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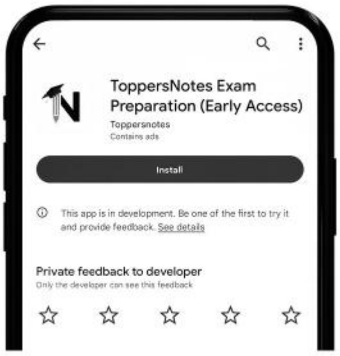

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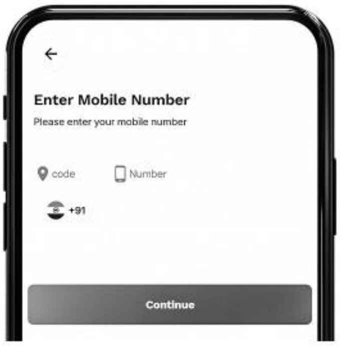

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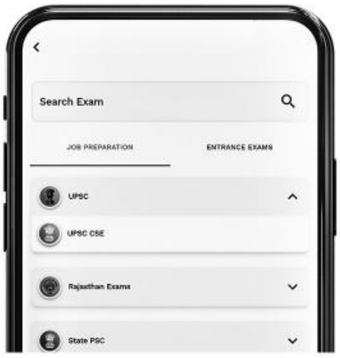

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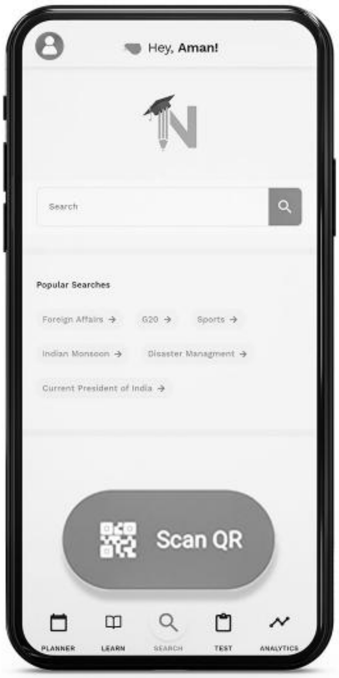

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CHAPTER
1
Coordination Compounds

CHAPTER OUTLINE

- Co-ordination Chemistry
- Terms Related to a Complex
- Isomerism in Coordination Compounds
- Stereo Isomerism
- Valence Bond Theory
- Crystal Field Theory
- Type of Organometallic Compounds
- Type of Co-ordination Complexes
- Nomenclature of coordination compounds
- Structural Isomerism
- Bonding in Complexes
- Structures and shapes of complexes on the basis of valence bond theory
- Organometallic Compounds
- Important points

CO-ORDINATION CHEMISTRY

When two or more saturated solutions of neutral compounds are mixed in stoichiometric proportion followed by standing a solid, adduct is formed.

This adduct or addition compound is of two types:

Double Salt	**Co-ordination Complex**
Formed by the combination of two salts.	A complex ion is an electrically charged radical generated by combining a simplication with one or more simple ions or neutral molecules, each of which has two constituents: **an acceptor (central metal atom) and a donor (ligand).**
Retains its identity only in solid state but losses in solution.	Retains its identity not only in solid state but also in solution state.
On dissolution in water, it dissociates into original ions.	Gives complex or different ions on dissociation.
Example: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O(s) + aq.\,solution \rightarrow$ Potash alum $2K^+(aq) + 2Al^{3+}(aq) + 4SO_4{}^{2-}(aq) + 24H_2O(l)$ $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O(s) + aq.\,solution \rightarrow$ Mohr salt $Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O(l)$	**Example**: $Fe(CN)_2(aq) + 4KCN(aq) \rightarrow K_4[Fe(CN)_6](aq)$ $\downarrow$ $4\,K^+(aq) + [Fe(CN)6]^{4-}(aq)$

TYPES OF CO-ORDINATION COMPLEXES

Perfect or Penetrating Complex	**Imperfect or Normal Complexes**
Complex ion is either completely stable i.e., undissociated or very feebly dissociated in solution also.	Complex ion is either less stable or dissociates appreciably.

Example:	**Example:**
$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$ Feebly dissociated $\cancel{\downarrow}$ $Fe^{2+} + 6CN^-$	$K_2[Cd(CN)_4] \longrightarrow 2K^+ + [Cd(CN)_4]^{2-}$ Appreciably dissociated $\updownarrow$ $Cd^{2+} + 4CN^-$

Representation of Co-ordinate Complex

$$\mathbf{A_x[M(K)_a(\,L)_b]B_Y}$$

- where, A and B = Cationic and anionic species which are ionizable and precipitable
- M = Central metal atom like Cr, Mn, Fe, Co, Ni etc
- K, L = Ligands i.e., electron pair donor species nonionizable and non-precipitable species
- Sum of a and b is equal to coordination number
- [ ] represents coordination sphere

TERMS RELATED TO A COMPLEX

Coordination Sphere

- The **coordination sphere** refers to the core metal atom and the ligands that are immediately linked to it.
- The central metal atom or ion, as well as the ligands around it, are denoted in **square brackets, [ ]** and are referred to as the **coordination sphere.**
- This sphere's atoms, ions, or molecules are not ionizable.

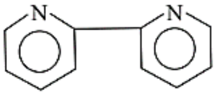
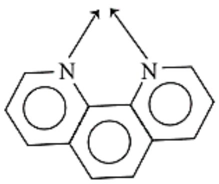
Central Metal Atom or Ion or Centre of Co-ordination

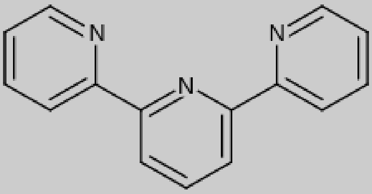
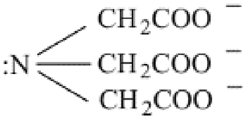
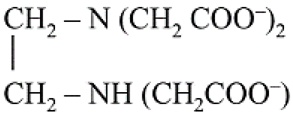
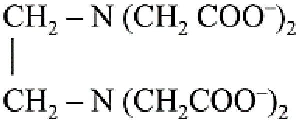
- The **centre of coordination** is the central metal atom or ion to which one or more neutral molecules or ions are connected.

Ligand

- **Ligands** or complexing agents are the molecules and ions that surround the metal ion in a complex.
- A single atom or a group of atoms that attaches to the core metal atom or ion through the lone pair of electrons on its donor atom.

