

CO-ORDINATION COMPOUNDS

JEE MAINS Syllabus

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2. *Molecular or Addition Compounds*
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KEY CONCEPTS

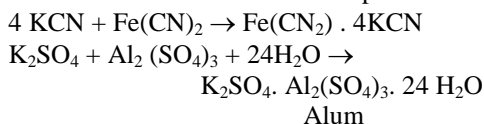
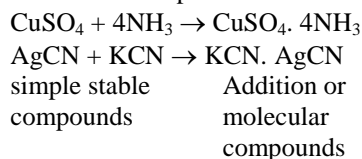
1. Introduction

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives, as chlorophyll of plants and haemoglobin of animal blood are also coordination compounds of Mg and Fe respectively
- (c) One of the earliest known coordination compound is prussian blue which was accidentally prepared by a Berlin color maker, Diebach in 1704.
- (d) The field of such compound is expanding due to their utilization in metallurgy, analytical chemistry and polymerisation.

2. 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.



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

2.1 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 solution 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

2.2 Coordination or complex compounds

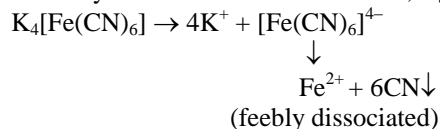
- (a) The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions are called coordination compounds

- (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.

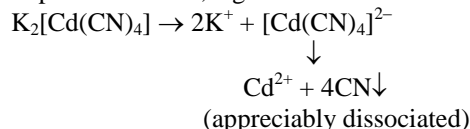
- (d) On the basis of stability of complex ion, complex ions are further divided as follows.

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



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.



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

3. Various terms used in Coordination Compounds

To understand concepts related to coordination compounds and their nature it is essential to discuss some important terms. These are as follows.

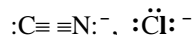
3.1 Central ion : (Centre of coordination)

- (a) The cation to which one or more neutral molecules or anions are attached is called as centre of coordination
- (b) Since the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atom of the ligands, it must have empty orbitals
- (c) This explains why the transition metals having empty d-orbitals form coordination compounds very readily.

(d) In the complexes $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central ions.

3.2 Ligand :

- The neutral molecules, anions or cations which are directly linked with the central metal atom or ion in a complex ion are called ligands.
- Ligand donate a pair of electrons to the central atom
- Ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage
- Ligands are normally polar molecules like $\ddot{\text{N}}\text{H}_3$; $\text{H}_2\ddot{\text{O}}$ or anions such as Cl^- , OH^- , CN^- etc. which contain at least one unshared pair of valency electrons.
- With few exceptions, free ligands have lone pair of electron that is not engaged in bonding for example.

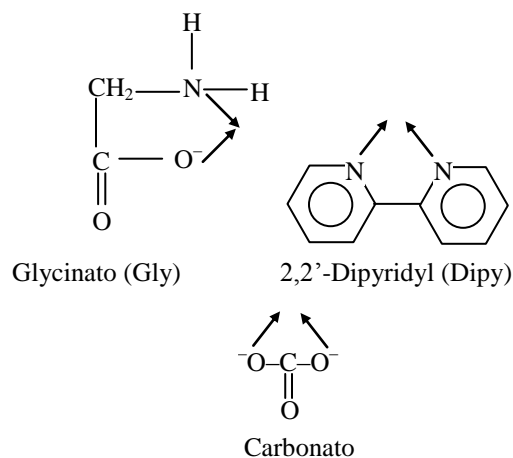
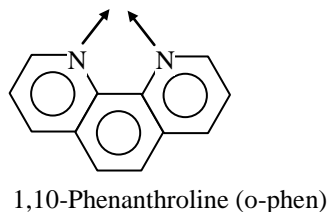
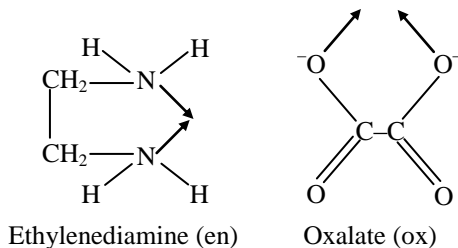


3.2.1 Types of Ligands on the basis of number of donor atoms present in them :

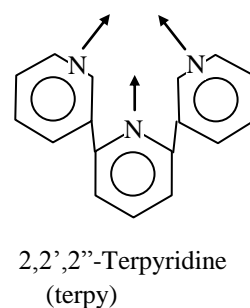
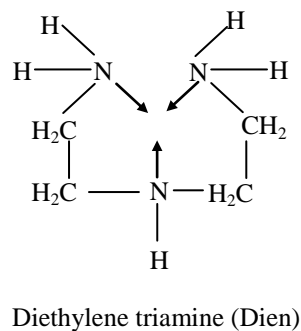
- (A) **Mono-or unidentate ligands** : They have one donor atom, i.e. they supply only one electron pair to central metal atom or ion.

