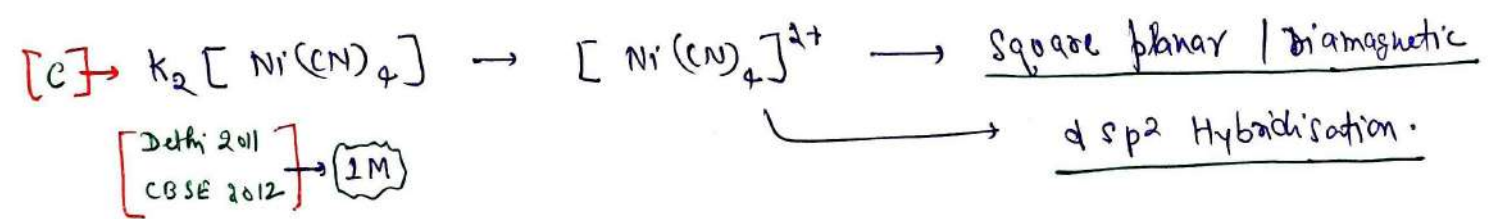
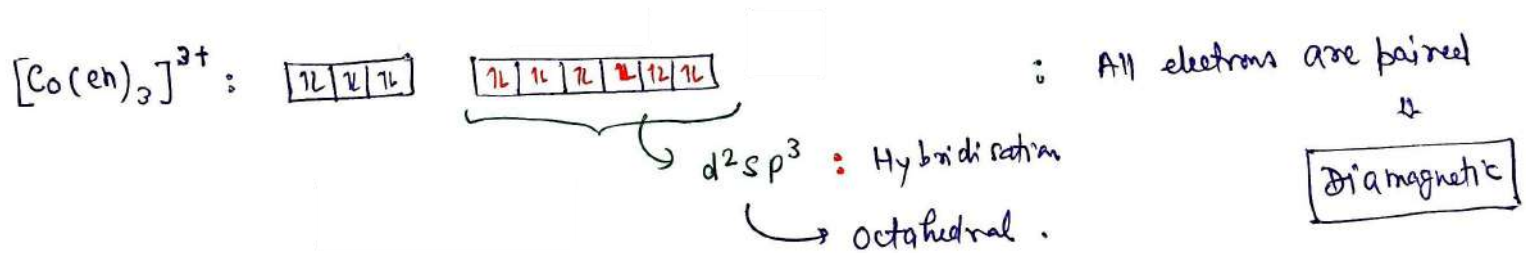
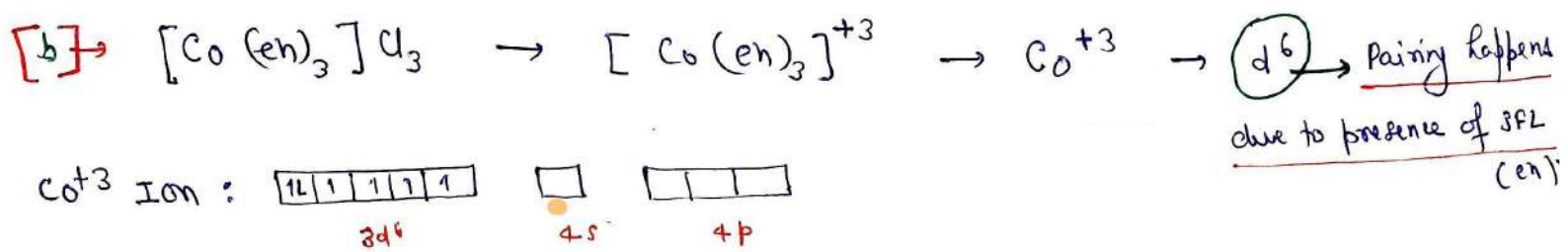
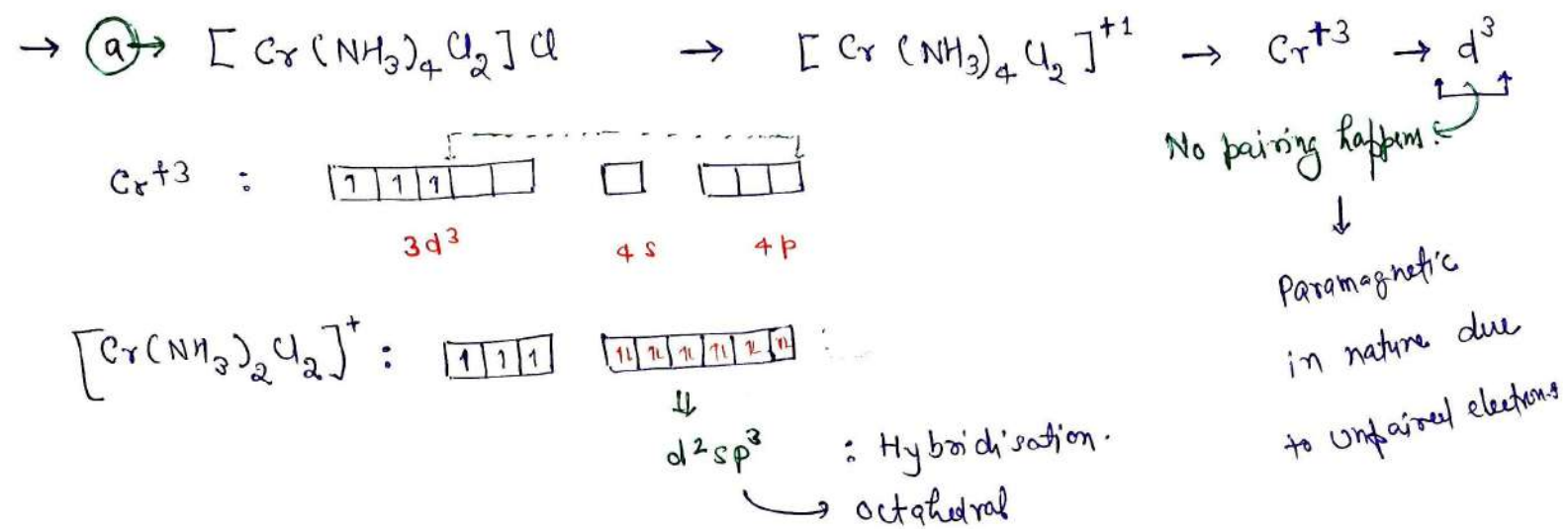
1M