Depending on number of pairs donated by different atoms, the ligands are classified as:

Types	**Meaning**	**Examples**
Unidentate	Have one electron pair to donate.	X^-, NH_2, CN^-, OH
Bidentate	Have two electron pairs to donate.	$C_2O_4^{-2}$ (Oxalato) $H_2NCH_2COO^-$(Glycinato) $H_2NCH_2CH_2NH_2$ or en (Ethylene diammine)  Bipyridyl (bipy)  1,10-phenanthroline (phen)

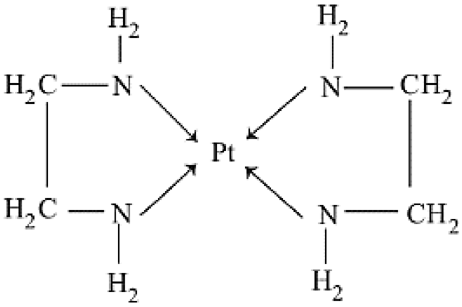
Tridentate	Have three electron pairs to donate.	$H_2\,N(CH_2)_2NH(CH_2)_2NH_2$ Di ethylene tri ammine (dien)  Ter pyridyl (terpy)
Tetradentate	Have four electron pairs to donate.	$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ Tri ethylene tetra amine or trien Tri amino tri ethyl amine or tren  $:N\begin{cases}CH_2COO^{-}\\CH_2COO^{-}\\CH_2COO^{-}\end{cases}$ Nitriloacetato
Pentadentate	Have five electron pairs to donate.	 $\begin{array}{l}CH_2-N(CH_2\,COO^{-})_2\\ \vert\\ CH_2-NH(CH_2COO^{-})\end{array}$ Ethylene di ammine tri acetate
Hexadentate	Have six electron pairs to donate.	 $\begin{array}{l}CH_2-N(CH_2\,COO^{-})_2\\ \vert\\ CH_2-N(CH_2COO^{-})_2\end{array}$ Ethylene diammine tetra acetate (E.D.T.A.)

Facts to Remember

The attachment of a symmetrical bidentate ligand to the central metal atom is shown by a curve $\overset{A}{A}\supset L$ where L is the abbreviation of the symmetrical bidentate ligand and two A's are two (similar) donor atoms.	The attachment of an unsymmetrical bidentate ligand to the central metal atom is shown by a curve $\overset{A}{B}\supset L$ where L is the abbreviation of the ligand and A and B are two (different) donor atoms.
Example: phen	**Example:** Glycinato (gly)

Chelating Ligand

- When a polydentate ligand attaches to the central metal atom via several donor sites, a cyclic ring-like structure, i.e., chelate, is created, and this ligand is referred to as a **chelating ligand.**



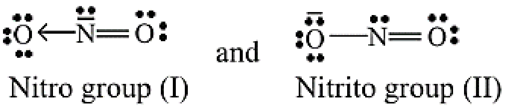
- Because of the chelating or macrocyclic action, such a cyclic or chelate complex is more stable than an open complex.
- Example: In case of $[Ni(en)_3]^{2+}$ stability is nearly 10^{10} more than$[Ni(NH_3)_6]^{2+}$.

Facts to Remember

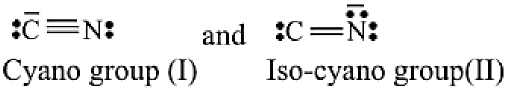
- These chelates are used to soften hard water and to separate lanthanides and actinides.
- In medicine, chelating drugs are used to remove metal ions such as Hg^{2+}, Pb^{2+}, and Cd^{2+}.
- E.D.T.A., for example, is used to treat lead poisoning.

Ambidentate Ligand

- These ligands have two or more donor sites, but only one is employed during complex formation.
- Examples:



Nitro group (I) and Nitrito group (II)



Cyano group (I) and Iso-cyano group(II)

SCN^- and NCS^-

Thio cyanide   Iso thiocyanide

Facts to Remember

Thio sulphato ($S_2O_3^{2-}$) can also act as an ambidentate ligand like ($O^- - S_2O_2^-$) ion and ($S^- - SO_3^-$) ion.

Flexidentate

- The ligand has numerous donor sites here, but not all of them are utilised.
- **E.D.T.A. is an example.**
- It frequently acts as a penta co-ordinate ligand, leaving one of the acetate groups free.

π - Acid Ligand

- Such ligands can accept a significant amount of electron density from the central metal atom into their empty π or π^* orbitals.
  Example: CO

Coordination Number or Ligancy

- The coordination number refers to the total number of ligands around the core metal atom in the coordination sphere.
- Examples:
  $[Ni(CN_4]^{-2}$, Coordination number is 4.
  $K_4[Fe(CN)_6]$, Coordination number is 6.
  $[Fe(C_2O_4)_3]^{-3}$, Coordination number is 6 , since $C_2O_4{}^{-2}$ is bidentate in nature.

Sidgwick Theory of Complexes

- **Lewis acids** are transition metals or ions.
- Ligands are electron donor species, often known as **Lewis bases.**
- By absorbing the lone pair of electrons from ligands, transition metal ions can build complex compounds.
- A co-ordinate covalent bond is established between the transition metal ion and the ligand (L → M Here L = ligand, M = central metal atom).
- To receive electron pairs from ligands, transition metal ions must have unoccupied orbitals.
- Ligands must have at least one single pair of electrons to contribute.

Effective Atomic Number (E.A.N.)

- It was introduced by Sidgwick and it is defined as "*Effective atomic number is the total number of electrons present around central metal ion in a complex*".
  E.A.N. = [Atomic number of the metal] − [**Number of electrons lost in the formation of its ion] + [Number of electrons gained from ligands].**
  Example:
  E.A.N. $= Z -$ Oxidation number $+ 2 \times$ Number of ligands
- Sidgwick postulated that a metal ion is stable if the atomic number of the closest inert gas is equal to E.A.N.
  Example:
  $K_4[Fe(CN)_6]$
  E.A.N = 26 – 2 + 12
  = 36

- The E.A.N of certain complexes is not equal to the atomic number of the closest inert gas.