Examples : F^- , Cl^- , Br^- , H_2O , NH_3 , CN^- , NO_2^- , ON^- , CO

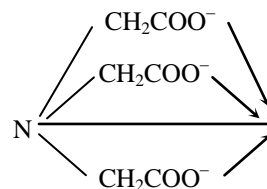
- (B) **Bidentate ligands** : Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are :



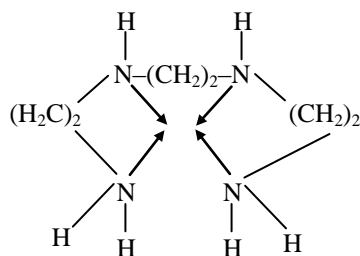
- (C) **Tridentate ligands** : The ligands having three donor atoms are called tridentate ligands. Examples are:



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

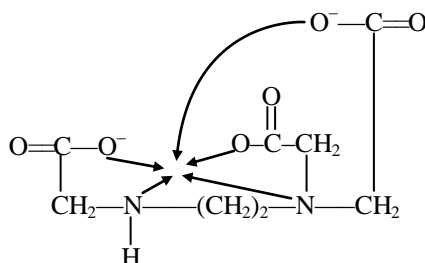


(Nitriloacetato)



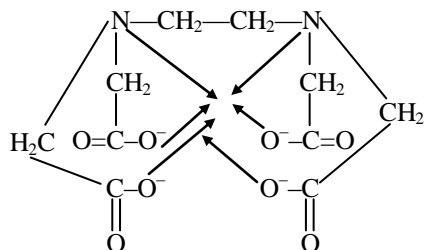
Triethylenetetramine (Trien)

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



Ethylenediamine triacetate ion

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



Ethylenediamine tetraacetate ion (EDTA)⁴⁻

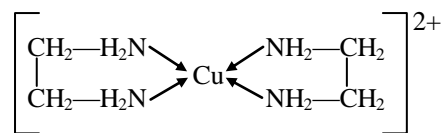
- (G) **Chelating ligands.**

- 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.
- 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.
- The process of formation of chelates is called chelation.

- Chelate complexes are more stable than ordinary complexes in which the ligand is a monodentate

- This increased stability of the compound due to chelation is called the chelate effect

- In the complex ion given below, 5 membered rings are formed. So all these are called chelate complexes



- Generally the chelate complexes with 5 or 6 membered rings are more stable.
- Out of these, 5 membered rings are very stable when they involve saturated ligands.
- 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.

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

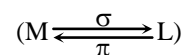
- (A) **Ligands having one (or more) lone pair (or pairs) of electrons**

- Ligands which contain vacant p-type orbitals that can receive back donated pe^- from M-ion in low oxidation state.

e.g.: CO, NO, CN, NC, R-N=C, R₃P, R₃As

a,a-dipyridyl, o-phenanthroline

- All these ligands also have filled donor orbital in addition to vacant p-type acceptor orbitals.
- Thus in there complexes both metal and ligand function as donors and acceptors



- Ligands which do not have vacant orbitals to receive back donated electron from metals eq. H₂O, NH₃ F.

- (B) **Ligands having no lone pairs of electrons but have p bonding electron eq. Ethylene, benzene, cyclopentadienyl-ion**

Note: (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) 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

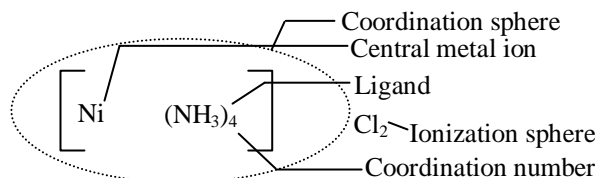
3.3 Coordination number :

- 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

3.4 Coordination sphere :

- 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 central metal atom and the ligands inside the square bracket behave as a single entity
- The part outside the bracket is called ionisation sphere.
- The species present in the coordination sphere are nonionizable

- (f) The species present in the ionization sphere are ionisable



3.5 Oxidation state

- It is a number which represents the electric charge on the central metal atom of a complex ion
- For example, the O.N. of Fe, Co and Ni in $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Ni}(\text{CO})_4$ is +2, +3 and zero respectively
- The charge of the complex is the sum of the charges of the constituent parts.

