

CO-ORDINATION COMPOUNDS

INTRODUCTION

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our life. Haemoglobin of animal blood and chlorophyll of plants are also coordination compounds of Fe and Mg respectively.

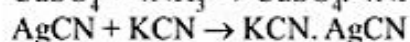
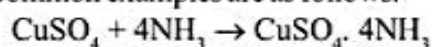
COMPLEX FORMATION

- Transition metal ions have maximum tendency to form complexes. In the formation of complexes they form coordinate covalent bonds and act as electron pair acceptors.
- Transition metal ions have smaller size and have high positive charge i.e., high charge density. Due to this they have maximum tendency to accept electrons. They have vacant 'd' orbitals available on them hence they can accept lone pairs of electrons forming coordinate covalent bond.
- The greater the charge density on the transition metal ion, the greater they have tendency to form complexes. Thus Ti^{+2} to Ni^{+2} the stability of complexes formed goes on increasing.
- Compounds like NaCl, $Al_2(SO_4)_3$ and K_2SO_4 provide only two types of ions in aqueous solution i.e., cations and anions, are called as simple salts.
- When two or more simple salt solutions are mixed and then subjected for crystallisation, the crystals which are obtained are of addition compounds.

MOLECULAR OR ADDITION COMPOUNDS

- (a) When solutions containing two or more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new substances are obtained. These substances are termed molecular or addition compounds.

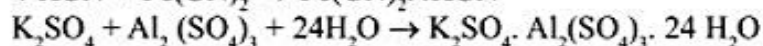
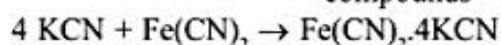
- (b) Some common examples are as follows.



simple stable Addition or

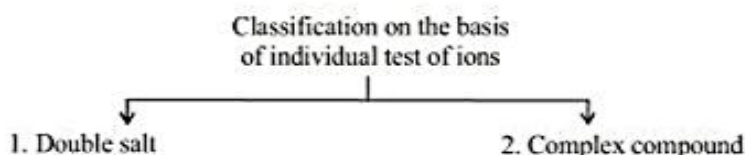
compounds molecular

compounds



Alum

- (c) The molecular or addition compounds are of two types : Double salts or lattice compound and coordination or complex compound



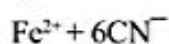
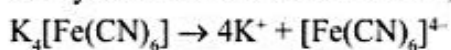
1. Double salts or lattice compounds

- (a) The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called double salts or lattice compounds.
- (b) Their solutions have the same properties as the mixture of individual compounds
- (c) For example when carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) is dissolved in water it exhibits the properties of KCl and MgCl_2

2. Coordination or complex compounds

- (a) The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions are called coordination compounds
- (b) The properties of their solutions are different than those of their constituents.
- (c) In such compounds there is complex ion which is a central metal ion with lewis bases attached to it through coordinate covalent bonds.
- (d) On the basis of stability of complex ion, complex ions are further divided as follows.

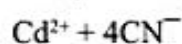
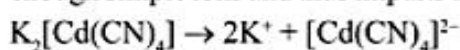
(i) Perfect complexes : Those in which complex ion is fairly stable and is either not dissociated or feebly dissociated in solution state, e.g.



(feebly dissociated)

The ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ is so insignificantly dissociated that it can be considered as practically undissociated and does not give the test of Fe^{2+} or CN^- ions

(ii) Imperfect complexes : Those in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus imparts their tests, e.g.



(appreciably dissociated)

Note : An imperfect complex may be too unstable to exist and may be completely dissociated in solution, it then becomes a double salts

Illustration

1. Study the following double salt and write the type of ions which can be tested in their aqueous solution.

Salt**Ions can be tested**

- (a) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (b) $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (c) $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (d) $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (e) $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$

Sol.**Salt****Ions can be tested**

- (a) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (b) $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (c) $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (d) $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (e) $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$

$\text{K}^+, \text{Al}^{3+}, \text{SO}_4^{2-}$

$\text{NH}_4^+, \text{Al}^{3+}, \text{SO}_4^{2-}$

$\text{K}^+, \text{Cr}^{3+}, \text{SO}_4^{2-}$

$\text{Fe}^{2+}, \text{Al}^{3+}, \text{SO}_4^{2-}$

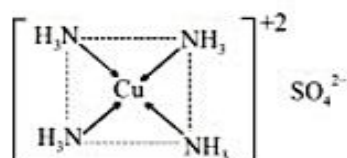
$\text{Al}^{3+}, \text{OH}^-, \text{PO}_4^{3-}$

Exercise

1. Predict which among the following properties given below belong to double salt and co-ordination compounds.
- The blue coloured solution prepared by $\text{Cu}^{+2}(\text{aq.})$ and $\text{NH}_3(\text{NH}_4^+ \text{aq.})$ does not show the presence of Cu^{+2} (.....)
 - Compounds which are stable in the solid state but break up into its constituents in aqueous solution (.....)
 - Aq. solution of carnallite (.....)
 - The Compounds in which central metal ion form dative bonds with species surrounding it. (.....)
 - Mohr's salt (.....)
- Sol. (a) Co-ordination (b) Double salt (c) Double salt (d) Co-ordination (e) Double salt

VARIOUS TERMS USED IN CO-ORDINATION COMPOUNDS

- Complex ion :** An aggregate of metal ion with anions cation or neutral molecules is called as complex ion. The metal ion which forms complex ion in combination with anions or neutral molecules is called as central metal ion. Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond. The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands. They act as electron pair donors or Lewis bases.
- Central metal ion :**
 - The metal ion which forms complex ion in combination with anions or neutral molecules is called as **central metal ion**.
 - Central metal ion acts as an electron pair acceptor and forms coordinate bond with ligands.
- Coordination Number :**
 - The number of atoms of the ligands that are directly bond to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.
 - It is actually the number of coordinate covalent which the ligands form with the central metal atom or ion
 - Some common coordination numbers exhibited by metal ions are 2,4,6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals may exhibit coordination number more than 6
 - For example, the coordination number of Ni in the complex $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$ is 4 and that of Pt in the complex $\text{K}_2[\text{PtCl}_6]$ is 6
- Coordination sphere-(entity) :**
 - The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.
 - Coordination sphere is written inside square bracket, for example $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - The part outside the bracket is called **ionisation sphere**.
 - The species present in the coordination sphere are nonionizable.
 - The species present in the ionization sphere are ionisable.



(e) Oxidation state :

- (i) It is number which represents the electric charge on the central metal atom of a complex ion.
- (ii) Example the oxidation number of Fe, Co and Ni in $[\text{Fe}(\text{CN})_6]^{+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Ni}(\text{CO})_4$ is +2, +3 and zero respectively.

(f) Charge on the complex ion :

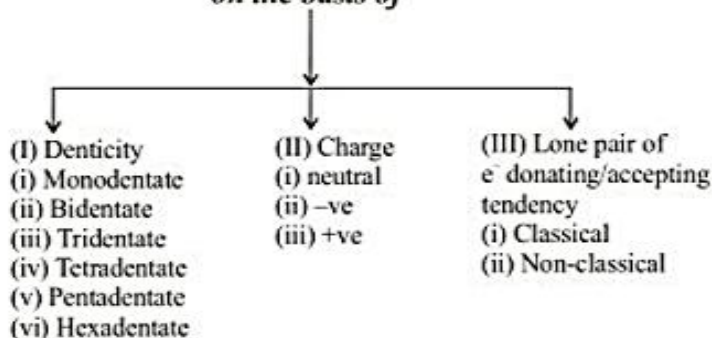
It is the algebraic sum of the total charge of the ligands and central metal ion.

Ex. $\text{K}_4[\text{Fe}(\text{CN})_6]$ total charge on the complex ion is -4 .

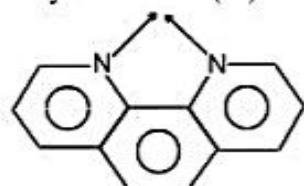
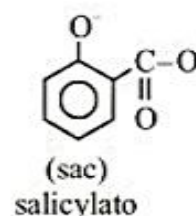
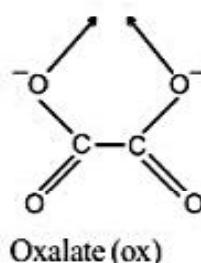
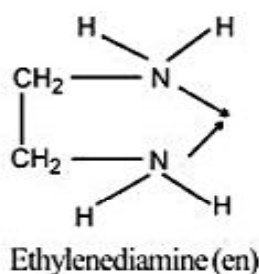
(g) Ligands :

- (i) The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands.
- (ii) They act as electron pair donor or Lewis bases, but strong crystal field ligands like CO, CN⁻ etc. can also accept electron pair from the metal ion, because these ligands are π -acids ligands.