  Examples:
- $K_4[Fe(CN)_6]$

  E.A.N = 26 – 3 + 12

  = 35
- $[Ni(CN)_4]^{2-}$

  E.A.N = 28 – 2 + 8

  = 34

Complex	Electrons lost in ion formation	Electrons gained from ligands	E.A.N
$[Ni(CO)_4]$	0	8	28 – 0 + 8 = 36
$[Cu(CN)_4]^{3-}$	1	8	29 – 1 + 8 = 36
$[Ag(NH_3)_4]^+$	1	8	47 – 1 + 8 = 54
$[Co(CN)_6]^{4-}$	2	12	27 – 2 + 12 = 37
$[Ni(NH_3)_6]^{2+}$	2	12	28 – 2 + 12 = 38
$[PdCl_4]^{2-}$	2	8	46 – 2 + 8 = 52
$[Pt(NH_3)_2 Br_2]$	2	8	78 – 2 + 8 = 84
$[Ni(py)(en)(NH_3)_3]^{2+}$	2	12	28 – 2 + 12 = 38

Preparation of Complexes

Complexes are mainly prepared by following methods:

(1) By Substitution Reaction

$$[Cu(H_2O)_4]SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

$$[Co(NO_2)_6]^{-3} + 2NH_2-CH_2-CH_2-NH_2 \rightarrow [Co(en)_2(NO_2)_2]^+ + 4NO_2$$

(2) By Direct Combination

$NiCl_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]Cl_2$

$CoCl_3 + 6NH_3 \rightarrow [Co(NH_3)_6]Cl_3$

$PtCl_4 + 2KCl \rightarrow K_2[PtCl_6]$

(3) By Redox Reactions

$$CoCl_2 + 2NH_4Cl + 10NH_3 + H_2O_2 \rightarrow 2[Co(NH_3)_6]Cl_3 + 2H_2O$$

$$2[Co(H_2O)_6](NO_3)_2 + 8NH_3 + 2NH_4NO_3 + H_2O_2 \rightarrow 2[Co(NO_3)_2(NH_3)_5](NO_3)_2 + 14H_2O$$

Stability of Complexes

The stability of a complex depends upon these factors.

Stability $\propto$ K (Stability Constant)

$M^{a+} + nL^{X-} \rightarrow (ML_n^{b+})$

$$K = \frac{(MLn)^{b+}}{[M^b][L^x]^n}$$

Example: $[Cu(CN)_4]^{2-}$, $K = 2 \times 10^{27}$

$[Fe(CN)_6]^{3-}$, $K = 7.7 \times 10^{43}$

- Stability $\propto$ Charge on cation or oxidation number
- Stability $\propto$ 1/ Size of cation i.e., cation with higher charge and smaller size will form more stable complex.

  Example:

  $Fe^{3+} > Fe^{2+}$
- Stability $\propto$ Basic nature of ligands or electron density

  Example: Cyano amine complex $>$ X-complexes more basic ligands
- Stability $\propto$ Number of chelate rings (macro cyclic effect)

Facts to Remember

Complex formation tendency of some divalent cations decreases as $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$

NOMENCLATURE OF CO-ORDINATION COMPOUNDS

The basic rules are:

- When naming salts, the **positive ion (cation)** comes first, then the **negative ion (anion).**

Example:
$[Co(NH)_5Br]Br_2$ in this case the name is first given for $[Co(NH_3)_5Br]^{2+}$ then Br^-.

- The non-ionic or neutral compound name must be written in a single word.
- The ligands in a complex species are named before the metal atom.
- The names of the neutral ligands should be written exactly as they are. There are several exceptions.

H_2O – aqua	NH_3 – ammine
CO – carbonyl	NO – nitrosyl
CS – thiocarbonyl	NH – thionitrosyl

- Names of the negative ligands must be ended with ' O '.

Examples:

Cl^-- chloro or chloride	CH_3COO^-- acetato
CO_3^{2-} - carbanato	$C_2O_4^{2-}$ - oxalate
NO⍰2⍰—nitro	NO_3^- —nitrato
S^{2-} - sulphido	SO_4^{2-} — sulphato
NH_2 - amine or amino	NH^-- imido
OH⍰—hydroxo	O_2^{2-} - peroxo

- The names of the positive ligands should be ended with "ium".

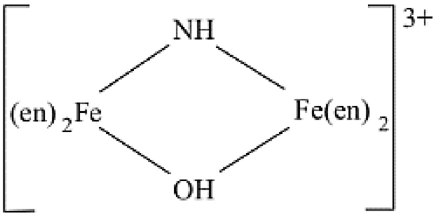
Examples:
H_3O^+ —hydronium
NO_2^+ —nitronium
$N_2H_5^+$- hydrazinium

- If the same complex compound contains different ligands, their names should be written in alphabetical order.
- The prefixes **di, tri, tetra, penta,** etc. are used before the **ligands** to **indicate their number.**
- The number of complex ligands such as bidentate, tridentate, and so on is indicated by bis, tris, tetakis, and so on, if their names already contain di, tri, and so on.
- When identifying ambidentate ligands, the ligands are named according to their place of attachment.

Example:
SCN^-, S - thio cyanato (here S is donor)
NCS^-, N — iso thio cyanato (here N is donor)

- If the complex comprises two or more metal atoms, the bridging ligands are denoted by a prefix μ before their names.

Examples:
$[(NH_3)_5Cr - OH - Cr(NH_3)_5]Cl_5$
Pentaamminechromium (III) – μ - hydroxopentaaminechromium (III) chloride



Bis (ethylenediamine) iron (III) -μ- hydroxo-μ-imido bis (ethylenediamine) iron (III)

Or

Tetrakis (ethylenediamine)-μ-hydroxo-μ-imido diiron (III) ion.

- The central metal ion's oxidation number should be provided in roman numerals in the parentheses immediately after the name of the metal ion.
- If the complex ion is positive, the metal ion's name is written exactly as it is.

Example: $[Cr(en)_3]Cl_3$ - Tris ethylene di amine cobalt(III) bromide

- If the complex ion is an anion and the metal's symbol is in Latin, their names should be in Latin as well.

Examples:
Ferrum – ferrate
Argentums – argenate
Stannum - stannate etc.

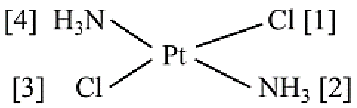
Example: $K_4[Fe(CN)_6]$ Potassium hexa cyano ferrate (II)

- The water molecules of crystallisation are mentioned after the complex name, with arabic numbers indicating the quantity of such molecules.

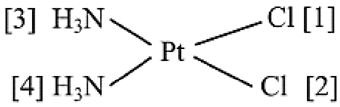
Example:
$AlK(SO_4)_2.12H_2O$
Aluminium potassium sulphate 12 -water

- Geometrical isomers are termed by prefixing the names of the ligands with the prefixes cis for adjacent (90°) positions and trans for opposite (180°) positions.
- The groups at locations (1,2) and (3,4) in square planar complexes are cis to each other, whereas those at positions (1,3) and (2,4) are trans to each other.

  Example:



trans-diammine dichloro platinum (II)



Cis-diammine dichloro platinum (II)

- In mono nuclear octahedral complexes of Ma_4b_2 type (1, 2), (1, 3), (1, 4), (1, 5), (6, 2), (6, 3), (6, 4), (6, 5), (2, 3), (3, 4) and (5, 2) are cis position while (1, 6), (2, 4) and (3, 5) are trans positions.
- In mono nuclear complexes of $\mathrm{Ma_3\ b_3}$ type $(1,2,5)$ are cis while $1,2,6$ are trans positions.
- Optically active dextro and leavo rotatory compounds are denoted by (+) and (-) or d and l, respectively.