3.6 Effective atomic number (EAN)

- In order to explain the stability of the complex, Sidgwick proposed effective atomic number
- It can be defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands.
- The EAN generally coincides with the atomic number of next noble gas in some case.
- EAN is calculated by the following relation $\text{EAN} = \text{atomic number of the metal} - \text{number of electrons lost in ion formation} + \text{number of electrons gained from the donor atoms of the ligands}$
- The EAN values of different metal in their respective complexes are tabulated as follows

Complex	Matal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number
$\text{K}_4[\text{Fe}(\text{CN})_6]$	+2	26	6	$(26 - 2) + (6 \times 2) = 36$ [Kr]
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	+2	29	4	$(29 - 2) + (4 \times 2) = 35$
$[\text{Co}(\text{CH}_3)_6]\text{Cl}_3$	+3	27	6	$(27 - 3) + (6 \times 2) = 36$ [Kr]
$\text{Ni}(\text{CO})_4$	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	$(78 - 4) + (6 \times 2) = 86$ [Rn]
$K_3[Cr(C_2O_4)_3]$	+3	24	6	$(24 - 3) + (6 \times 2) = 33$
$K_3[Fe(CN)_6]$	+3	26	6	$(26 - 3) + (6 \times 2) = 35$
$K_2[HgI_4]$	+2	80	4	$(80 - 2) + (4 \times 2) = 86$ [Rn]
$[Ag(NH_3)]Cl$	+1	47	2	$(47 - 1) + (2 \times 2) = 50$
$K_2[PdCl_4]$	+2	46	4	$(46 - 2) + (4 \times 2) = 52$

4. 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

4.1 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 o.s.
- In case the complex is non ionic, it is named as one word e.g. $[Ni(CO)_4]$ 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.

4.2 Name of the ligand :

- If there are two or more different kinds of ligands, they are named in alphabetical order without separation by hyphen.

(b) When there are several ligands of same kind, they are listed alphabetically

(c) Anionic ligands ending with 'ide' are named by replacing 'ide' by suffix 'O'.

e.g.	Symbol	Name as ligand	N^{3-}	Nitrido
	Cl^-	Chloro	O_2^{2-}	Peroxo
	Br^-	Bromo	O_2H^-	Perhydroxo
	CN^-	Cyano	S^{2-}	Sulphido
	O^{2-}	Oxo	NH_2^-	Amido
	OH^-	Hydroxo		

(d) Ligands whose names end in 'ite' or 'ate' become 'ito' or 'ato' i.e., by replacing the ending 'e' with 'o' as follows

Symbol	Name as ligand
CO_3^{2-}	Carbonato
$C_2O_4^{2-}$	Oxalato
SO_4^{2-}	Sulphato
NO_3^-	Nitrato
SO_3^{2-}	Sulphito
CH_3COO^-	Acetato
NO_2^-	(bonded through oxygen) nitrite (bonded through nitrogen) nitro

(e) Neutral ligands are given the same names as the neutral molecules. For example. Ethylene diamine as a ligand is named ethylene diamine in the complex. However some exceptions to this rule are

H_2O	Aquo
NH_3	Ammine
CO	Carbonyl
NO	Nitrosyl
CS	Thiocarbonyl

(f) Names of positive ligands ends in 'ium' e.g.

NH_4^+ Ammonium

NO^+ Nitrosylium

NH_2NH_3^+ Hydrazinium

(g) 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

(h) 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 paranthesis

(i) 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 *m* before its name.

5. Bonding in Coordination Compounds

5.1 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 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.

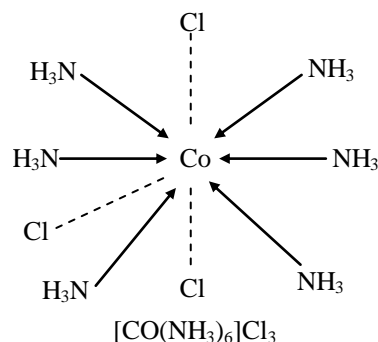
(f) Every central ion tends to satisfy its primary as well as secondary valencies.