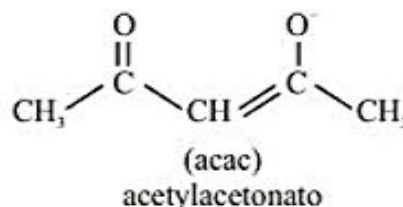
**Classification of the Ligand
on the basis of**

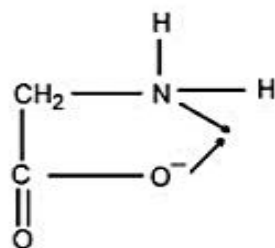
**(I) CLASSIFICATION ON THE BASIS OF DENTICITY**

- (i) **Mono-or unidentate ligands :** They have one donor atom, i.e. they supply only one electron pair to central metal atom or ion.
Examples : F^- , Cl^- , Br^- , H_2O , NH_3 , CN^- , NO_2^- , OH^- , CO, Py, H^-
- (ii) **Bidentate ligands :** Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are :

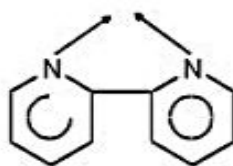


1,10-Phenanthroline (o-phen)

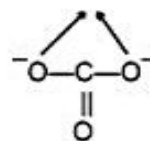




Glycinato (Gly)

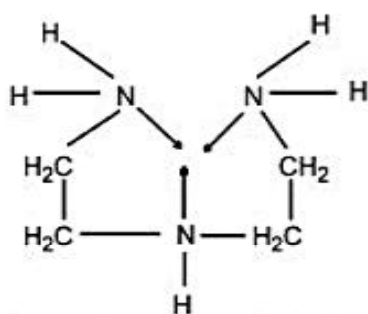


2,2'-Dipyridyl (Dipy)

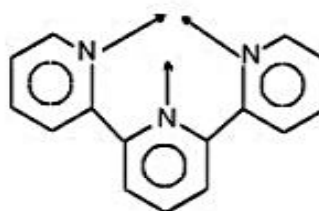


Carbonato

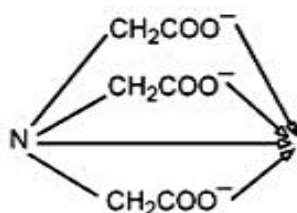
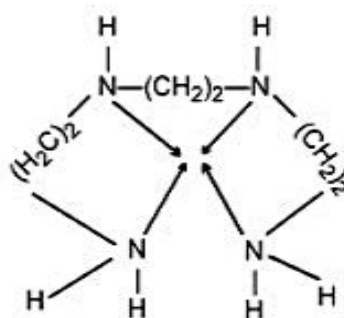
(iii) **Tridentate ligands** : The ligands having three donor atoms are called tridentate ligands. Examples are:



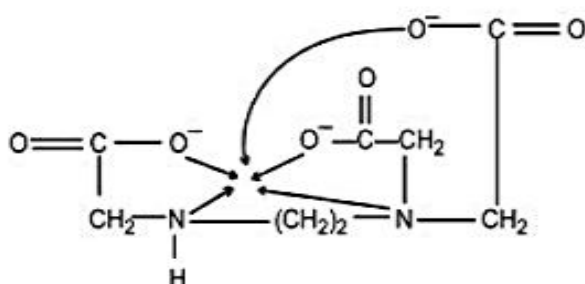
Diethylene triamine (Dien)

2,2',2''-Terpyridine
(terpy)

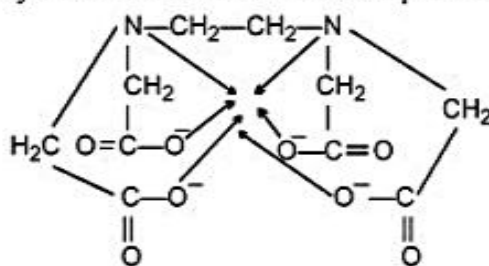
(iv) **Tetradentate ligands** : These ligands possess four donor atoms. Examples are:

(Nitrilotriacetato)
(NTA)Triethylene tetramine
(Trien)

(v) **Pentadentate ligands** : They have five donor atoms. For example, ethylenediamine triacetate ion.

Ethylenediamine triacetato ion (EDTA)³⁻

- (vi) **Hexadentate ligands:** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



Ethylenediamine tetraacetate ion (EDTA)⁴⁻

Classification of ligands on the basis of donor and acceptor properties of the ligands

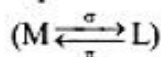
(A) Ligands having one (or more) lone pair (or pairs) of electrons

- (a) Ligands which contain vacant π -type orbitals that can receive back donated π electron from metal ion in low oxidation state.

e.g.: CO, NO, CN^- , NC^- , $\text{R}-\text{N} \equiv \text{C}$, R_3P , R_3As

α, α -dipyridyl, o-phenanthroline

- (b) All these ligands also have filled donor orbital in addition to vacant π -type acceptor orbitals.
 (c) Thus in these complexes both metal and ligand function as donors and acceptors



- (d) Ligands which do not have vacant orbitals to receive back donated electron from metals
 e.g. H_2O , NH_3 , F^- .

(B) Ligands having no lone pairs of electrons but have π bonding electron

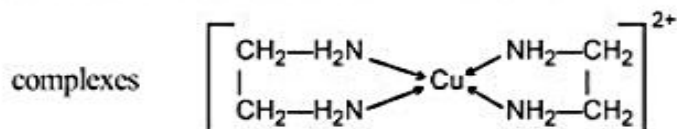
e.g. Ethylene, benzene, cyclopentadienyl-ion

$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ Zises salt

SPECIAL LIGAND

- (1) **Polydentate ligands:** have Flexidentate character, it is not necessary that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion.
- (2) **Ambidentate Ligand:** Ligands which can ligate through two different atoms present in it are called ambidentate ligands. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds. There are certain ligands which have two or more donor atoms but during formation of complexes only one donor atom is attached to metal ion. Such ligands are called **ambidentate ligands** such as CN^- , CNS^- .
- (3) **Chelating ligands.**
 - (a) Polydentate ligands whose structures permit the attachment of two or more donor sites to the same metal ion simultaneously, thus closing one or more rings are called chelating ligands and the compounds formed are known as chelate compounds.
 - (b) A chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms with a metal ion forming part of the ring.

- (c) The process of formation of chelates is called chelation.
 (d) Chelate complexes are more stable than ordinary complexes in which the ligand is a monodentate
 (e) This increased stability of the compound due to chelation is called the chelate effect
 (f) In the complex ion given below, 5 membered rings are formed. So all these are called chelate



- (g) Generally the chelate complexes with 5 or 6 membered rings are more stable.
 (h) Out of these, 5 membered rings are very stable when they involve saturated ligands.
 (i) On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bond. This is due to the resonance effects involving metal d-orbitals and ligand p-orbital electrons.

Illustration

1. Match the Column.

A	B
(i) Ligand contains one donor site	(a) hexadentate
(ii) Ligand contains two donor site	(b) tridentate
(iii) Ligand contain three donor site	(c) tetradentate
(iv) Ligand contain four donor site	(d) bidentate
(v) Ligand contain six donor site	(e) unidentate

Sol. (i) - (e); (ii) - (d); (iii) - (b); (iv) - (c); (v) - (a)

Exercise

1. In the coordination compound, $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is :
 (A) -1 (B) 0 (C) +1 (D) +2

Ans. (B)

2. Which of the following species is not expected to be a ligand
 (A) NO^+ (B) NH_4^+ (C) $\text{NH}_2-\text{NH}_3^+$ (D) CO

Ans. (B)

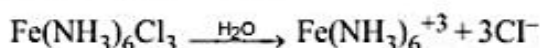
WERNER'S COORDINATION THEORY

Alfred Werner (considered as the father of coordination chemistry) studied the structure of coordination complexes such as $\text{CoCl}_3 \cdot 6\text{NH}_3$ and $\text{CuSO}_4 \cdot 4\text{NH}_3$ in 1893.

According to him :

- (a) Each metal in coordination compound possesses two types of valencies :
 (i) primary valency or principal valencies or ionisable valencies.
 (ii) Secondary valency or nonionisable valencies
 (b) Primary valencies are satisfied by anions only. The number of primary valencies depends upon the oxidation state of the central metal. It may change from one compound to other. These are represented by dotted lines between central metal atom and anion.

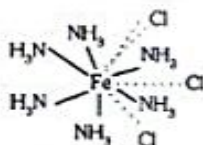
- (c) Secondary valencies are satisfied only by electron pair donor, the ions or the neutral species. These are represented by thick lines.
- (d) Each metal has a fixed number of secondary valencies, also referred to as coordination number. The coordination number depends mainly on the size and the charge on the central atom. The maximum number of ions or molecules that the central atom can hold by secondary valencies is known as coordination number.
- (e) The ions attached to primary valencies possess ionising nature whereas the ions attached to secondary valencies do not ionise when the complex is dissolved in a solvent.
- (f) Every central ion tends to satisfy its primary as well as secondary valencies.
- (g) The secondary valencies are directional and are directed in space about the central metal ion. The primary valencies are non-directional. The presence of secondary valencies gives rise to stereoisomerism in complexes.
- (h) Initially, Werner had pointed out coordination number of a metal atom to be four or six.
- (i) The six valencies were regarded to be directed to the corners of a regular octahedron circumscribed about the metal ion. For metals having four coordination number, the four valencies are either arranged in a planar or tetrahedral nature.
- (j) $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$ forms 3 moles of AgCl in the form of precipitate on addition of AgNO_3 solution. This indicates that the complex ionises as



- (i) Electrical conductance of complexes - More the number of ions provided greater is the electrical conductance of the complex in aqueous medium.