  Example:

  $(+)$ or $\mathrm{d} - \mathrm{K_3[Ir(C_2O_4)_3]}$ is potassium $(+)$ or d-trioxalato iridate (III).
- The names of several coordination compounds according to IUPAC regulations are provided below.

(a) Complex Cations IUPAC Name

Formula	Name
$K_3[Cr(CN)_6]$	potassium hexa cyano chromate (III)
$[Ti(H_2O)_6]Cl_3$	hexa aqua titanium (III) chloride
$[Cr(NH_3)_6]Cl_3$	hexa amine chromium (III) chloride
$[CrSO_4(NH_3)_4]NO_3$	tetra ammine sulphato chromium (III) nitrate
$[Co(en)_2\ F_2]\ ClO_4$	bis-(ethylenediamine)-di fluorocobalt (III) perchlorate
$[Cu(acac)_2]$	bis (acetylacetonato) copper(II)
$[CoCl.CN.NO_2.(NH_3)_3]$	triamminechloro cyano nitro cobalt (III)
$[Pt(NH_3)_4(NO_2)Cl]SO_4$	tetra ammine chloro nitro platinum (IV) sulphate
$[Cr(NO_2)_3\ (NH_3)_3]$	triammine nitro chromium (III)
$[Co(en)_2\ Cl(ONO)]^+$	chloro-bis-(ethylenediamine)-nitro-cobalt-(III) ion

(b) Complex Anions

Formula	Name
$[Pt(NH_3)_4\ (ONO)Cl]^{2-}$	tetraammine chloro nitrito palatinate (IV) ion
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	potassium amminedicyano dioxoperoxo chromate (VI)
$Na[ZnCl_4]$	sodium tetrachlorozincate (II)
$(NH_4)_3[Co(C_2O_4)_3]$	ammonium tris-(oxalato)- cobaltate – (III)
cis $[PtBrCl(NO_2)_2]^{2-}$	cis-bromochloronitro palatinate (II) ion
$Na_3[Ag(S_2O_3)_2]$	sodium bis(thiosulphato) argentite (I)
$K_2[OsCl_5N]$	potassium pentachloronitrido osmate (VI)

$K_3[Fe(CN)_5NO]$	potassium pentacyanonitrosyl ferrate (II)
$K_2[OSCl_5N]$	potassium tetrafluoro borate (IV)

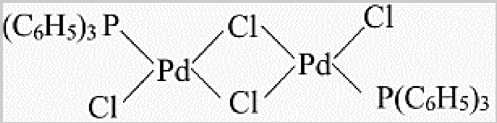
(c) Neutral Complexes

Formula	Name
$[Cr(C_6H_6)_2]$	bis-(benzene) chromium-(0)
$[Ni(CO)_4]$	tetracarbonyl nickel-(0)
$[Cr(en)_3]Cl_3$	d or ℓ tris (ethylenediamine) chromium (III) chloride
$[CoCl_2((NH_2)_2CO)_2]$	dichloro-bis-(urea)-cobalt- (II)
$Fe(C_5H_5)_2$	bis(cyclopentadienyl)iron(II)
$[Fe(C_2H_5N)_2]$	dipyridineiron-(0)

(d) Cationic as well as Anionic Complexes $[\,]^{n+}$ $[\,]^{n-}$

Formula	Name
$[Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4]$	tetraamine dichloro latinum (IV) tetrachloro palatinate (II)
$[Pt(py)_4]$ $[PtCl_4]$	Tetrapyridineplatinum-(II) Tetrachloroplatinate-(II)

(e) Bridging Groups

Formula	Name
$[Be_2O(CH_3COO)_6]$	Hexa-μ-acetato (O,O')-μ oxo-tetraberylium (II)
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonylbis [tricarbonyl iron (0)]$^{4-}$
$[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)_5$	
	μ-amidobis[pentaammine cobalt (III)] nitrate
	trans-chloro triphenylphospine palladium (II) –μ-dichloro-chloro triphenyl palladium (II) or trans bis-μ-chloro chloride triphenyl phosphine palladium (II)

(f) Hydrates

Formula	Name
$AlK(SO_4)_2.12H_2O$	Aluminium potassium sulphate 12-water
$[Cr(H_2O)_4Br_2]Br_2H_2O$	tetra aqua dibromo chromium (III) bromide 2-water
$AlCl_3.4(C_2H_5OH)$	aluminium trichloride-4-ethanol

ISOMERISM IN CO-ORDINATION COMPOUNDS

- Isomers are compounds with the same chemical formula but distinct structural arrangements.
- Isomerism is of two types:
  - Structural Isomerism
  - Stereo isomerism

STRUCTURAL ISOMERISM

1. Ionization Isomerism

- Compounds with have identical compositions but distinct ions in solution are referred to as **ionisation isomers**.
- By exchanging the position of ligands inside and outside the coordination sphere, ionisation isomers are formed.
- Ionisation isomers are detectable via conductance measurement or chemical analysis.

Example 1

$[Co(NH_3)_5SO_4]Br$: red colour
$[Co(NH_3)_5Br]SO_4$: violet colour
The ions precipitable are $Br^-$and $SO_4{}^{2-}$.

Example 2

$[Pt(NH_3)_4Br_2]Cl_2$
$Pt(NH_3)_4Cl_2]Br_2$
Here the ions precipitable are $Cl^-$and Br^-.

2. Hydrate Isomerism

It is caused by a difference in the location of water molecules in a complex as ligand and hydrated molecules, i.e., the amount of water molecules in the coordination sphere varies.

Example 1

$CrCl_3.6H_2O$ has 3 isomers: i.e.,

$[Cr(H_2O)_6]Cl_3$: violet
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$: green
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$: dark green

Example 2

$CoCl_3(H_2O)_6$ has 3 isomers i.e.,

$[Co(H_2O)_6]Cl_3$
$[CoCl_2(H_2O)_4]Cl_2.H_2O$
$[CoCl_3(H_2O)_3] \cdot 3H_2O$

3. Linkage Isomerism

This isomerism happens when more than one atom in a ligand may function as a donor site, as in the case of an ambidentate ligand.

Examples: CN, NC
SCN, NCS
NO_2, ONO
$O^-S_2O_2^-$, $S_2O_3^{2-}$

$[(NH_3)_5 CoONO]Cl_2$: Red colour
$[(NH_3)_5 CoNO_2]Cl_2$: Yellow colour
$[Cr(NH_3)_5 (SCN)] Cl_2$; $[Cr(NH_3)_5 (NCS)]Cl_2$

4. Co-ordination Isomerism

This isomerism happens when compound include both cationic and anionic complexes and the ligands of these complexes interchange.