(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) Thus on the basis of werner theory, the $\text{CoCl}_3 \cdot 6\text{NH}_3$ is called hexamminecobalt (III) chloride because there are six ammonia ligands and the cobalt is in the +3 oxidation state, i.e. cobalt has three primary valencies and six secondary valencies. The complex can therefore be represented as shown.



Note: Now, it has been proposed that coordination number of a metal may be any whole number between 2 and 9

5.2 Sidgwick Theory and EAN rule

Sidgwick suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of the next noble gas.

This total number of electrons is called EAN of the metal which we have already discussed.

5.3 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 n d-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.

$$m = \sqrt{n(n+2)} \text{ where } n = \text{no of lone pair}$$

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.

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Draw back of V.B. 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.

5.4 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.

6. Shape of Complexes

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

6.1 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.

6.1.1 Inner orbital complexes :

We have already discussed that in these type of complexes the d-orbitals used are of lower

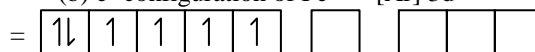
quantum number i.e. (n - 1) various examples are as follow

- (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

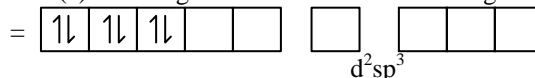
6.1.1.1 $[\text{Fe}(\text{CN})_6]^{4-}$

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

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

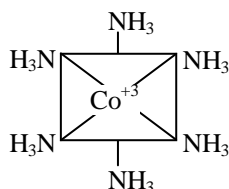


(c) e^- configuration of Fe^{+2} after rearrangement



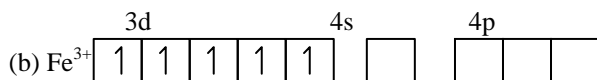
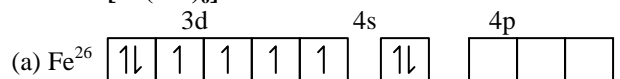
d^2sp^3

- (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

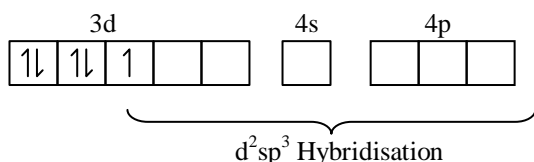


Octahedral shape of $[\text{Co}(\text{NH}_3)_6]^{3+}$

6.1.1.2 $[\text{Fe}(\text{CN})_6]^{3-}$



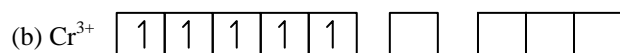
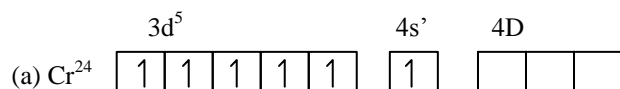
(c) Fe^{3+} (rearranged due to presence of CN^-)



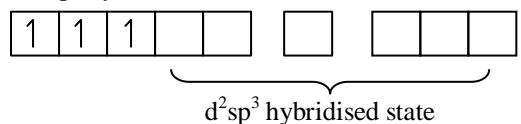
(d) The resulting complex is octahedral due to d^2sp^3 hybridization

(e) due to presence of unpaired e^- it is paramagnetic

6.1.1.3 $[\text{Cr}(\text{NH}_3)_6]^{3+}$



(c) Cr^{3+} in d^2sp^3 hybridized state



(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 it must be paramagnetic which is founded to be so

(f) Other complexes of chromium with similar inner structure are $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

6.1.2 Outer orbital complexes.

(a) In these complexes s, p as well as d orbitals involved in hybridization, belong to the highest quantum number (n)

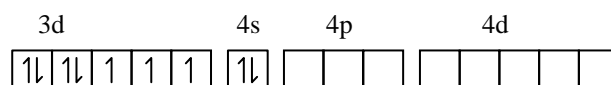
(b) complexes formed by the use of outer n, d orbitals will be paramagnetic.

(c) These complexes are called high- spin or spin free complexes

(d) The outer orbital complexes have greater number of unpaired electrons.