$\hookrightarrow$ More stable due to chelate effect

[iii] CO is stronger complexing agent than NH_3 , why? [Delhi 2012] 1M

$\rightarrow$ There exist a backbonding in CO complexes in which CO accepts electron density from the filled d orbitals of metal atom into their π^* orbital. So, there are σ as well as π interaction with metal in case of CO. But NH_3 makes only σ bond with metal. Therefore CO is a stronger complexing agent than NH_3 .

(iv) → Write the state of hybridisation, the shape and the magnetic behaviour of following complex entities. [CBSE 2011] → (3M)



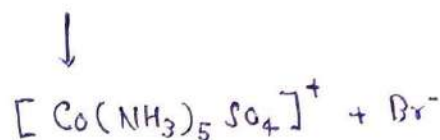
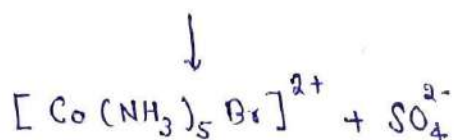
Isomerism in Coordination Compounds

→ Isomerism arises due to different structural arrangements [Structural Isomerism] or spacial arrangements [Stereoisomerism] of compounds having same formula.

Structural Isomerism :-

(i) Ionisation Isomerism :- When the complexes with same composition give different ions in solution.

Example: $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ Delhi 2010
1M



(ii) Solvate / Hydrate Isomerism :- When complex differ in the number of water (solvent) molecules present as ligand.

Example :- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
[CBSE 2015] 1M

(iii) Linkage Isomerism :- When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom.

Example :- $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ [Delhi 2010] 1M



(iv) Coordination Isomerism :- When the interchange of the ligands take place between ionic and anionic entities of different metal ions present in a complex.

Example :- $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$

[Delhi 2010] 1M

→ $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$ and $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$

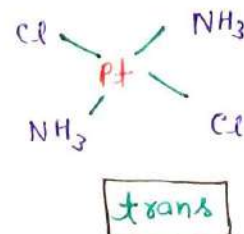
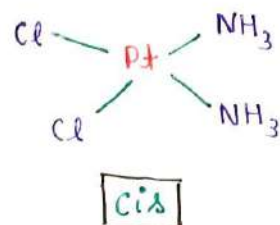
[CBSE 2010] 1M

Stereo-isomerism :-

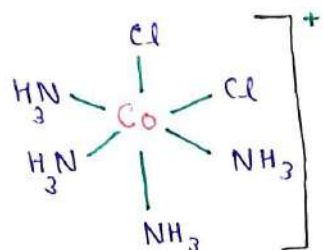
(a) Geometrical Isomerism :- When similar groups are present in adjacent position, it is cis. When they are present in opposite position, it is trans.

→ It occurs in square planar compounds and octahedral compounds.

→ Geometrical Isomers of $[Pt(NH_3)_2Cl_2]$

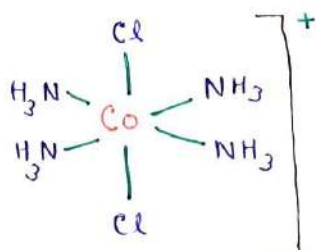


→ Geometrical Isomers of $[Co(NH_3)_4Cl_2]^+$



cis

[Delhi 2013] (1M)

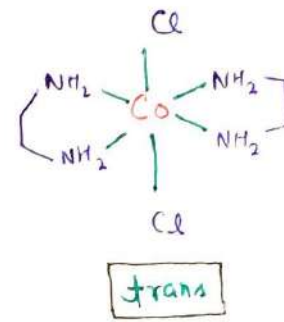
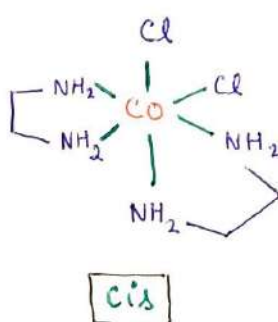


trans

[Delhi 2012] (1M)