Example 1

$[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(CN)_6][Co(NH_3)_6]$

Example 2

$[Cu(NH_3)_4][PtCl_4]$ and $[Cu(NH_3)_3Cl][Pt(NH_3)Cl_3]$

5. Polymerization Isomerism

It refers to compounds that have the same stoichiometric composition but have molecular compositions that are multiples of the simplest stoichiometric arrangements.

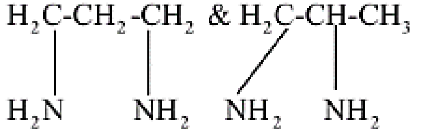
Example:

$[Pt(NH_3)_2Cl_2]$
$[Pt(NH_3)_4][PtCl_4]$

6. Ligand Isomerism

If we consider following two ligands

Example:



1,3-diaminopropane(tn) 1,2-diaminopropane(pn)

In this condition when such ligands form complexes ligand isomerism is observed.

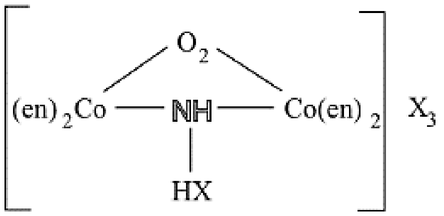
Example:

$[Co(tn)_2Cl_2]^+$ and $[Co(pn)_2Cl_2]^+$

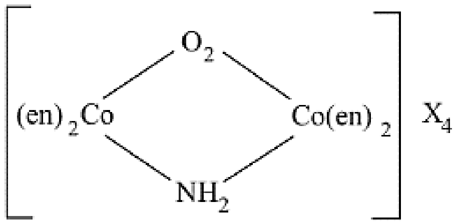
7. Valency Isomerism

- It occurs when the ligand is bound together by multiple types of valence bonds, which might be primary or secondary.

  Example:



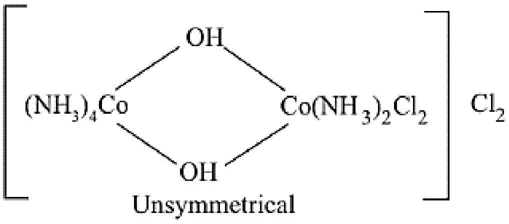
and

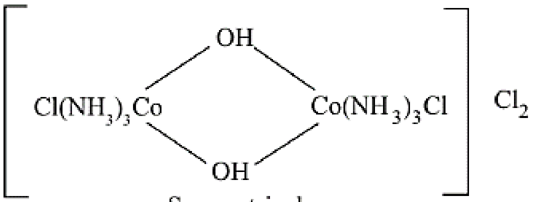


8. Coordination Position Isomerism

- It forms in polynuclear complexes as a result of ligand exchange between metal atoms.

  Example:





Symmetrical

STEREO ISOMERISM

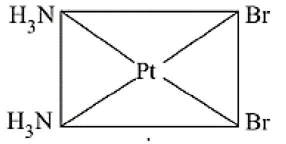
- It forms when the isomers differ in the arrangement of the atoms in space.
- It is of two types:-
  - Geometrical isomerism
  - Optical isomerism

1. Geometrical Isomerism

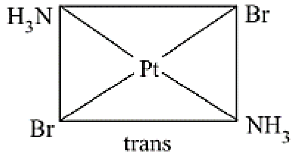
- It occurs when the complex's geometry is altered by the exchange of atoms, groups, or ions inside its coordination sphere.
- When two identical ligands are present in neighbouring positions in geometrical isomers, this is known as **cis-isomerism,** and when such ligands are placed diagonally (opposite), this is known as **trans-isomerism.**
- Complexes with a **tetrahedral** structure with a coordination number of 2, 3, or 4 **do not show geometrical isomerism**.
- Complexes with a **square planar** structure and a coordination number of 4 for the central metal ion will **display geometrical isomerism**.
  - Square planar complexes of the type $Ma_4, Ma_3b, Mab_3, M(aa)_2$ do not exhibit geometrical isomerism.
  - $Ma_2\ b_2, Ma_2bc, M(aa)b_2$ or $M(ab)_2$ and Mabcd type square planar complexes exhibit geometrical isomerism.

    Example:

    [Pt $(NH_3)_2Br_2$] and [Pt$(NH_3)_2$ (Cl) (Br)]

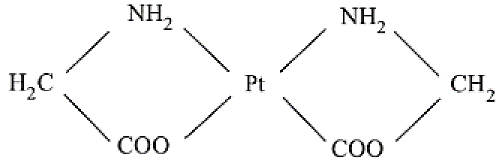


cis

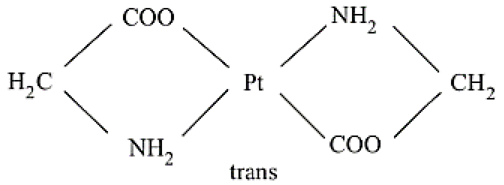


trans

e.g., [Pt (gly)$_2$]

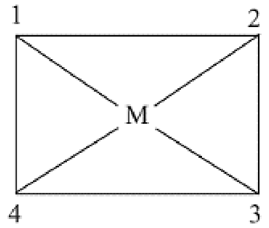


cis



trans

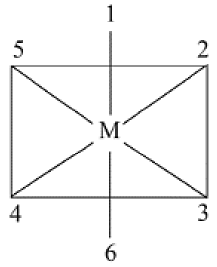
Mabcd type square planar complexes exists in three isomerism forms.



- In square planar complexes positions 1, 4 and 2, 3 are cis while 1,3 and 2,4 are trans.

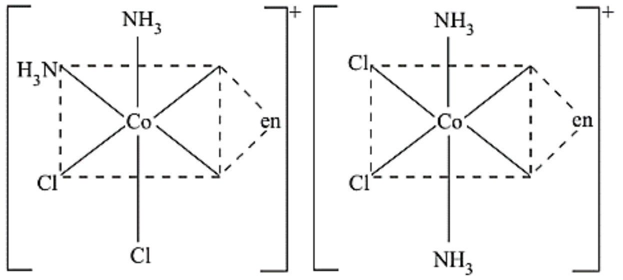
  Example:

  $[Pt(NH_3)(Py)(Cl)(Br)]$
- Octahedral complexes of the type Ma_6, Ma_5b, or Mab_5, $M(aa)_3$ do not exhibit geometrical isomerism.



- Octahedral complexes of the type $Ma_4\ b_2, Ma_4bc, Ma_3\ b_3$, $Ma_2\ b_2c_2$, etc., type complexes exhibit geometrical isomerism.
- In octahedral complexes positions 1, 6 and 2, 4 and 3, 5 are trans.