6.1.2.1 $[\text{CoF}_6]^{3-}$

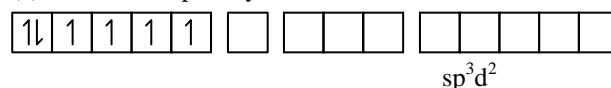
(a) Co^{27}



(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 is 3d orbital $[\text{CoF}_6]^{3-}$ ion has paramagnetic character

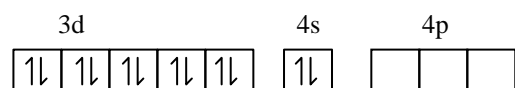
(f) Other examples are $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cu}(\text{NH}_3)_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

6.2 Tetrahedral Complexes :

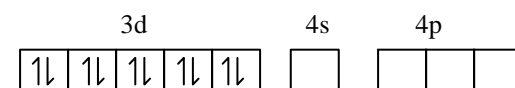
These are formed by sp^3 hybridisation. Complexes of Zn^{2+} are invariable tetrahedral because they involve sp^3 hybrid orbitals

6.2.1 $[\text{Zn}(\text{NH}_3)_4]^{2+}$

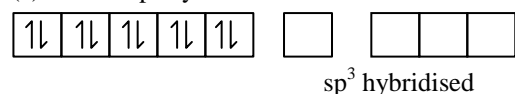
(a) configuration of Zn^{30}



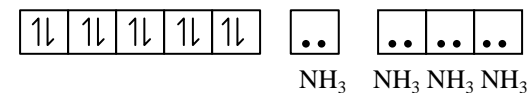
(b) e^- configuration of Zn^{2+}



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



(d) $\text{Zn}(\text{NH}_3)_4]^{2+}$

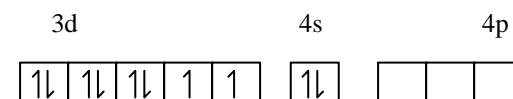


(e) Since the complex is formed by sp^3 hybridisation, it is tetrahedral

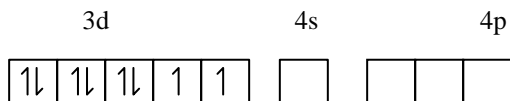
(f) Since all electrons are paired it is diamagnetic

6.2.2 $[\text{Ni}(\text{CO})_4]$

(a) Ni^{28}



(b) Ni after rearrangement

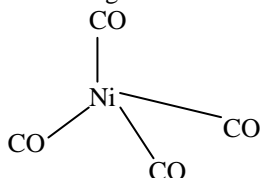


(c) The empty one 4s and three 4p orbitals mix to form four sp^3 hybridised orbitals

(d) each orbital accepts one electron pair from carbon monoxide molecule forming $[\text{Ni}(\text{CO})_4]$

(e) The shape of nickel tetra carbonyl is tetrahedral as shown below

(f) It is diamagnetic in nature



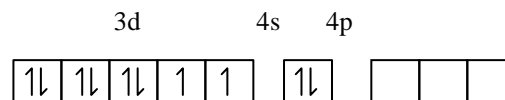
6.3 Square planar complex.

These are formed due to dsp^2 hybridisation.

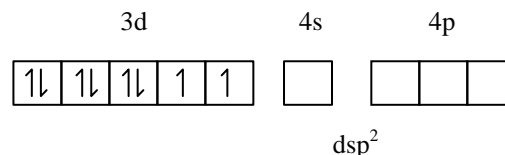
These complexes tend to be formed when the central ion has only one d orbital available in the inner shell

6.3.1 $[\text{Ni}(\text{CN})_4]^{2-}$

(a) e^- configuration of Ni



(b) e^- configuration of Ni^{2+}



(d) The rearrangement is due to presence of strong ligand CN^- . The four orbitals make dsp^2 hybridisation

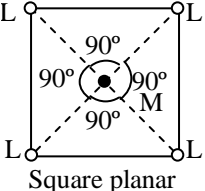
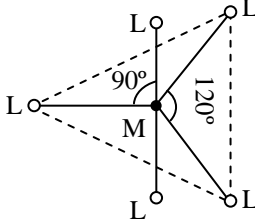
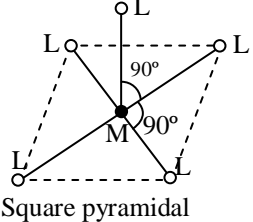
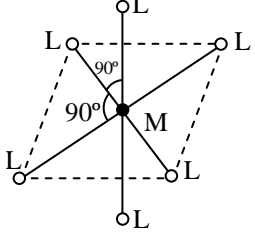
(e) The shape of resulting complex is square planar

(d) due to paired electrons it is diamagnetic.

L = Ligands indicated by white circles (same or different) M = Central metal indicated by black circles.