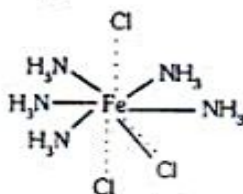
e.g. - The electrical conductance of aqueous $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$ is greater than that of aqueous solution of $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Fe}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$ Total 3 ions

Representation of complexes – Werner's representation for $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$

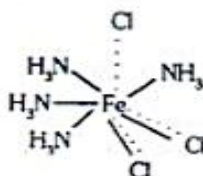


(Dotted lines indicate primary Valency and continuous lines indicate secondary valency of metal ion.) If the complex is

- (ii) $\text{Fe}(\text{NH}_3)_5\text{Cl}_3$ Then in this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation for this complex will be



- (iii) $\text{Fe}(\text{NH}_3)_4\text{Cl}_3$ In this complex 'Cl' groups act as primary valencies and two of the 'Cl' group act as secondary valencies also. Thus this complex is represented as



Complex	Metal (Oxidation State)	Atomic Number of Metal	Coordination number	Effective atomic number (E.A.N.)
$K_4[Fe(CN)_6]$	+2	26	6	$(26-2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29-2) + (4 \times 2) = 35$
$[Co(CH_3)_6]Cl_3$	+3	27	6	$(27-3) + (6 \times 2) = 36$ [Kr]
$Ni(CO)_4$	0	28	4	$(28-0) + (4 \times 2) = 36$ [Kr]
$K_2[Ni(CN)_4]$	+2	28	4	$(28-2) + (4 \times 2) = 34$
$K_2[PtCl_6]$	+4	78	6	$(78-2) + (6 \times 2) = 86$ [Rn]
$K_3[Cr(C_2O_4)_3]$	+3	24	6	$(24-3) + (6 \times 2) = 33$
$K_3[Fe(C_2O_4)_3]$	+3	26	6	$(26-3) + (6 \times 2) = 35$
$K_2[HgI_4]$	+2	80	4	$(80-2) + (4 \times 2) = 86$ [Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47-1) + (2 \times 2) = 50$
$K_2[PdCl_4]$	+2	46	4	$(46-2) + (4 \times 2) = 52$

Illustration

1. Calculate the EAN of the following complex.

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number $EAN = (At. No. - O.N) + 2 \times$
$K_4[Fe(CN)_6] + 2$ $[Cu(NH_3)_4]SO_4$ $[Co(NH_3)_6]Cl_3$ $[Ni(CO)_4]$ $K_2[Ni(CN)_4]$ $K_2[PtCl_6]$ $K_3[Cr(C_2O_4)_3]$ $K_3[Fe(CN)_6]$ $K_2[HgI_4]$ $[Ag(NH_3)_2]Cl$	26		6	$(26 - 2) + (6 \times 2) = 36$ [Kr]

Sol. Calculate the EAN of the following complex.

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number $EAN = (At. No. - O.N) + 2 \times$
$K_4[Fe(CN)_6]$	+2	26	6	$(26 - 2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29 - 2) + 2 \times 4 = 35$ [Br]
$[Co(NH_3)_6]Cl_3$	+3	27	6	$(27 - 3) + 2 \times 6 = 36$ [Kr]
$[Ni(CO)_4]$	+4	28	4	$(28 - 4) + 2 \times 4 = 32$ [Ge]
$K_2[Ni(CN)_4]$	+2	28	4	$(28 - 2) + 2 \times 4 = 34$ (Se)
$K_2[PtCl_6]$	+4	78	6	$(78 - 4) + 2 \times 4 = 82$ [Pb]
$K_3[Cr(C_2O_4)_3]$	+3	24	3	$(24 - 3) + 2 \times 3 = 29$ [Cu]
$K_3[Fe(CN)_6]$	+3	26	6	$(26 - 3) + 2 \times 6 = 35$ [Br]
$K_2[HgI_4]$	+2	80	4	$(80 - 2) + 2 \times 4 = 84$ [Po]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47 - 1) + 2 \times 2 = 50$ [Sn]

Exercise

1. In the complex $Fe(CO)_x$, the value of x is, if it follows sidwick EAN rule :

(A) 3

(B) 4

(C) 5

(D) 6

Ans. (C)

I.U.P.A.C. NAMING OF COORDINATION COMPOUNDS

Due to wide variety of coordination compounds it is essential to use a unified system of nomenclature. Though a lot of compounds are known by their trivial names only, but I.U.P.A.C. has introduced rules for the naming of coordination compounds as follows :

The order of listing the ions

- In common salts cation is named first and then the anion.
- In the complex ion (Cation or anion) ligands are named first followed by the name of central atom
- The oxidation state of the central metal is indicated by Roman numeral in brackets immediately after its name; (0) indicates zero oxidation state.
- In case the complex is non ionic, it is named as one word e.g. $[\text{Ni}(\text{CO})_4]$ is called tetracarbonyl nickel (0)
- The suffix -ate is added to the name of central metal forming anionic complex ion. In cationic complex ion, the name of metal (usual name) is followed by the oxidation number in bracket. However in some metals Latin names are preferred in place of English names e.g. iron as ferrate, lead as plumbate and silver as argentate.

Name of the ligand

- If there are two or more different kinds of ligands, they are named in alphabetical order without separation by hyphen.
- When there are several ligands of same kind, they are listed alphabetically

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo
CN^-	Cyanido	S^{2-}	Sulphido
O^{2-}	Oxido	NH^{2-}	imido
OH^-	Hydroxido	NH_2^-	amido
H^-	Hydridido	SO_3^{2-}	Sulphito
CO_3^{2-}	Carbonato	CH_3COO^-	Acetato
$\text{C}_2\text{O}_4^{2-}$	Oxalato	NO_2^-	(bonded through oxygen) nitrito (bonded through nitrogen) nitro
SO_4^{2-}	Sulphato		
NO_3^-	Nitrato		
$\text{S}_2\text{O}_3^{2-}$	Thiosulphato		

- Names of positive ligands ends in 'ium' e.g.
 NO^+ Nitrosylium
 NH_2NH_3^+ Hydrazinium
- If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc. However, when the name of the ligand includes a number, e.g. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc
- In case of chelating ligands or ligands having di, tri, tetra, etc, in their name the prefixes bis, tris, tetrakis are used before ligands placed in parenthesis
- In poly nuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of complex by hyphens and adding before its name or in poly nuclear complex (a complex with two or more metal atoms) bridging ligands (which links two metal atoms) is denoted by the prefix μ before its name.

S.No.	Complex Compounds	IUPAC Name
(i)	$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate (II)
(ii)	$K_2[PtCl_6]$	Potassium hexachloridoplatinate (IV)
(iii)	$[Co(NH_3)_6]Cl_3$	Hexammine cobalt (III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichloridochromium (III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum (IV)
(vi)	$[Co(NH_3)_3Cl_3]$	Triamminetrichloridocobalt (III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitridocobaltate (III)
(viii)	$Na_3[Fe(CN)_5NO]$	Sodium pentacyanido nitrosyl ferrate(II)
(ix)	$[NiCl_4]^{2-}$	Tetrachloridonickelate (II) ion
(x)	$[Ru(NH_3)_5Cl]^{+2}$	Pentamminechloridoruthenium (III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris(ethylenediamine) iron (III) chloride
(xii)	$[Ni(Gly)_2]$	Bis(glycinato)nickel (II)

Illustration

1. Write the systematic names of the following coordination entities and compounds:
 (i) $[CoCl_2(NH_3)_4]^+$ (ii) $[CrCl_3(NH_3)_3]$ (iii) $K_3[Cr(C_2O_4)_3]$ (iv) $K_4[Fe(CN)_6]$
 (v) $[PtCl(NH_3)_5]Cl_3$
- Sol. (i) tetraamminedichlorido Cobalt(III) (ii) triamminetrichloridochromium(III)
 (iii) potassium trioxalatochromate(III) (iv) potassium hexacyanoferrate(II)
 (v) pentaamminechloridoplatinum(IV) chloride

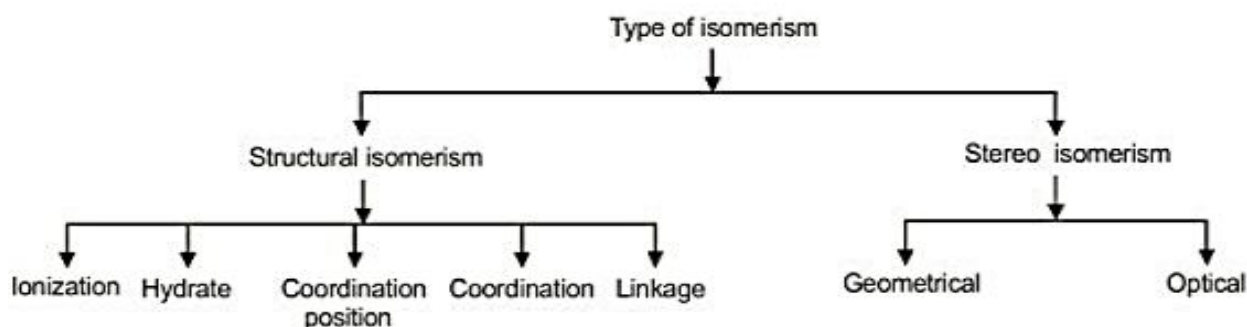
Exercise

1. The IUPAC name $[Co(NH_3)_6][Cr(CN)_6]$ is –
 (A) Hexaammine cobalt (III) hexacyanochromate (III)
 (B) Hexacyanochromium cobalt hexaammine (VI)
 (C) Hexaammine cobalt (III) hexacyanochromium (VI)
 (D) Hexacyanochromium (III) hexaammine cobalt (III)
- Ans. (A)
2. The IUPAC name for $[Co(NCS)(NH_3)_5]Cl_2$ is –
 (A) Pentaammine (thiocyanato-N) cobalt (III) chloride
 (B) Pentaammine (thiocyanato-S) cobalt (III) chloride
 (C) Pentaamine (isothiocyanato-N,S) cobalt (III) chloride
 (D) Pentaammine (mercapto-N) cobalt (III) chloride
- Ans. (A)

ISOMERISM IN COORDINATION COMPOUND

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

(c) **Classification of isomerism :**



STRUCTURAL ISOMERISM

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

1. Ionisation isomers :

The type of isomerism is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere

Ex.

- (a) $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$ can represent
 (i) $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$ (red violet)
 (ii) $[\text{Co}(\text{NH}_3)_4]\text{SO}_4[\text{Br}_2]$ (red).