  Example: $[Co(NH_3)_4Cl_2]^+$
- Complexes of the type [M (aa) x_2y_2] can show geometrical (cis and trans) isomerism. Example: [Co (en) $(NH_3)_2Cl_2]^+$exhibits cis and trans isomerism.

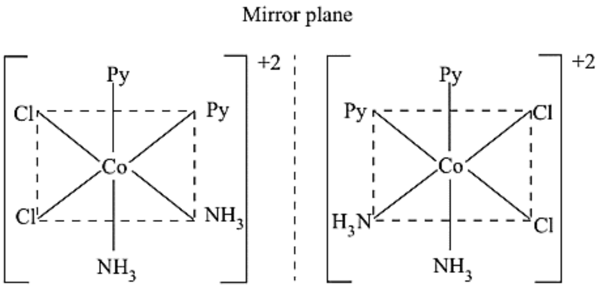


cis trans

- Octahedral complexes of the type $\mathrm{M}(aa)_2\,\mathrm{b}_2$ where, (aa) is a symmetric bidentate ligand also exhibit geometrical isomerism.
  Example: $[\mathrm{Co(en)_2Cl_2}]^+$
- Octahedral complex of the type [M(abcdef)] has 15 different geometrical isomers with a pair of enantiomers.
  Example: $[\mathrm{Pt(py)\ (NH_3)(Cl)(Br)(I)(NO_2)}]$

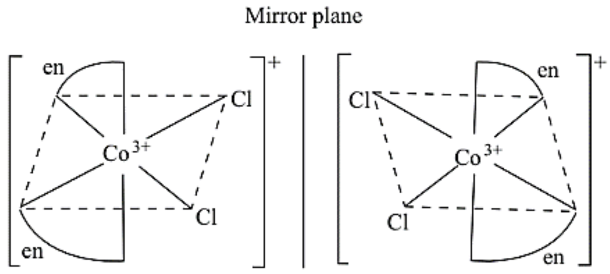
2. Optical Isomerism

- Complexes that lack a centre of symmetry, a plane of symmetry, or an axis of symmetry display optical isomerism.
- When all four ligands are of various types, complexes with coordination number four and tetrahedral structure might display optical isomerism.
- Compound of type $Ma_2x_2y_2$, Ma_2x_2yz, Ma_2xyzl, Mabcxyz, $M(aa)_3$, $M(aa)_2x_2$ show optical isomerism.
- Octahedral complexes of the type $\mathrm{Ma_2b_2c_2}$ type can exist in two optical isomers.
  Example: $[\mathrm{Pt\ (NH_3)_2\ (Py)_2\ Cl_2}]^{+2}$ exhibits optical isomerism.



- The cis isomer occurs in two optical isomers in octahedral complexes of the form $M(aa)_2\,b_2$. Optical isomerism is not feasible in the case of trans isomers.

Example: $[\mathrm{Co(en)_2Cl_2}]^+$

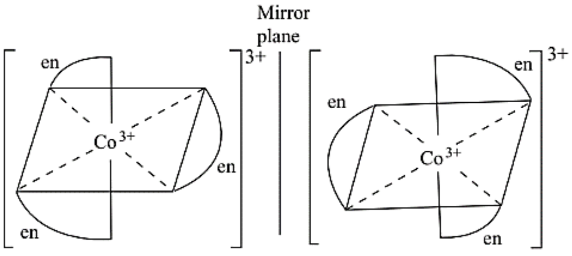


Cis-d-isomer Cis-l-isomer

Figure: Optical isomer of $[\mathrm{Co\ (en)_2Cl_2}]^+$ion

$\mathrm{M(aa)_3}$ type octahedral complexes also exists in two optical isomers.

Example: $[\mathrm{Co(en)_3}]^{3+}$



d-form i-form

Figure: Optical isomer of $[\mathrm{Co(en)_3}]^{3+}$ ion

[Mabcd] type Complexes

- This complex ion/compound should have optical activity. Due to its unstable nature, it has not been able to segregate optically active d - and l - forms of such a compound.
- Example:
  $[\mathrm{As(CH_3)(C_2H_5)(S)(C_6H_5COO)}]^{2+}$ ion.
- It is optically active because it lacks a plane of symmetry.

BONDING IN COMPLEXES

Werner's Theory

- In coordination compounds, the central metal atom has two types of valencies: **Primary (Principle valency)** and **Secondary (Auxillary valency),** and the metal atom seeks to fulfil both of its valencies.

Secondary Valency

- Secondary valency is represented by the coordination number of the central metal atom and is fulfilled by ligands (anions and neutral molecules).

Examples

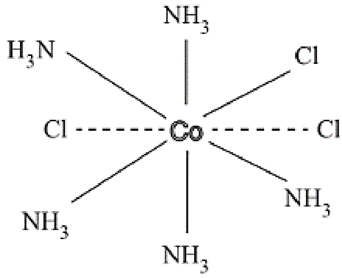
(a) In $K_4[Fe(CN)_6]$ here the secondary valency of **Fe is 6** and it is satisfied by **6 CN ligands**.

(b) $[Co(NH_3)_6]Cl_3$ here secondary valency of Co is 6 and it is satisfied by **$6NH_3$ molecules**.

(c) $[Co(NH_3)_5Cl]Cl_2$ here Co has secondary valency 6 and it is satisfied by **$5NH_3$ and Cl^-ion molecule.**

- Secondary valencies are basically written inside the **coordination sphere**.

  Example: $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]$ Cl



$[Co\ (NH_3)_5Cl]\ Cl_2$

- Secondary valency is **directional** in nature and gives a **definite geometry** to coordination compounds.
- Secondary valency is 2 linear, 3 trigonal planar, 4 square planar or tetrahedral, 6 octahedral.

  Example: $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]\ Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ will have octahedral shape.
- Secondary valency cannot be achieved in the free-state by ionising coordination compound aqueous solutions.

  Example:

  $[Co(NH_3)_4Cl_2]Cl \rightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$
- Secondary valency is shown by thick (—) lines.

Primary Valency

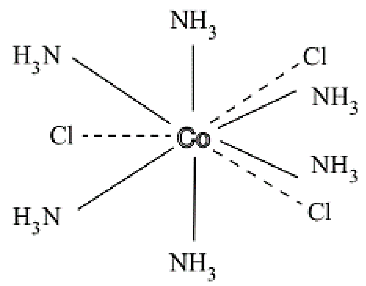
- Primary valency denotes the oxidation number of the core metal atom.
- Anions always fulfill the primary valency. Example:

  $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, the primary valency is 3 and it is satisfied by $3Cl^-$ ions.
- Primary valency is written outside the coordination sphere, but if a species has both primary and secondary valency, it is also written inside the coordination sphere.
- Outside of the coordination sphere, **primary valency is non-directional.**
- The primary valency does not indicate the geometry of the coordination compounds.
- Primary valency achieving species can be produced in the free state by ionising coordination compound aqueous solutions.