Co-ordination numbers, Hybridised orbitals and geometry of some co-ordination compounds

Coordination Number	Hybridised orbital	Geometrical shape of the complex	Examples of complex
2.	sp	<p style="text-align: center;">Linear</p>	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3.	sp^2		$[\text{HgI}_3]^-$
4.	sp^3	<p style="text-align: center;">Tetrahedral</p>	$[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]^0$ $\text{Zn}(\text{NH}_3)_4^{+2}$ $[\text{ZnCl}_4]^{2-}$, $[\text{CuX}_4]^{2-}$ where X = CN^- Cl^- , Br^- , I^- , CNS

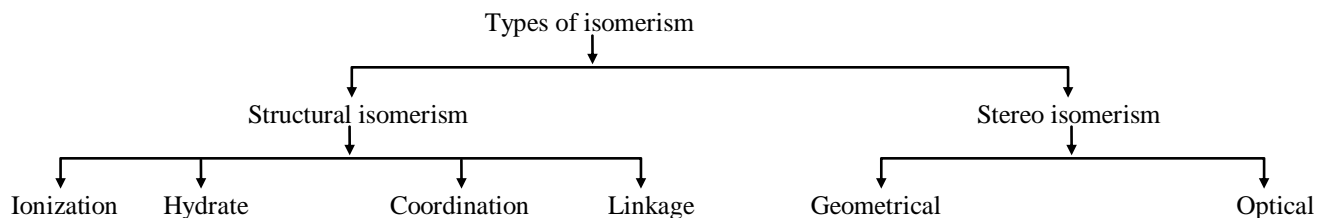
4.	dsp^2 The d-orbital involved is $d_{x^2-y^2}$ orbital is $(n-1) d_{x^2-y^2}$ orbital	 <p>Square planar</p>	$[\text{Ni}(\text{CN})_4]^{-2}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$
5.	dsp^3 The d-orbital is $(n-1) d_{z^2}$ orbital		$[\text{CuCl}_5]^{-3}$ $[\text{MoCl}_5]^0$ $[\text{Fe}(\text{CO})_5]^0$
5.	sp^3d The d-orbital is $nd_{x^2-y^2}$ orbital	 <p>Square pyramidal</p>	$[\text{SbF}_5]^{-2} \text{IF}_5$
6.	d^2sp^3 When d-orbitals are $(n-1)$ d-orbitals (Inner orbital complexes) or sp^3d^2 When d-orbitals are nd orbital (Outer orbital complexes) In both cases p-orbitals are d_{z^2} and $d_{x^2-y^2}$ orbitals	 <p>Octahedral</p>	$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{-2}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{-2} [\text{CoF}_5]^{-3}$

7. Isomerism in Complexes

(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 frequency among inorganic substances.

(c) **Classification of isomerism :**



8. Structural Isomerism

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

8.1 Ionisation isomers :

The type of isomerism is due to the exchange of groups of 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

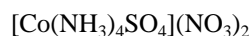
(i) $[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$ (red violet)

(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



8.2 Hydrate isomers :

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

(a) $\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$ 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) $[\text{Co}(\text{NH}_3)_4] \text{H}_2\text{O Cl}] \text{Cl}_2$

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

8.3 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^- Nitrogen ligand) or through oxygen (i.e. ONO Nitrogen ligand)

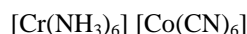
(iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

8.4 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. **Ex.**

(i) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]'$



(ii) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{C}_2\text{O}_4)_3]'$



9. 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.

9.1 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.

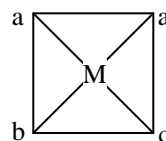
(e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.

(f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-Trans isomerism.

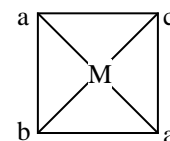
(g) It is exhibited by 4-coordinated complexes with square planar geometry.

9.2 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.

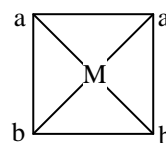


Cis-isomer

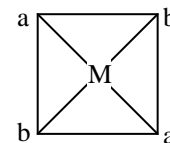


Trans-isomer

(ii) Complexes with general formula Ma_2bc can have Cis-and trans-isomers.