These complexes give sulphate ion and bromide ion respectively

- (b) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
 (c) $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4\text{SO}_4](\text{NO}_3)_2$

2. Hydrate isomers :

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Ex. $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ has three possible structure

- (i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) (ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (green)
 (iii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green)

These complexes differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are –

- (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ (ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

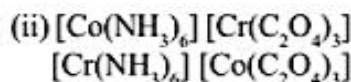
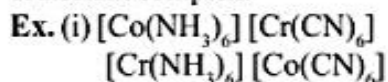
3. Linkage or salt isomers :

- (a) This type of isomerism arises due to presence of ambidentate ligands like NO_2^- , CN^- and SCN^-
 (b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.
 (c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Ex. (i) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$
 (ii) In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^-) or through oxygen (i.e. ONO)
 (iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

4. Coordination isomers :

- (a) This type of isomerism is exhibited when the complex has two complex ions in it, cationic and anionic.
- (b) This type of isomerism is caused by the interchange of ligands and metal ions between the two complex ions of the same complex.

**Illustration**

1. Select correct code about complex $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$
 (I) IUPAC name of the compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)
 (II) It shows geometrical isomerism
 (III) It shows linkage isomerism
 (IV) It shows co-ordination isomerism
 (A) III, IV (B) I, III & IV (C) II, III & IV (D) I, II, III & IV

Ans. (B)

- Sol.** (I) $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$
 IUPAC name of the compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)
 (III) It shows linkage isomerism due to presence of ambident ligands
 $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$
 $[\text{Cr}(\text{ONO})(\text{NH}_3)_5][\text{ZnCl}_4]$
 (IV) Because both complex ions have different ligands

Exercise

1. Which of the following is pair of ionization isomers –
 (A) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
 (B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
 (C) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
 (D) cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Ans. (A)**STEREO ISOMERISM**

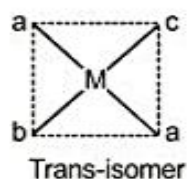
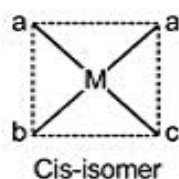
- (a) They have same molecule formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
- (b) The two stereo isomers which are possible are - Geometrical and optical.

1. Geometrical or cis - Trans isomers :

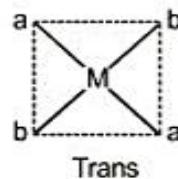
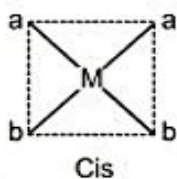
- (a) The ligands occupy different positions around the central metal ion.
- (b) When two identical ligands are coordinated to the metal ion from the same side then it is **cis isomer**. (Latin, cis means same).
- (c) If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across)
- (d) These geometrical isomers differ in physical as well as in chemical properties.
- (e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
- (f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-Trans isomerism.
- (g) It is exhibited by 4-coordinated complexes with square planar geometry.

Geometrical isomers with coordination number = 4 (Square planar complexes)

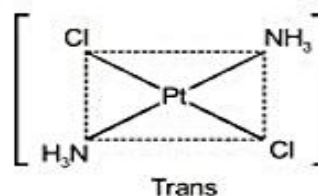
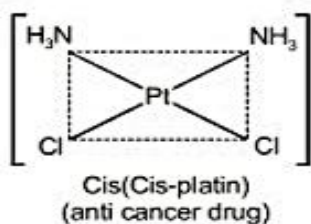
- (i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis-and trans isomers.



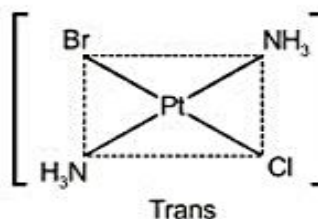
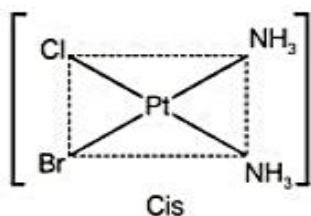
- (ii) Complexes with general formula $\text{Ma}_2\text{b}_2\text{c}$ can have Cis-and trans-isomers.



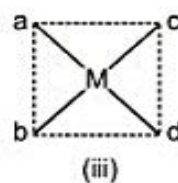
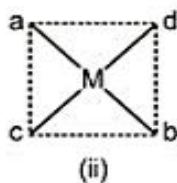
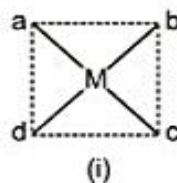
e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



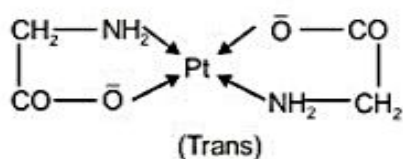
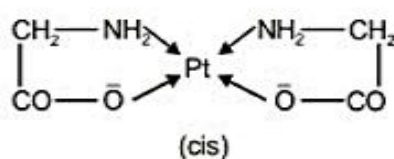
e.g. $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



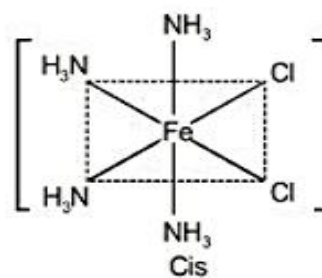
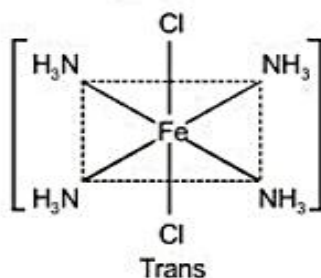
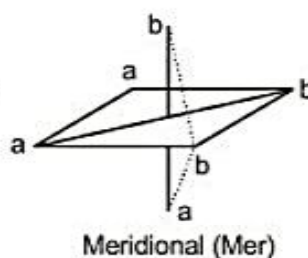
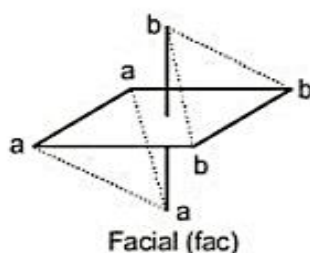
- (iii) Complexes with general formula, Mabcd can have three isomers.



- (vi) Diglycinato platinum (II) complexes



Geometrical isomers with coordination number = 6

(i) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$ (ii) Facial and Meridional isomerism (Ma_3b_3)

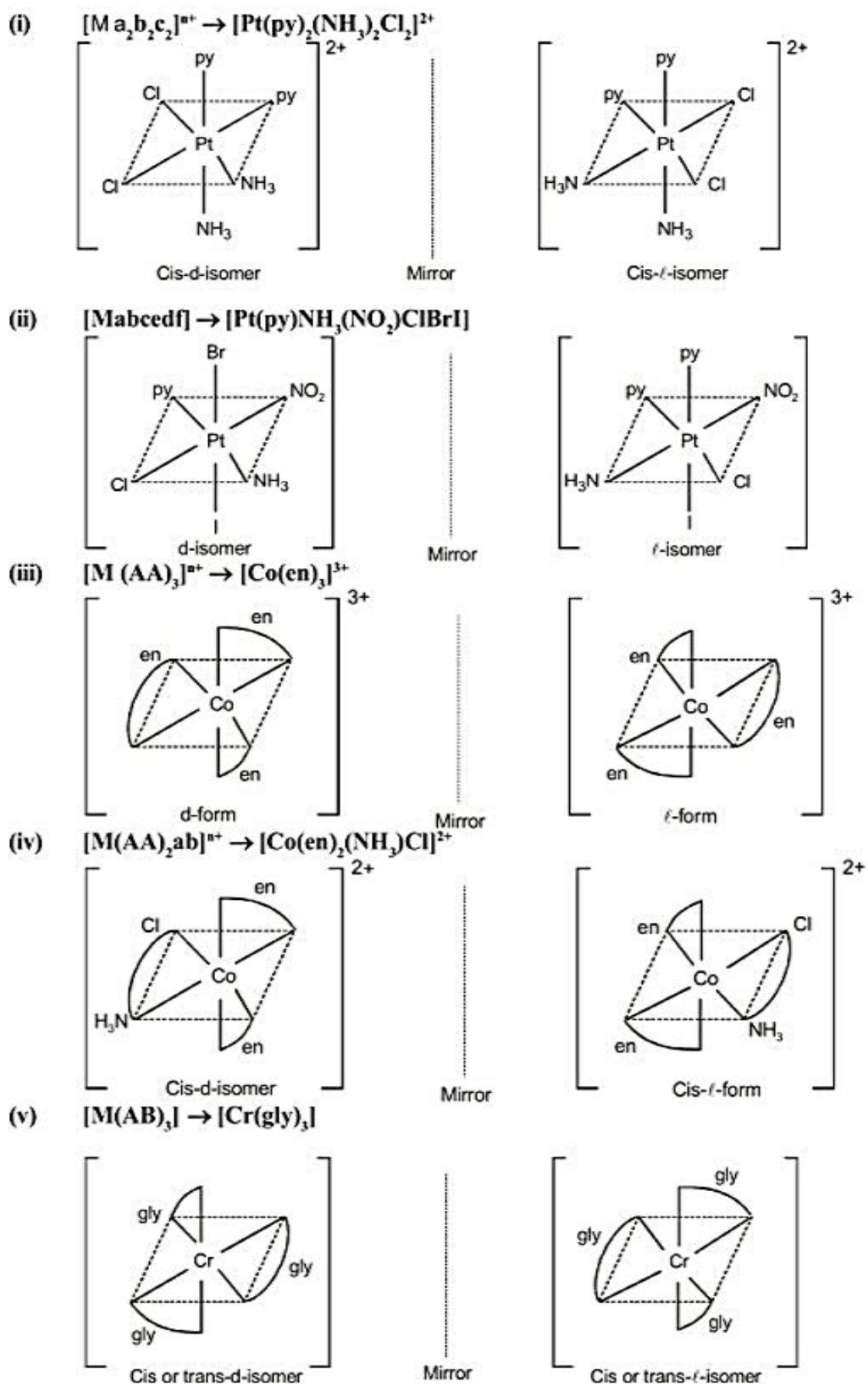
Other 6-Coordinated geometrical isomers are