→ Geometrical Isomers of $[CoCl_2(en)_2]^-$

[CBSE 2012] (1M)

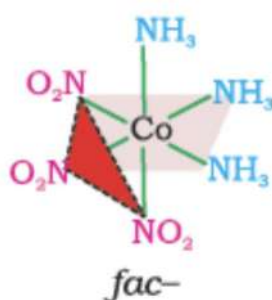


→ Geometrical Isomers of $[Ma_3b_3]$

→ Facial [fac]

→ Meridional [mer]

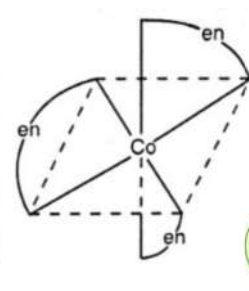
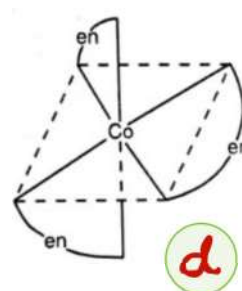
Example —: $[Co(NH_3)_3(NO_2)_3]$



(b) Optical Isomerism —: This is shown by complexes whose mirror images are non-superimposable. Such complexes are called optical isomers.

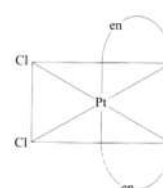
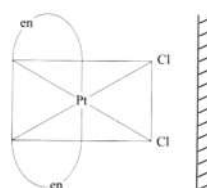
→ Optical isomers (d and l) of $[Co(en)_3]^{3+}$

[Delhi 2013] (1M)

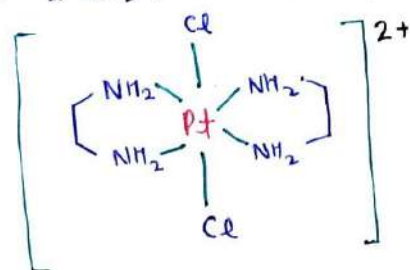


→ Optical isomers (d and l) of cis $[PtCl_2(en)_2]^{2+}$

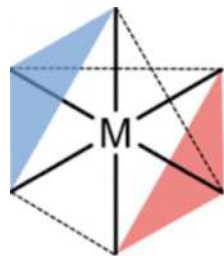
(1M) [CBSE 2015]



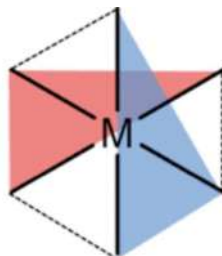
→ trans $[PtCl_2(en)_2]^{2+}$ is optically inactive.



[CBSE 2014] (1.5M)



facial

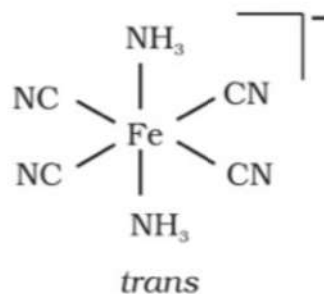
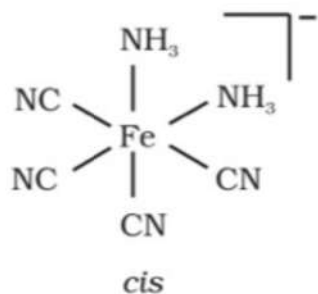


meridional

Example 9.5

Draw structures of geometrical isomers of $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$

Solution



Example 9.6

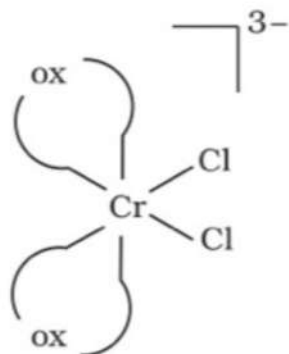
Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*- $[\text{CrCl}_2(\text{ox})_2]^{3-}$

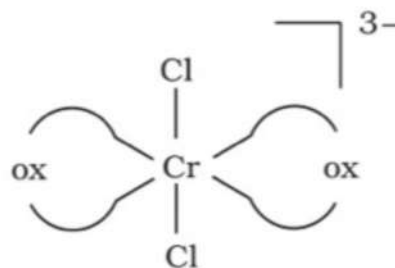
(b) *trans*- $[\text{CrCl}_2(\text{ox})_2]^{3-}$

Solution

The two entities are represented as



(a) *cis* - $[\text{CrCl}_2(\text{ox})_2]^{3-}$



(b) *trans* - $[\text{CrCl}_2(\text{ox})_2]^{3-}$

Out of the two, (a) *cis* - $[\text{CrCl}_2(\text{ox})_2]^{3-}$ is chiral (optically active).