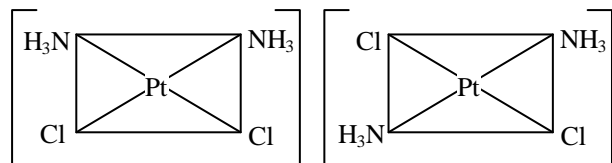


Cis



Trans

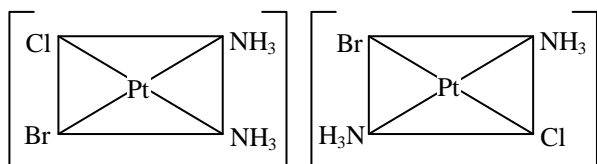
(iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



Cis (Cis-platin) anti cancer

Trans

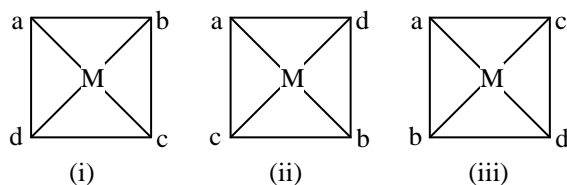
(iv) $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



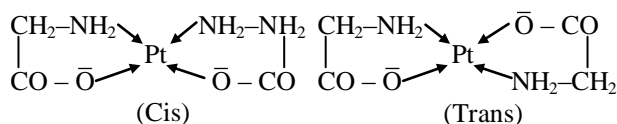
Cis

Trans

(v) Complexes with general formula, Mabed can have three isomers.

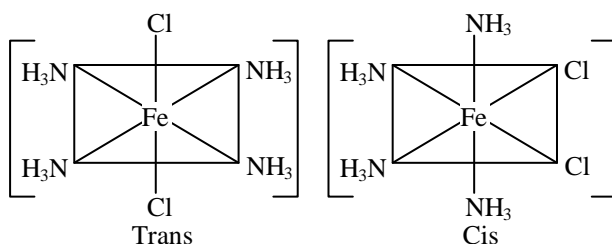


(vi) Diglycinato platinum (iv) complexes

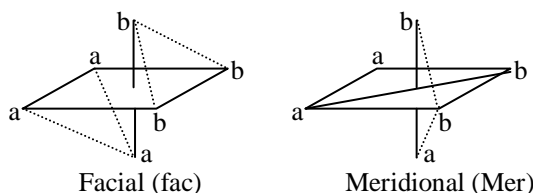


9.3 Geometrical isomers with coordination number = 6

(i) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



(ii) Facial and Meridional isomerism (Ma_3b_3)

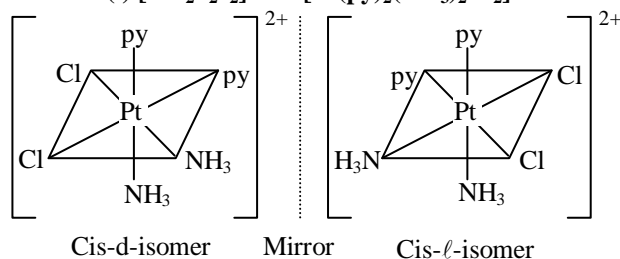


Optically isomers :

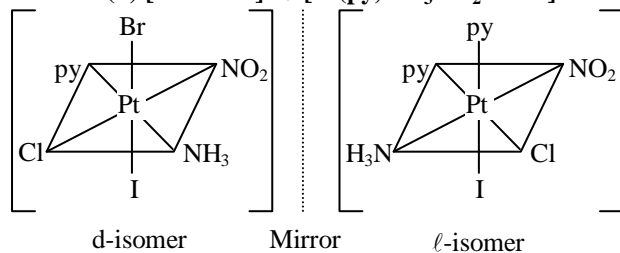
- Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- The complex which rotates plane polarised light to left hand side is laevo rotatory i.e., 'l' or '-' and if the complex rotates the plane polarized light to right hand side then it is **dextrorotatory** '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.