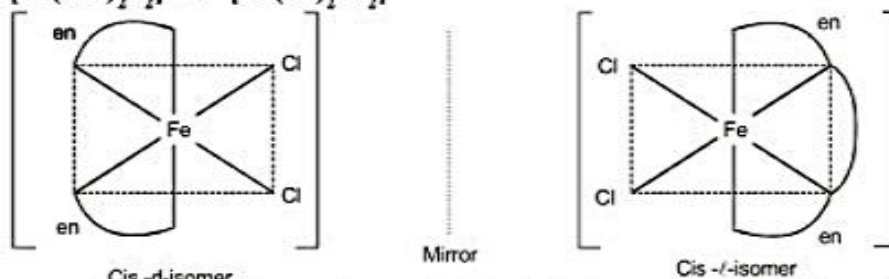
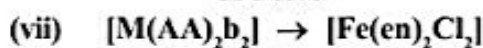
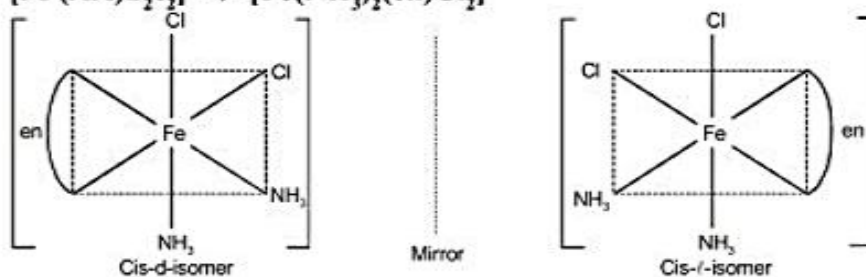
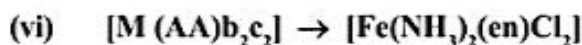
General formula	Total No. of geometrical isomers
Mabcdef	15
$\text{Ma}_2\text{b}_2\text{c}_2$	5
Ma_2bcde	9
Ma_4b_2	2
Ma_4bc	2
Ma_3b_3	2
$\text{Ma}_6, \text{Ma}_5\text{b}$	Nil
Here M = central atom a, b, c, d, e, f = ligands (unidentate)	

2. Optical isomers :

- Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- The complex which rotates plane polarised light to left hand side is laevo rotatory i.e., ' ℓ ' or '-' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.
- Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- The 'd' and ' ℓ ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.
- Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isomerism. This is due to the absence of elements of symmetry in the complex.
- Optical isomerism is not found in square planar complexes on account of the presence of axis of symmetry.

Optical isomer with Coordination number = 6



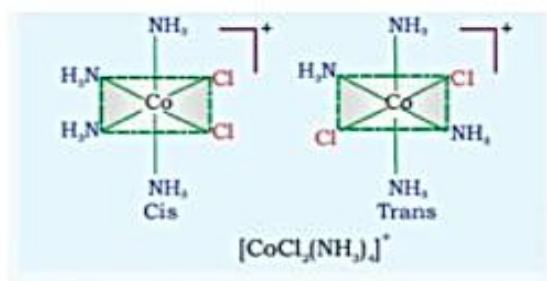


- (i) Trans- $[Fe(en)_2Cl_2]$ do not show optical activity due to superimposition of their mirror image.
 (ii) Some more examples are optically active:
 $[Cr(ox)_3]^{3-}$; $[Fe(dipy)_3]^{2+}$; $[Cr(ox)_2(H_2O)_2]$; $[Pt(en)_3]^{4+}$ etc.

Illustration

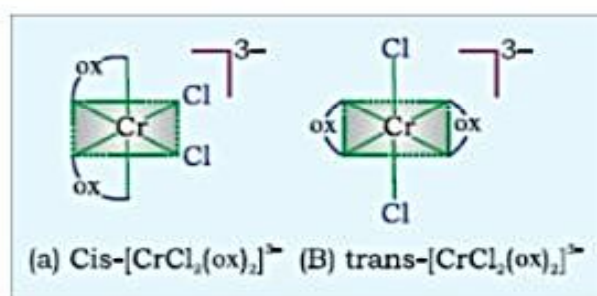
1. Draw structures of geometrical isomers of $[CoCl_2(NH_3)_4]^+$.

Sol.



2. Which out of the following two coordination entities is chiral (optically active)?
 (a) cis - $[CrCl_2(ox)_2]^{3-}$ (b) trans - $[CrCl_2(ox)_2]^{3-}$.

Sol. The two entities are represented as



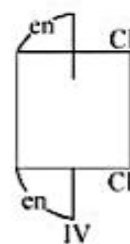
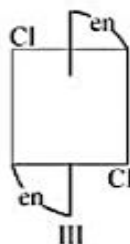
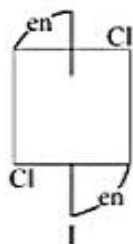
Out of the two, (a) cis- $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

Exercise

1. $[\text{Co}(\text{en})_3]^{3+}$ ion is expected to show
 (A) two optically active isomers: d and l forms
 (B) three optically active isomers: d, l and meso forms
 (C) four optically active isomers: cis, d and l isomers and trans d and l isomers
 (D) none of these

Ans. (A)

2. Of the following configurations, the optical isomers are



(A) I and II

(B) I and III

(C) II and IV

(D) II and III

Ans. (C)

BONDING IN COORDINATION COMPOUNDS

1. **Valence Bond Theory**

The salient features of the theory are summarised below.

- (a) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.
- (b) The atomic orbitals (s, p or d) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.
- (c) The d-orbitals involved in the hybridization may be either inner $(n-1)$ d orbitals or outer nd-orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.
- (d) Each ligand contains a lone pair of electrons.
- (e) A covalent bond is formed by the overlap of a vacant hybridized metal orbital and a filled orbital of the ligand. The bond is also sometimes called as a coordinate bond.
- (f) If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electrons, it is diamagnetic in nature.
- (g) The number of unpaired electrons in the complex, points out the geometry of the complex as well as hybridisation of central metal ion and vice-versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as illustrated below.

$$\mu_s = \sqrt{n(n+2)}, \text{ where } n = \text{no of unpaired electron}$$

Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex

- (h) Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.
-

Draw back of valence bond Theory

- (i) It describes bonding in coordination compounds only qualitatively
- (ii) It does not offer any explanation for the optical absorption spectra of complex
- (iii) It does not describe the detailed magnetic properties of coordination compounds.

Crystal field Theory

This is the more advanced theory and satisfactorily explains the optical absorption spectra and magnetic properties of complexes which were not explained by V.B.T. But its details are beyond the scope of this text.

The shape of complexes depends upon hybridization state of central atom, it is described as follows:

Octahedral complexes

On the basis of hybridized orbitals it can be of two type as d^2sp^3 (inner orbital) or sp^3d^2 (outer orbital) hybridized. Let us assume that the six ligands are positioned symmetrically along the cartesian axes, with the metal atom at the origin. As the ligands approach, first there is an increase in the energy of d orbitals relative to that of the free ion just as would be the case in a spherical field. Next, the orbitals lying along the axes (d_{z^2} and $d_{x^2-y^2}$) get repelled more strongly than d_{xy} , d_{yz} and d_{zx} orbitals, which have lobes directed between the axes. The d_{z^2} and $d_{x^2-y^2}$ orbitals get raised in energy and d_{xy} , d_{yz} , d_{zx} orbitals are lowered in energy relative to the average energy in the spherical crystal field. Thus, the degenerate set of d orbitals get split into two sets: the lower energy orbital set, t_{2g} and the higher energy, e_g set. The energy separation is denoted by Δ_o (the subscript o is for octahedral) :

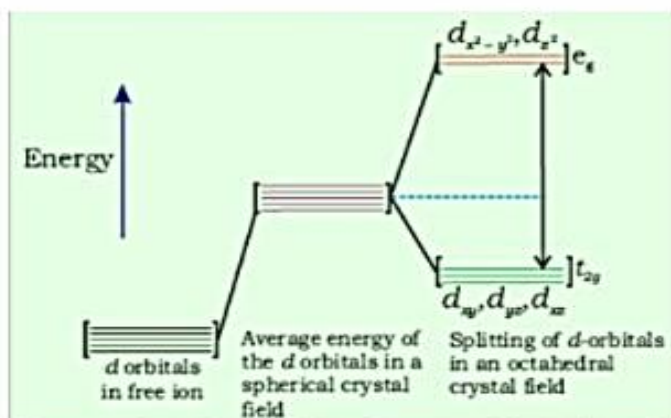


Figure : d-orbital splitting in an octahedral crystal field

Inner orbital complexes :

We have already discussed that in these type of complexes the d-orbitals used are of lower quantum number i.e. $(n - 1)$ various examples are as follow

- (a) Complexes formed by the use of inner orbitals are diamagnetic or have reduced paramagnetism.
- (b) These are called as low spin or spin paired complexes