  $[Co\ (NH_3)_5\ Cl]\ Cl_2 + 2AgNO_3 \rightarrow$ …………

  $2Cl^- + 2Ag^+\ 2AgCl$

  White ppt.



$[Co\ (NH_3)_6]\ Cl_3$

Primary valency is shown by dotted (...........) lines.

	Molecular formula	Colour	No. of Cl^- ion ppt. by $AgNO_3$	Molar conductance ohm^{-1} cm2 mol^{-1}	No. of ions	Structural formula
	$CoCl_1$ Ammine Complexes					
1	$CoCl_3.6NH_3$	Orange	3	430	4	$[Co(NH_3)_6]Cl_3$
2	$CoCl_2.5NH_3.H_2O$	Pink	3	430	4	$[Co(NH_3)_5H_2O]Cl_3$
3	$CoCl_2.5NH_3$	Violet	2	250	3	$[Co(NH_3)_3Cl]Cl_2$

4	$CoCl_3.4NH_3$	Green or violet	1	100	2	$[Co(NH_3)_4Cl_2]Cl$
5	$CoCl_3.3NH_2$	Blue green	0	0	-	$[Co(NH_3)_3Cl_3]$
	$PtCl_4$ Ammine Complexes					
1	$PtCl_4.6NH_3$		4	520	5	$[Pt(NH_3)_6]Cl_3$
2	$PtCl_4.5NH_3$		3	410	4	$[Pt(NH_3)_5Cl]Cl_3$
3	$PtCl_4 \cdot 4NH_3$		2	240	3	$[Pt(NH_3)_4Cl_2]Cl_2$
4	$PtCl_4 \cdot 3NH_3$		1	100	2	$[Pt(NH_3)_4Cl_3]Cl$
5	$PtCl_4.2NH_3$		0	0	-	$[Pt(NH_3)_2Cl_4]$

VALENCE BOND THEORY

- Linus Pauling proposed Valence bond theory to explain bonding in complicated molecules. The following are the major postulates of valence bond theory:
    - To produce the cation, the centre atom loses the required number of electrons. The number of electrons lost is equal to the cation's oxidation number.
    - For the formation of dative bonds with the ligands, the central cation makes accessible a number of vacant orbitals equal to its co-ordination number.
    - The cation orbitals fuse to generate a new set of equivalent hybrid orbitals with distinct directional properties.

Co-ordination no.	**Type of hybridization**	**Molecular geometry**	**Examples**
2	sp.	Linear	$[CuCl_2]^–$, $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$
3	sp^2	Trigonal planar	$[CuCl\ (Cu)_2]$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiCl_4]^{2+}$, $[Cu(CN)_4]^{3–}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2–}$, $[PdCl_4]^{2–}$, $[Cu(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$
5	sp^3d or dsp	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3–}$, $[Ni(CN)_5]^{3–}$
6	sp^3d^2 or d^2sp^3	Octahedral	$[Fe(CN)_6]^{3–}$, $[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{4–}$, $[Co(NO_2)_6]^{3–}$, $[CoF_6]^{3–}$m, $[FeF_6]^{3–}$, $[Fe^+\ (NO^+)\ (H_2O)_5]^{2+}$, $[Ni(NH_3)_6]^{2+}$

- Non-bonding metal electrons reside in the inner d orbitals and are not involved in hybridization.
- If the ligands are strong, such as $C\bar{N}$, CO, NH_3 the d-electrons are rearranged, vacating some d-orbitals (when there are more than three) that can participate in hybridization.
- The d-electrons are not rearranged if the ligands are weak, such as F^-, Cl^-, and H_2O.
- The hybridised d-orbitals might be either (n-1) d orbitals or outer nd-orbitals.
- **Inner orbital complexes** or **low spin complexes** are created by the participation of **(n-1)d orbitals** in hybridization.
- **Outer orbital complexes** or **high spin complexes** are the complexes created by the participation of **nd-orbitals** in hybridization.
- Each ligand has a single pair of electrons. A dative bond is created by the overlap of a metal ion's unoccupied hybrid orbital and a ligand's filled orbital.
- If there are any **unpaired** electrons in the complex, it will be **paramagnetic**; **otherwise**, it will be **diamagnetic**.

- The number of unpaired electrons in a complex determines its geometry, or vice versa.

Inner orbital octahedral complexes	**Outer orbital octahedral complexes**
These are formed by dsp^2, d^2sp^3 type of hybridisation.	These are formed by sp^3, sp^3d^2 type of hybridisation.
These complexes have less number of unpaired electrons therefore show low magnetic moment or no magnetic moment.	These complexes have greater number of unpaired electrons therefore show high magnetic moment.
These are less reactive, therefore substitution of ligands is fairly difficult.	These are more reactive, therefore substitution of ligands is easy.
These are formed by strong ligands.	These are formed by weak ligands.

Examples

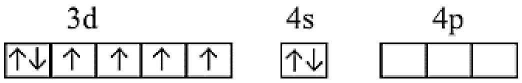
Complex	**Hybridisation**		**Magnetic behaviour**	**Nature**
(CN = 6)				
$[Cr(NH_3)_6]^{3+}$	d^2sp^3		Paramagnetic	Inner orbital
$[Fe(CN)_0]^{3-}$	d^2sp^3	octahedral	Slightly paramagnetic	Inner orbital
$[Fe(CN)_6]^{4-}$	d^2sp^3		Diamagnetic	Inner orbital
$[CoF_6]^{3-}$			Paramagnetic	Outer orbital
(CN = 4)	sp^3d^2			
$[Ni(CO)_4]^0$	sp^3	[tetrahedral]	Diamagnetic	–
$[Zn(NH_3)_4]^{2+}$	sp^3		Diamagnetic	–
$[Ni(CN)_4]^{2-}$	dsp^2	Square planar	Diamagnetic	–
$[Cu(NH_3)_4]^{2+}$	dsp^2		Paramagnetic	–
(CN = 5)				
$Fe(CO)_5$	dsp^3	[trigonal bipyramidal]	Diamagnetic	

STRUCTURES AND SHAPES OF COMPLEXES ON THE BASIS OF VALENCE BOND THEORY

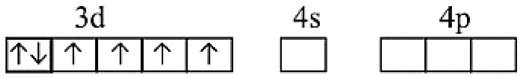
- **$K_4Fe(CN)_6$ or Hexacyano ferrate (II) ion, $[Fe(CN)_6]^{4-}$**