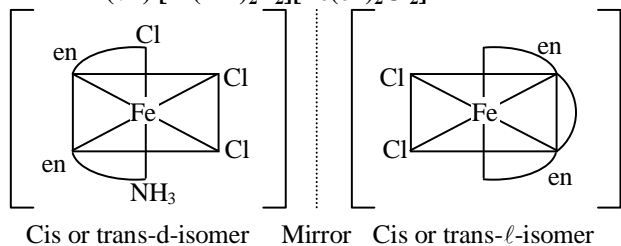
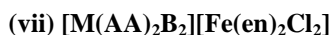
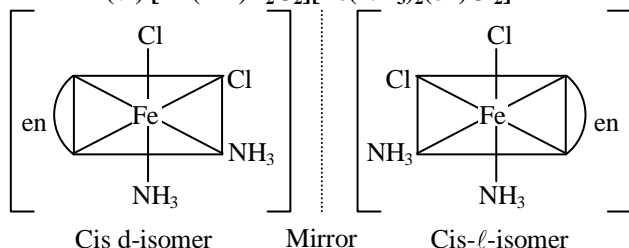
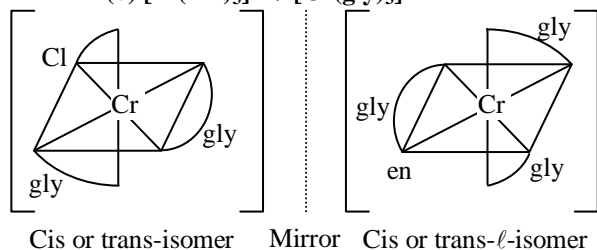
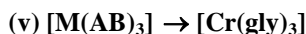
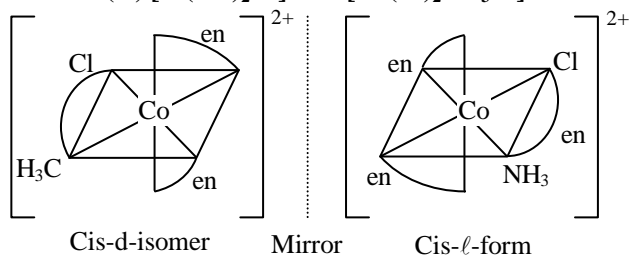
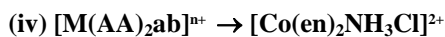
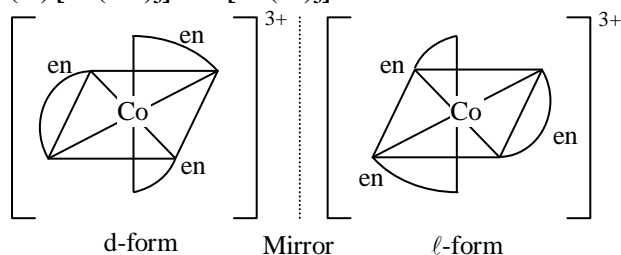
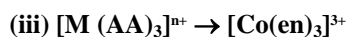
Optical isomer with Coordination number = 6

(i) $[\text{Ma}_2\text{b}_2\text{c}_2]^{n+} \rightarrow [\text{Pt}(\text{py})_2(\text{NH}_3)_2\text{Cl}_2]^{2+}$



(ii) $[\text{Mabcedf}] \rightarrow [\text{Pt}(\text{py})\text{NH}_3\text{NO}_2\text{ClBrI}]$





(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.

10. 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
 $ML + L \rightleftharpoons ML_2$
- The forthcoming stability constant K' is
 $K_1 = \frac{[ML_2]}{[ML][L]}$ 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}

10.1 Factors influencing the stability of complex

10.1.1 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

10.1.2 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.

11. 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.

11.1 σ - b and organometallic compounds :

In σ - b onded compound organic group is bonded to metal atoms through a normal 2 electron covalent bond. Some example of σ - b onded 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 –

$\text{R} - \text{Mg} - \text{X}$	$(\text{CH}_3\text{CH}_2)_2\text{Zn}$
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

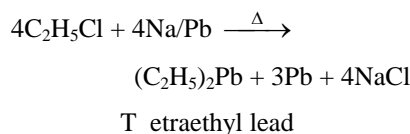
Trimethyl aluminium exists as stable dimer. In this, two methyl groups act as bridges between two aluminium atoms. The alkyl bridge is formed by multicentre bonding.

transition metals. Some examples of π -complexes are –

Transition metals usually form the π -bonded complexes. Ferrocene, Dibenzene chromium, Zeise's salt, etc. are some well known examples of the complexes belonging to this class.

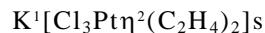
Metal carbonyls of transition metals constitute another important class of organometallic compounds. The first metal carbonyls, $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ were discovered by **A. Mond** in 1890 and 1891. Few more examples of metal carbonyls are $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$. 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 possesses both σ and π character.

Tetraethyl lead :

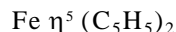


A colourless poisonous liquid, immiscible with water but miscible with ether. It is used as an antiknock compound in petrol engines.

Ziesse salt :



Ferrocene :



11.2 π -bonded organometallic compounds : This type of compounds are generally formed by