$[\text{Fe}(\text{CN})_6]^{4-}$

- (a) electronic configuration of $\text{Fe}^{26} = [\text{Ar}] 3d^6 4s^2$

- (b) electronic configuration of $\text{Fe}^{+2} = [\text{Ar}] 3d^6$ =

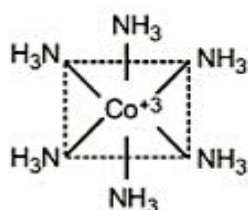
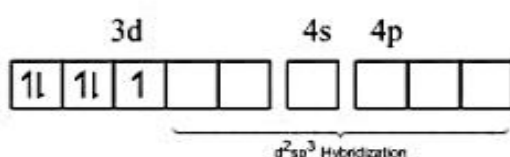
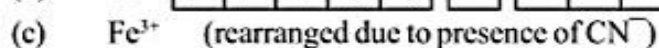
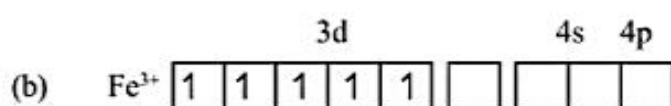
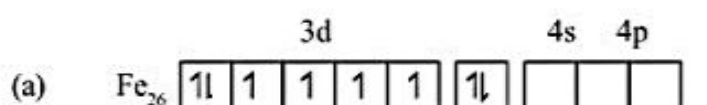
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- (c) electronic configuration of Fe^{+2} after rearrangement =

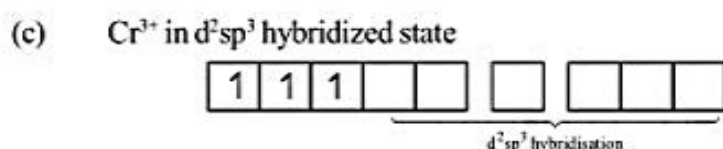
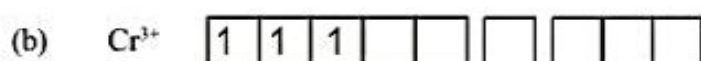
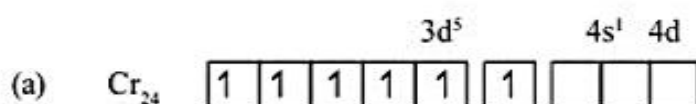
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 d^2sp^3
- (d) The above rearrangement is due to presence of cyanide ligand
- (e) In this state Fe^{2+} undergoes d^2sp^3 hybridisation to form six d^2sp^3 hybrid orbitals, each of which accepts electron pair donated by CN^- ions.
- (f) The resultant complex is inner octahedral as shown in figure and it should be diamagnetic as it has no unpaired electron. Formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$ takes place in the same manner

Octahedral shape of $[\text{Co}(\text{NH}_3)_6]^{3+}$ $[\text{Fe}(\text{CN})_6]^{1-}$ 

- (d) The resulting complex is octahedral due to d^2sp^3 hybridization
- (e) Due to presence of unpaired electron it is paramagnetic

 $[\text{Cr}(\text{NH}_3)_6]^{3+}$ 

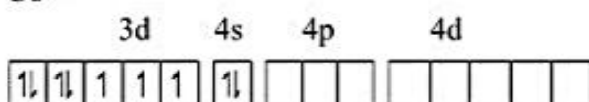
- (d) This d^2sp^3 hybridisation leads to octahedral geometry, the complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ will be octahedral in shape
- (e) Since the complex ion has 3 unpaired electrons so it must be paramagnetic.
- (f) Other complexes of chromium with similar inner structure are $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

Outer orbital complexes

- (a) In these complexes s, p as well as d orbitals involved in hybridization, belong to the highest quantum number (n)
- (b) Complexes formed by the use of outer n, d orbitals will be paramagnetic.
- (c) These complexes are called high-spin or spin free complexes
- (d) The outer orbital complexes have greater number of unpaired electrons.

$[\text{CoF}_6]^{3-}$

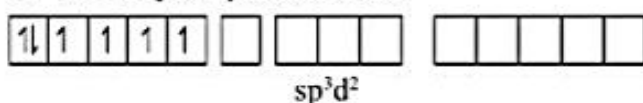
- (a) Co^{27}



- (b) Co^{3+} ion



- (c) Co^{3+} ion in sp^3d^2 hybridised state



- (d) Due to octahedral orientation of six sp^3d^2 hybridised orbitals shape $[\text{CoF}_6]^{3-}$ complex ion is octahedral
- (e) Due to presence of four unpaired electrons in 3d orbital $[\text{CoF}_6]^{3-}$ ion has paramagnetic character
- (f) Other examples are $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cu}(\text{NH}_3)_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

Tetrahedral Complexes :

In tetrahedral coordination entity formation, the 'd' orbital splitting is inverted and smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = -(4/9)\Delta_o$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

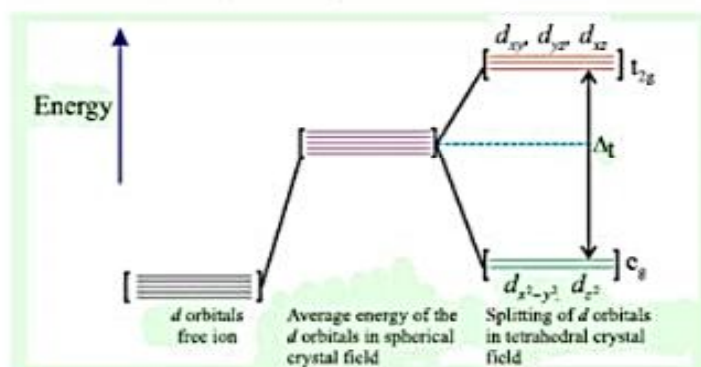
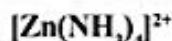
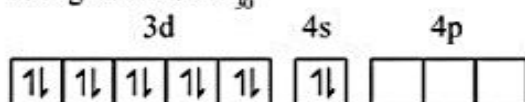


Figure : d-orbital splitting in an tetrahedral crystal field

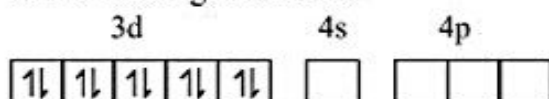
These are formed by sp^3 hybridisation. Complexes of Zn^{2+} are invariable tetrahedral because they involve sp^3 hybrid orbitals



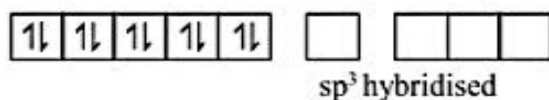
- (a) configuration of Zn_{30}



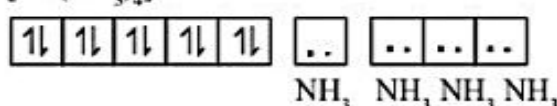
- (b) electronic configuration of Zn^{2+}



- (c) Zn^{2+} in sp^3 hybridised state



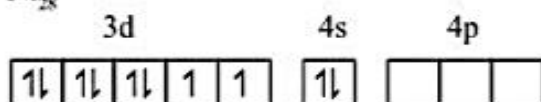
- (d) $[Zn(NH_3)_4]^{2+}$



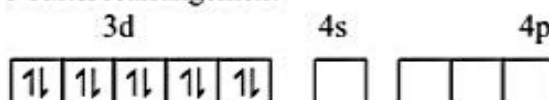
- (e) Since the complex is formed by sp^3 hybridisation, it is tetrahedral
 (f) Since all electrons are paired it is diamagnetic



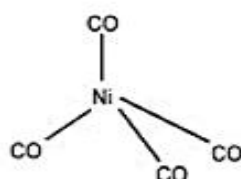
- (a) Ni_{28}



- (b) Ni after rearrangement



- (c) The empty one 4s and three 4p orbitals mix to form four sp^3 hybridised orbitals
 (d) each orbital accepts one electron pair from carbon monoxide molecule forming $[Ni(CO)_4]$
 (e) The shape of nickel tetra carbonyl is tetrahedral as shown below
 (f) It is diamagnetic in nature



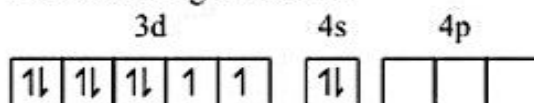
Square planar complex.

These are formed due to dsp^2 hybridisation.

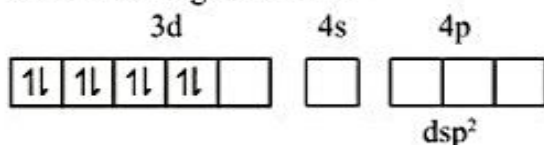
These complexes tend to be formed when the central ion has only one d orbital available in the inner shell



(a) electronic configuration of Ni



(b) electronic configuration of Ni^{2+}

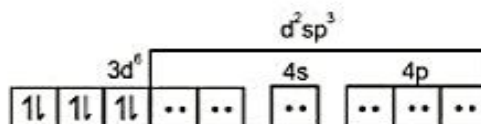
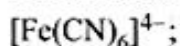


- (c) The rearrangement is due to presence of strong ligand CN^- . The four orbitals make dsp^2 hybridisation
 (d) The shape of resulting complex is square planar
 (e) Due to paired electrons it is diamagnetic.

Illustration

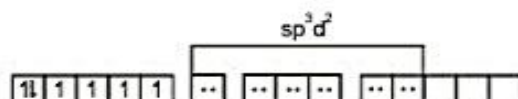
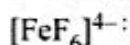
1. $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic while $[\text{FeF}_6]^{4-}$ is strongly paramagnetic. Why?

Sol. CN^- is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

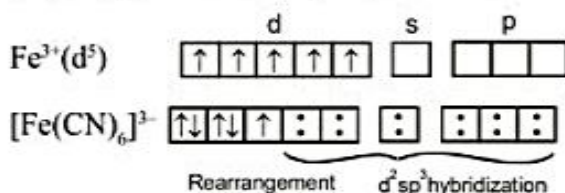
F^- is weak field ligand so it forms high spin paramagnetic complex.



Octahedral, paramagnetic complex

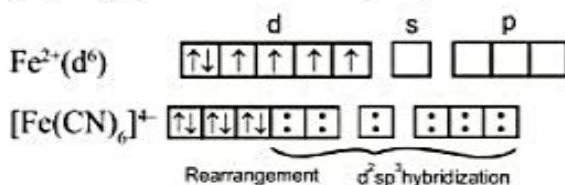
2. $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic, why?

Sol. $[\text{Fe}(\text{CN})_6]^{3-}$ involves d^2sp^3 hybridization



One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$ involves also d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.



All orbitals are doubly occupied, hence it is diamagnetic in nature.

Exercise

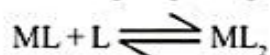
- Hexafluorocobaltate(III) ion is found to be high spin complex, the hybridisation state of cobalt is –
 (A) d^2sp^3 (B) sp^3 (C) sp^3d (D) sp^3d^2
Ans. (D)
- The number of unpaired electrons calculated in $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are :
 (A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4
Ans. (D)
- For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (μ) is –
 (A) 2.83 B.M. (B) 1.73 B.M. (C) 3.87 B.M. (D) 4.92 B.M.
Ans. (A)
- Which of the following electronic arrangement gives the highest value of the magnetic moment in case of octahedral complex ?
 (A) d^6 , strong field (B) d^7 , high spin (C) d^4 , weak field (D) d^2 , strong field
Ans. (C)

STABILITY OF COMPLEX

- A complex is formed in solution by the stepwise addition of ligands to a metal ion
- This can be expressed as follows $M + L \rightleftharpoons ML$, where M = metal and L is ligand
- The stability constant K for this reaction is as shown

$$K = \frac{ML}{[M][L]}$$

- This metal can again get a ligand



- The forthcoming stability constant K_1 then $K_1 = \frac{[ML_2]}{[ML][L]}$ its value is less than K
- The higher the value of stability constant stabler is the complex.
- The value of stability constants for some of the complexes are given below :

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$[Ag(NH_3)_2]^+$	1.6×10^7
$[Co(NH_3)_6]^{2+}$	1.12×10^6
$[Co(NH_3)_6]^{3+}$	5.0×10^{33}
$[AgCl_2]^-$	1.11×10^5
$[AgBr_2]^-$	1.28×10^7
$[Ag(CN)_2]^-$	1.0×10^{22}
$[Cu(CN)_4]^{2-}$	2.0×10^{27}
$[Fe(CN)_6]^{3-}$	7.69×10^{43}

Factors influencing the stability of complex

Nature of central ion -

- The complex will be more stable for higher values of charge density $\left(\frac{\text{Charge}}{\text{radius}}\right)$
- The higher the electronegativity of the central ion, the greater is the stability of its complexes
- The higher the oxidation state of the metal the more stable is the compound

Nature of ligand

- A basic ligand is likely to easily donate its electrons. Thus a more basic ligand will form more stable complex.
- Chelating ligands form more stable complexes as compared to monodentate ligands.

ORGANOMETALLIC COMPOUNDS

Compounds containing at least one metal-carbon bond may be called organometallic compounds. These compounds may be defined as those compounds in which the carbon atoms of organic groups are linked to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium, tellurium and antimony with organic groups are also included in the organometallics.

1. σ -bonded organometallic compounds :

In σ -bonded compound organic group is bonded to metal atoms through a normal 2 electron covalent bond. Some example of σ -bonded organometallic compounds are as below –

$\text{Al}_2(\text{CH}_3)_6$, $\text{Al}_2(\text{C}_6\text{H}_5)_6$, $\text{Pb}(\text{CH}_3)_4$, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $\text{Zn}(\text{C}_2\text{H}_5)_4$, $(\text{CH}_3)_4\text{Sn}$ etc.

Examples :

R – Mg – X	$(\text{CH}_3\text{CH}_2)_2\text{Zn}$
Grignard reagent (Alkyl magnesium halide)	Diethyl zinc
$(\text{CH}_3)_4\text{Si}$	$(\text{CH}_3)_4\text{Sn}$
Tetramethyl silane	Tetramethyl tin
$(\text{C}_2\text{H}_5)_4\text{Pb}$	$(\text{CH}_3)_2\text{Cd}$
Tetraethyl lead	Dimethyl cadmium

Trimethyl aluminium exists as stable dimer. In this, two methyl groups act as bridges between two aluminium atoms. The alkyl bridge is formed by multicentre bonding.

2. π -bonded organometallic compounds :

This type of compounds are generally formed by transition metals. Some examples of π -complexes are: Ferrocene, Dibenzene chromium, Zeise's salt, etc. are some well known examples of the complexes belonging to this class.

3. σ - and π -bonded organometallic compounds :

Metal carbonyls of transition metals constitute another important class of organometallic compounds. The first metal carbonyls, $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, were discovered by A. Mond in 1890 and 1891. Few more examples of metal carbonyls are $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$. In addition to mononuclear of metal carbonyls mentioned above, transition metals form various polynuclear metals carbonyls such as $\text{Fe}(\text{CO})_{12}$, $\text{Mn}_2(\text{CO})_{10}$. The metal carbonyl bond in metal carbonyls posses both σ and π character.

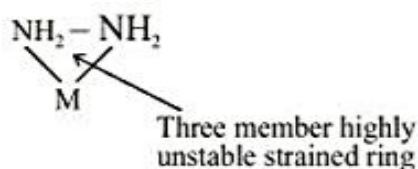
Application of Organometallic Compounds :

- (a) **Ziese's salt** is used in the treatment of cancer.
- (b) Nickel tetracarbonyl is used in purification of nickel.
- (c) Ethylmercuricchloride is used as a fungicide.
- (d) As homogeneous Catalyst
Wilkinsons catalyst for hydrogenation of olefins is $[P(Ph)_3RhCl]$
- (e) As heterogeneous catalyst
Zeigler-Natta Catalyst ($R_3Al + TiCl_4$)
 (Tri alkyl Aluminium + Titanium tetrachloride) used for polymerisation of alkene.
- (f) **Organic synthesis:** OMC like $RMgX$, R_2Cd , CH_3Li etc. are used for preparation of almost all type of organic compounds.
- (g) **Cyclopentadienyl manganesetricarbonyl** and **TEL** (Tetraethyl lead) is used as antiknock agent in petrol.
- (h) In medicine – Organo arsenic compounds are used as medicine for syphilis disease.
- (i) In agriculture– Seeds are treated with ethyl mercury Chloride commercially known as **CERESSAN** to protect the plants against infection.

SOLVED EXAMPLES

Q.1 $\text{NH}_2.\text{NH}_2$ although possesses two electron pair for donation but not acts as chelating agent. Why?

Sol. The co-ordinating by $\text{NH}_2.\text{NH}_2$ leads to a three member highly unstable strained ring and thus it does not acts as chelating agent.



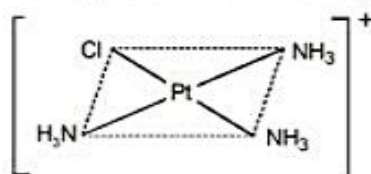
Q.2 Square planar complexes with co-ordination number four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

Sol. In tetrahedral complexes, the relative position of atoms with respect to each other is same thus these do not show geometrical isomerism. Square planar complexes show cis, trans isomerism.

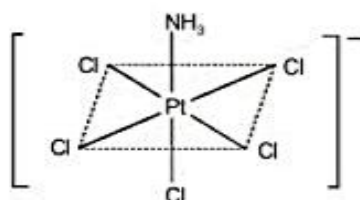
Q.3 Platinum (II) forms square planar complexes and plantinum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures -

(a) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ (b) $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$ (c) $[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$ (d) $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{2+}$

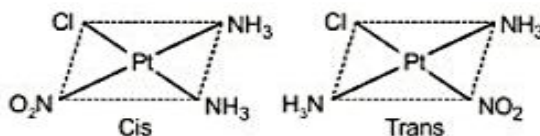
Sol. (a) Square planar complex of the type Ma_3b shows no isomerism.



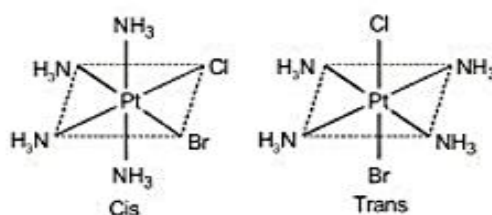
(b) An octahedral complex of the type Ma_5b shows no isomerism.



(c) A square planar complex of the type Ma_2bc exists as cis and trans isomers

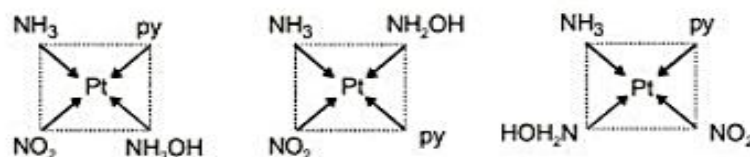


(d) An octahedral complex of the type Ma_4bc shows cis and trans isomerism.



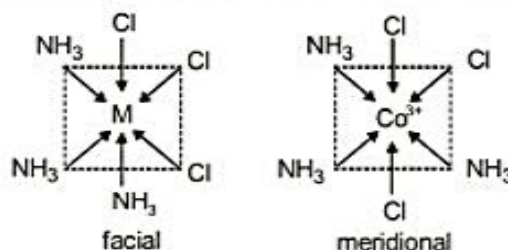
Q.4 How many geometrical isomers with formula $[MABCD]$ e.g., $[\text{Pt}(\text{NH}_3)\text{py}(\text{NH}_2\text{OH})\text{NO}_2]^+$ are possible?

Sol. Three isomers



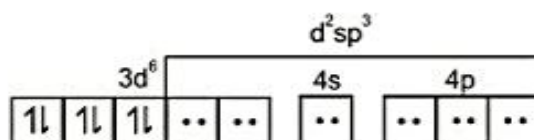
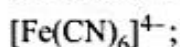
Q.5 What are facial and meridional isomers? Explain with examples.

Sol. For the complexes of the type $[\text{Ma}_3\text{b}_3]$ e.g., $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{Rh}(\text{py})_3\text{Cl}_3]$; the isomer is called facial (fac) when all similar ligands occupy same face of an octahedron as shown below. When all similar ligands are not on the same face then isomer is called meridional (mer).



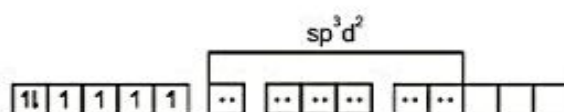
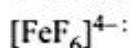
Q.6 $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic while $[\text{FeF}_6]^{4-}$ is strongly paramagnetic. Why?

Sol. CN^- is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

F^- is weak field ligand so it forms high spin paramagnetic complex.



Octahedral, paramagnetic complex

Q.7 If excess of AgNO_3 solution is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride, how many mol of AgCl be precipitated:

- (A) 0.0012 (B) 0.0016 (C) 0.0024 (D) 0.0048

Ans. (C)

Sol. $[\text{CoCl}_2(\text{en})_2]\text{Cl} \xrightarrow{\text{AgNO}_3} [\text{CoCl}_2(\text{en})_2]\text{NO}_3 + \text{AgCl}$

Mole of $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ = molarity \times v(Lt.)

0.0024 mole of $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ gives

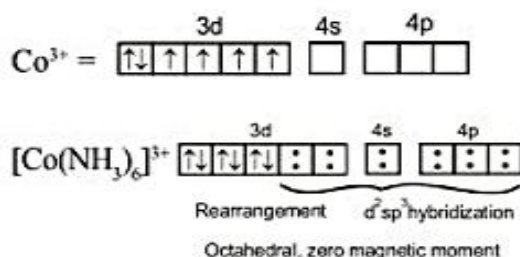
$$\frac{100}{1000} \times 0.024 = 0.0024 \text{ mole of } \text{Cl}^-$$

Which precipitate 0.0024 mole of AgNO_3 because 1 mole Ag^+ required 1 mole Cl^- to precipitate

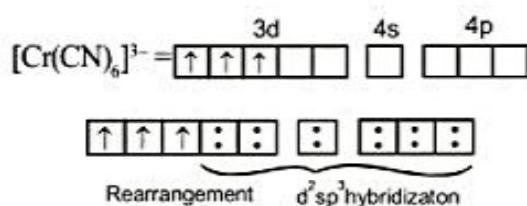
Q.8 Find out the hybridization, geometry and magnetic moment of the complexes :



Sol. (i) The oxidation state of cobalt in the complex is +3. The electronic configuration of Co^{3+} ions is



(ii) The oxidation state of chromium in the complex is +3. The electronic configuration of Cr^{3+} ion is



Octahedral, magnetic moment

$$= \sqrt{3 \times (3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

Q.9 The magnetic moment of $[\text{MnCl}_4]^{2-}$ is 5.92 B.M. On the basis of its magnetic moment, write configuration of Mn^{2+} in this complex.

Sol. For an atom/ion

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)}$$

(n = No. of unpaired electrons)

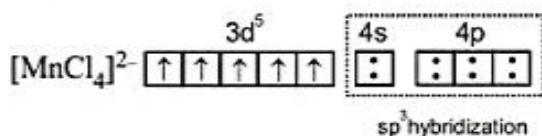
Given that $\mu = 5.92 \text{ B.M.}$

$$\therefore 5.92 = \sqrt{n(n+2)}$$

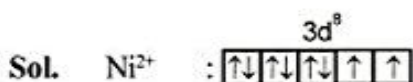
or $n = 5$

Thus in this complex Mn contains five unpaired electrons and so its possible configuration may be Mn^{2+} in $[\text{MnCl}_4]^{2-} = [\text{Ar}] 3d^5 4s^0$

so hybridisation of Mn^{2+} in the given complex must be sp^3 .



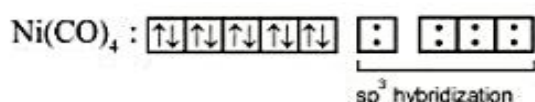
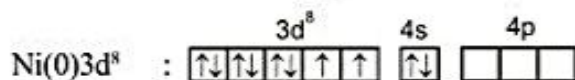
Q.10 All the octahedral complexes of Ni^{2+} are outer orbital complexes, why?



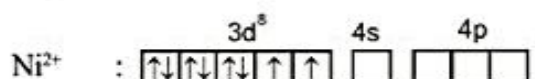
Thus only one vacant 3d-orbital is available after pairing up of electrons due to strong field ligand. Therefore, d^2sp^3 hybridisation is not possible. Only sp^3d^2 is possible which represents an outer complex.

Q.11 $\text{Ni}(\text{CO})_4$ possesses tetrahedral geometry while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar, why?

Sol. In the formation of $\text{Ni}(\text{CO})_4$, nickel undergoes sp^3 hybridization, hence it is tetrahedral in shape.



In the formation of $[\text{Ni}(\text{CN})_4]^{2-}$, Ni^{2+} ion undergoes dsp^2 hybridisation, hence it is square planar in shape.



Q.12 Consider the following complexes –

(i) K_2PtCl_6 (ii) $\text{PtCl}_4 \cdot 2\text{NH}_3$ (iii) $\text{PtCl}_4 \cdot 3\text{NH}_3$ (iv) $\text{PtCl}_4 \cdot 5\text{NH}_3$

Their electrical conductances in aq. solutions are –

(A) 256, 0, 97, 404 (B) 404, 0, 97, 256 (C) 256, 97, 0, 404 (D) 404, 97, 256, 0

Sol. (A) Coordination number of Pt is 6 hence

I $\text{K}_2[\text{PtCl}_6]$ – Three ions

II $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ – Zero ions

III $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$ – Two ions

IV $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ – Four ions

Conductivity \propto no. of ions

Q.13 Determine the oxidation state of metal in the complex ion, $[\text{PtCl}_6]^{2-}$.

Sol. Charge on the complex ion = Oxidation state of metal + charge on ligands

$$-2 = x + 6 \times (-1)$$

$$\text{or } x = +4$$

The oxidation of Pt in the complex ion is +4.

Q.14 The pair in which both species have same magnetic moment (spin only value) is –

(A) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$ (B) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(C) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{CoCl}_4]^{2-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Ans. (B)

Sol. Same magnetic moment = same number of unpaired electrons = $\sqrt{n(n+2)}$

where n = number of unpaired electrons

$\text{Co}^{2+} = 3d^7$, 3 unpaired electrons

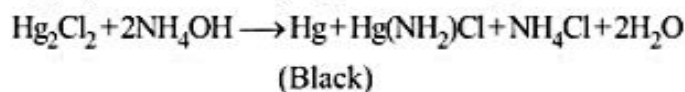
$\text{Cr}^{2+} = 3d^4$, 4 unpaired electrons

$\text{Mn}^{2+} = 3d^5$, 5 unpaired electrons

$\text{Fe}^{2+} = 3d^6$, 4 unpaired electrons

Q.15 The colour of Hg_2Cl_2 changes from white to black when treated with NH_3 . Why?

Sol. Hg_2Cl_2 reacts with NH_3 to give black complex.



Q.16 Write the formula of the following complexes.

(i) Pentamminechlorocobalt (III) ion

(ii) Lithium tetrahydridoaluminate (III)

Sol. (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$; (ii) $\text{Li}[\text{AlH}_4]$

Q.17 Identify the complexes which are expected to be coloured and explain.

(A) $\text{Ti}(\text{NO}_3)_4$

(B) $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$

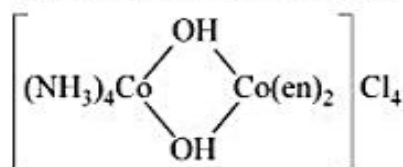
(C) $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$

(D) $\text{K}_3[\text{VF}_6]$

Ans. (C) and (D)

Sol. Are coloured because Cr^{3+} in $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and V^{3+} in $[\text{VF}_6]^{3-}$ have $3d^3$ and $3d^2$ configuration respectively and thus show d-d transition.

Q.18 Write the IUPAC name of the given compound.

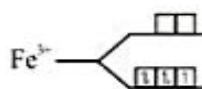


Sol. Tetraamine cobalt (III) di- μ -hydroxo bis ethylenediamine cobalt (III) chloride.

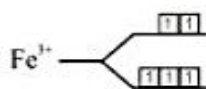
Q.19 Explain the following with appropriate reasons :

$[\text{Fe}(\text{CN})_6]^{3-}$ ion has magnetic moment 1.73 BM, while $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has a magnetic moment 5.92 BM.

Sol. $1.73 = \sqrt{n(n+2)}$ $5.92 = \sqrt{n(n+2)}$
 $n = 1$ $n = 5$



Due to strong field ligands (CN^-)



Due to weak ligands (H_2O)