  The formation of $[Fe(CN)_6]^{4-}$ complex ion by valence bond method:

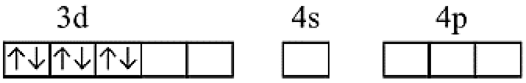
  (1) Fe atom



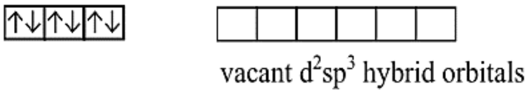
  (2) Fe^{2+} ion



  (3) Fe^{2+} ion under the influence of strong CN ligands



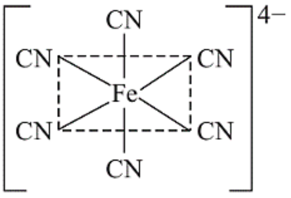
  (4) d^2sp^3 hybrid orbitals of Fe^{2+} ion



  (5) d^2sp^3 hybrid orbitals in $[Fe(CN)_6]^4$

6 pairs of electrons from 6 CN⁻ ligands

  (6) Octahedral shape of $[Fe(CN)_6]^{4-}$ ion

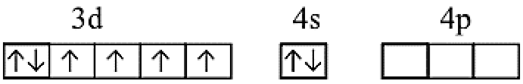


  (7) It has no unpaired electron i.e., $\mathbf{n = 0}$, $\mu = 0$ hence, it is **diamagnetic.**

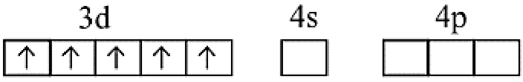
- **$K_3[Fe(CN)_6]$ or Hexacyano ferrate (III) ion, $[Fe(CN)_6]^{3-}$**

  Formation of $[Fe(CN)_6]^{3-}$ complex ion by valence bond method:

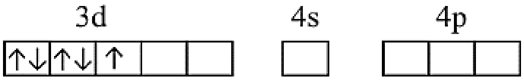
  (1) Fe atom



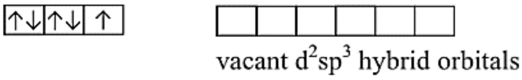
  (2) Fe^{3+} ion



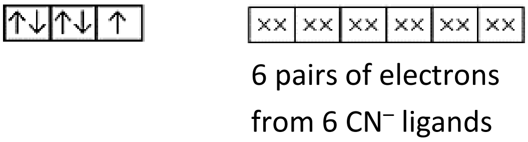
  (3) Fe^{3+} ion under the influence of strong CN^-ligands



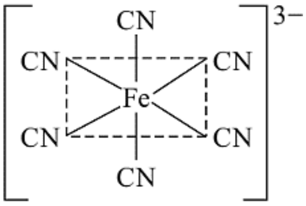
  (4) d^2sp^3 hybrid orbitals of Fe^{3+} ion



  (5) d^2sp^3 hybrid orbitals in $[Fe(CN)_6]^{3-}$



  (6) Octahedral shape of $[Fe(CN)_6]^{3-}$ ion is given as



  (7) It has one unpaired electron i.e., $\mathbf{n = 1}$,

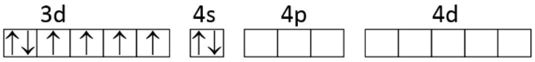
  $\mu = \sqrt{1(1+2)} = \sqrt{3}$

  Hence, it is **paramagnetic in nature**.

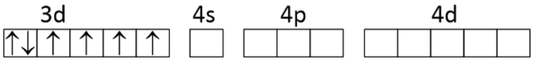
- **Hexaaqua iron (II) ion, $[Fe(H_2O)_6]^{2+}$**

  The formation of $[Fe(H_2O)_6]^{2+}$ complex ion by valence bond method:

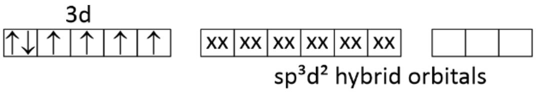
  (1) Fe atom



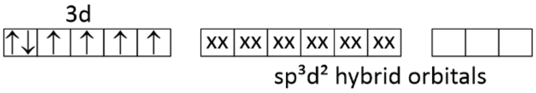
  (2) Fe^{2+} ion



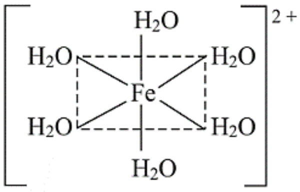
  (3) sp^3d^2 hybrid orbitals of Fe^{2+} ion



  (4) sp^3d^2 hybrid orbitals in $[Fe(H_2O)_6]^{2+}$



  (5) Octahedral shape of $[Fe(H_2O)_6]^{2+}$ ion is given as,



  (6) It has four unpaired electrons i.e., $\boldsymbol{n = 4}$,

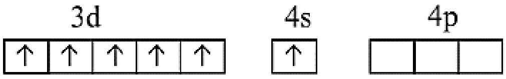
  $\mu = \sqrt{4(4+2)} = \sqrt{24}$

  Hence, it is **highly paramagnetic (ferromagnetic)** in nature.

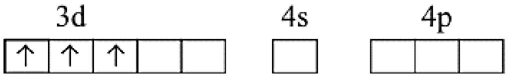
- **Hexa ammine chromium (III) ion, $[Cr(NH_3)_6]^{3+}$**

  The formation of $[Cr(NH_3)_6]^{3+}$ complex ion by valence bond method:

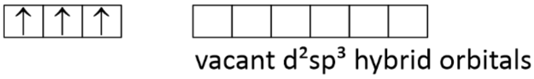
  (1) Cr atom



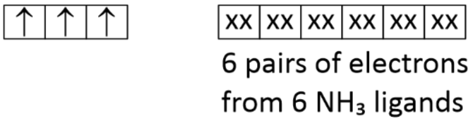
  (2) Cr^{3+} ion



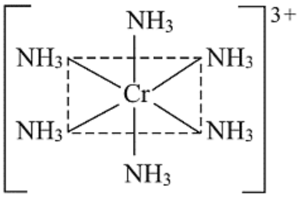
  (3) d^2sp^3 hybrid orbitals of Cr^{3+} ion



  (4) d^2sp^3 hybrid orbitals in $[Cr(NH_3)_6]^{3+}$



  (5) Octahedral shape of $[Cr(NH_3)_6]^{3+}$ ion is given as,



  (6) It has three unpaired electrons i.e., n = 3,

  $\mu = \sqrt{3(3+2)} = \sqrt{15}$

  Hence, it is **paramagnetic** in nature.

- **Hexa ammine cobalt (III) ion, $[Co(NH_3)_6]^{3+}$**

  The formation of $[Co(NH_3)_6]^{3+}$ complex ion by valence bond method: