Unit 4

Basic Concept of Co-ordination Chemistry

(By Dr. B.C. Dixit)

In 1893 the swiss chemist werner proposed theroy called Werner's theory of coodination compounds to explain the bonding in coordination complexs. He was able to explain the nature of bonding of complexs and he concluded that in complexes molecule the metal shows two different type of valency.

(i) **Primary valencies :** These are non-directional. The complex commonly exists as a positive ion. The primary valency is the number of charge on the complex ion.

(ii) **Secondary valencies :** These are directional. The number of secondary valencies is equal to the number of ligand atoms coordinated to the metal ion. This is called the coordination number.

Generally, in coordination compounds, metals are surrounded by groups that are called ligands. Finally, Werner developed the concept of ligands surrounding to a central metal ion i.e. the concept of coordination complex and he determined the geometrical structures of many compounds. Due to his contribution in coordination chemistry he won Nobel prize for chemistry in 1913.

❇ General terminology to understand coordination chemistry :

(i) Simple Salts :

When an acid reacts with an alkali it produce salt and water. This types of reactions are known as neutralization reactions. e.g.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

When such types of salts are dissolved in water it give ions in solution. The nature of salt (acid or basic or normal) depends on extent of neutralization. Mixed salts contain more than one acidic or basic radicals e.g. $NaKSO_4$.

(ii) Molecular or Addition compounds :

When solutions having two or more kinds of salts (simple molecule) in stoichiometric amounts and are evaporated then we will obtain crystals of new compounds know as molecular or addition compounds.

There are two types of compounds depending on their behaviour in aqueous solution.

(a) Double salts or Lattice compounds : The addition compounds having the following characteristics are called double salt.

- They exist in crystalline state.
- When they dissolved in water it produces ions which are the same as the individual components of the double salts. e.g.

$$FeSO_4(NH_4)_2SO_4{\cdot}6\,H_2O \rightarrow Fe^{+2} + 2\,NH^{+}{}_4 + 2\,SO_4^{-2} + 26\,H_2O \quad \text{(aqueous state)}$$

(Mohr's salt)

$$K_2SO_4Al_2(SO_4)_3 \cdot 24\,H_2O \rightarrow 2\,K^{+} + 2\,Al^{+3} + 4\,SO_4^{-2} + 24\,H_2O \quad \text{(aqueous state)}$$

(Potash alum)

In aqueous solution double salts give the test of all their individual components and do not lose their identity.

(b) Coordination compounds (complex) : When solution of $Fe(CN)_2$ and KCN are mixed together and evaporated to dryness; give new compound $Fe(CN)_2{\cdot}4KCN$ (Potassium ferrocyanide). It dissociate in water but do not exibit the test of Fe^{+2} and CN^{-} ions, but gives the test for K^{+} and $Fe(CN)_6^{-4}$ ions.

$$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 \cdot 4KCN \rightleftharpoons 4K^{+} + Fe(CN)_6^{-4}$$

It is observed that the molecular compound $Fe(CN)_2{\cdot}4KCN$ lose their individual properties. Such molecular compounds are called coordination (or complex) compounds. Coordination compounds contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and complex anion. e.g. $K_2[Pt^{IV}Cl_6]$ $[Pt^{IV}(NH_3)_4Br_2]Br_2$ and $[Co^{III}(NH_3)_6]\,[Cr^{III}(C_2O_4)_3]$.

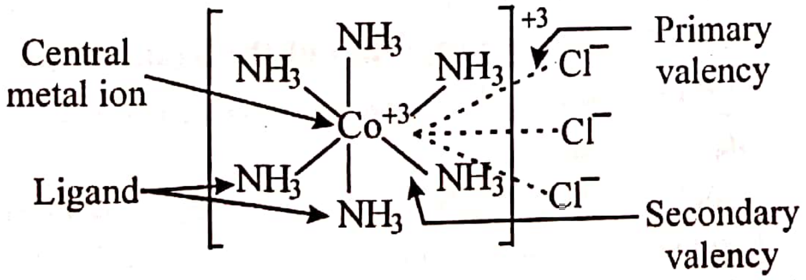
In the above complex compounds, the ions $[Pt^{IV}Cl_6]^{-2}$, $[Pt^{IV}(NH_3)_4\,Br_2]^{+2}$, $[Co^{III}(NH_3)_6]^{+3}$ and $[Cr^{III}(C_2O_4)_3]^{-3}$ are called **complex ions.**

(iii) Complex ion :

It is an electrically charged radical which is formed by the union of a metal cation with one or more neutral molecules or anions e.g. $[Pt^{IV}Cl_6]^{-2}$, $[Co^{III}(NH_3)_6]$ etc.

(iv) Coordination compound :

The compound in which the central metal atom or ion is attached to neutral molecules and / or ions in number exceeding the charge or oxidation number of atom/ion is called coordination compound e.g. $[Co(NH_3)_6]Cl_3$.



The central metal atom or ion have two types of valencies like (i) primary and (ii) secondary valencies. A definite number of lignds are bonded to the central metal atom or ion by secondary valencies and it has definite directions. The secondary valencies is also known as coordination number.

(v) Ligands :

The neutral molecules or ions (anions) bonded to the central metal ion by coordinate bond in the first coordination sphere are called ligand. e.g. $[Fe(CN)_6]^{-3}$. Here six CN^- ions are the ligands. Ligand generally acts as a donor partner i.e. it donates one or more pair of an electron to the central metal ion. But in metallic carbonyl CO molecule acts both as donor and acceptor, ($M \rightleftharpoons CO$). Ligands are arranged around the metal ion inside the first sphere of attraction in preferred geometries. The common geometries may be linear, equilateral triangular, tetrahedral, square planar, trigonal bipyramidal, square pyramidal and octahedral.

(vi) Coordination number (C.N.) or Ligancy :

The total number of donor atoms (coordinating atoms) directly attached to the central atom/ion is called coordination number. It represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands. e.g. In $[Fe^{III}(CN)_6]^{-3}$, the C. N. of Fe^{+3} is six. Similarly in $[Ni^{II}(NH_2-CH_2CH_2-NH_2)_3]^{+2}$, the C.N. of Ni^{+2} is also six, since each ethylene diamine molecule $NH_2CH_2CH_2NH_2$ has two donor nitrogen atoms. The number of ligand in $[Ni^{II}(NH_2CH_2CH_2NH_2)_3]^{+2}$ is only three.

(vii) Coordinating atom :

An atom of a ligand through which the ligand is attached to central metal atom or ion is called coordinating atom. e.g. $[Co(NH_3)_6]Cl_3$ (see page No. 117), NH_3 is ligand and it is attached to central metal atom through its nitrogen (N) atom. Thus nitrogen (N) atom of NH_3 is coordinating atom. There are six coordinating atoms.

(viii) Coordination sphere :

The central metal ion and a ligands that are directly attached to it are enclosed in a square bracket, which Werner called coordination sphere or first sphere of attraction. The anions outside the square bracket form the second sphere of attraction. e.g. $[Co(NH_3)_6]Cl_3$ (See page No. 117). Here Cl atoms are outside the square bracket, so it is in second sphere of attraction.

Classification of Ligands :

Ligands can be classify in the following two ways :

(1) Classification based on donor and acceptor properties of the ligands.

(i) Ligands having one or more lone pair of electrons.

Such ligands are further classified as under :

(a) Ligand which contain vacant π–type orbitals receive back donated π–electrons from the metal ion having low oxidation state such ligands are CO, NO, CN, isocyanides ($R-N=C$), R_3P, R_3As, α,α–dipyridyl, o–phenanthroline and unsaturated organic molecules. Such ligands also have filled donor orbitals in addition to vacant π–type acceptor orbitals. Thus in the complexes formed by these ligands have both type of (metal and ligand) function as donors and acceptors ($M \underset{\pi}{\overset{\sigma}{\rightleftharpoons}} L$).

(b) Ligand which do not contain vacant π–type orbitals. Such types of ligands have not vacant orbitals to receive back donated π–electrons from the metal e.g. H_2O, NH_3, F.

(ii) Ligands do not having lone pairs of electrons but having π–bonding electrons i.e. ethylene, benzene, cyclopentadienyl ion.

(2) Classification based on the number of donor atoms present in ligands.

Such types of ligands are further classify as under :

(i) **Monodentate or unidentate ligands :** The ligand having only one coordinating atom (one donor atom) are called monodentate ligands. e.g. NH_3, H_2O, Cl, OH, etc. These ligands may be neutral molecules, negatively charged (anions) or positively charged ions (cations) e.g.

(a) **Neutral monodentate ligands :** The names of such ligands are not systematic. e.g. H_2O (aquo), NH_3 (amine), CO (carbonyl), CS (thiocarbonyl), NO (nitrosyl), NS (thionitrosyl) etc.

(b) **Negative (anionic) monodentate ligands :** In naming of such ligands in which suffix ending 'e' is replaced by "o". e.g. –ite, –ate, –ide gives ito, –ato, –ido respectively.

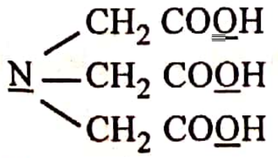
Some example of negative (anionic) ligands are : CH_3COO^- (acetato), F^- (fluoro), Cl^- (chloro), Br^-(bromo), I^- (iodo), CN^- (cyano), OCN^- (cyanato), SCN^- (thiocyanato) (When S–atom of the ligand coordinates with the metal ion), NCS – (isothiocyanato) (When N–atom coordinates with the metal ion), NO_2 (nitro) (when N – atom coordinate with metal ion), NO_2^- (nitrito) (when O–atom coordinate with metal ion), $\bar{O}H$ hydroxo or sometimes hydroxy), H^- (hydrido) etc.

(c) **Positive (cationic) monodentate ligands :** The name of ligands in which end 'in' is replaced by 'ium' e.g. NO^+ (nitrosylium) and $NH_2\,NH_3^+$(hydrazium).

(ii) **Bidentate Ligands :** The ligand containing two coordinating atoms are called bidentate ligands. e.g. ethylene diamine (en) $H_2\underline{N}CH_2CH_2\underline{N}H_2$. The underlined atom represent the coordinating atom.

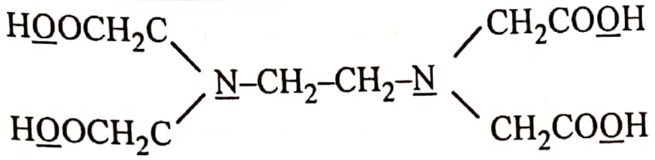
(iii) **Tri (ter) dentate ligands :** The ligand containing three coordinating atoms are called tri/ter dentate ligand, e.g. diethylene triamine (dien) $H_2\underline{N}CH_2\,CH_2\,\underline{N}HCH_2\,CH_2\,\underline{N}H_2$.

(iv) **Tetra (quardi) dentate ligands :** The ligand containing four coordinating atoms are called quardi dentate ligand. e.g. nitrilotriacetic acid (nta).

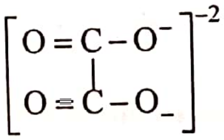


$$\underline{N}\begin{cases} CH_2\,CO\underline{O}H \\ CH_2\,CO\underline{O}H \\ CH_2\,CO\underline{O}H \end{cases} \quad \text{i.e.} \quad N(CH_2COOH)_3$$

(v) **hexa (sexa) dentate ligands :** The ligand containing six coordinating atoms are called hexa dentate ligand. e.g. ethylenediamine tetra acetic acid (edta).

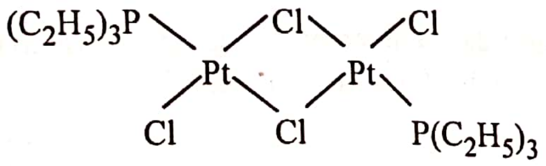


(vi) polydentate or multidentate ligands :

The ligand containing two or more coordinating atoms are called polydentate ligand (poly = many). The polydentate ligands may be further subdivided according to the nature of their donor atoms e.g. ethylene diamine $\underline{N}H_2(CH_2)_2\ \underline{N}H_2$ is a bidentate ligand with two neutral donor N – atoms, whereas oxalate ion  $\left[\begin{array}{c} O=C-O^- \\ | \\ O=C-O^- \end{array}\right]^{-2}$ is bidentate having two anionic donor oxygen atoms, Glycinato $[H_2\underline{N}\ CH_2CO\underline{O}^-]^-$ is also a bidentate with one neutral donor N–atom and one acidic donor oxygen atom.

Bridging ligands (polynuclear complex) :

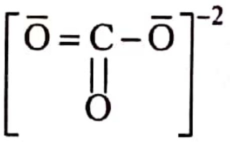
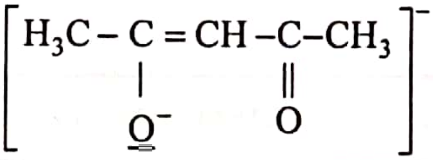
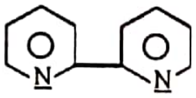
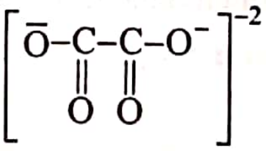
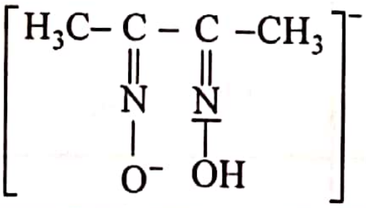
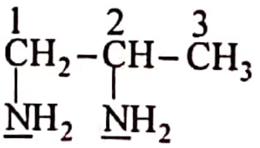
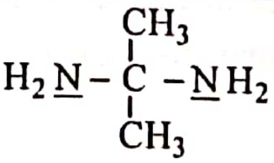
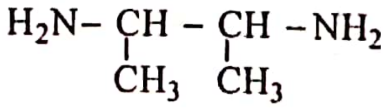
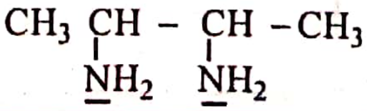
A complex with more than one central metal atom is called a polynuclear complex or bridge complex. i.e. a monodentate ligand may have more than one free electron pairs, may be simultaneously coordinate with two or more atoms. The ligand forms two σ–bonds with two metal atoms / ions and acts as a bridge between metal atoms. Such ligand is called a bridge ligand and a complex is known as a bridge complex. e.g.

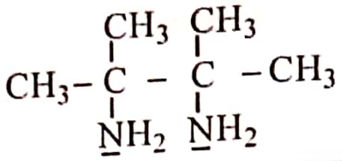
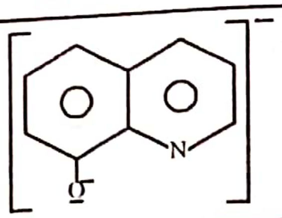
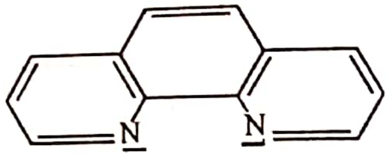
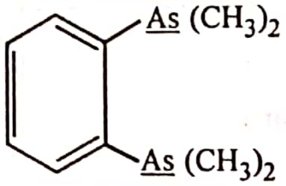
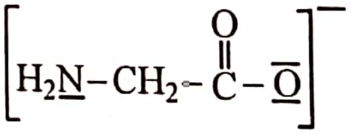
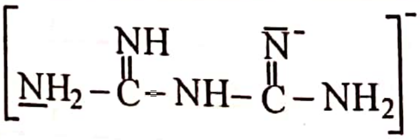
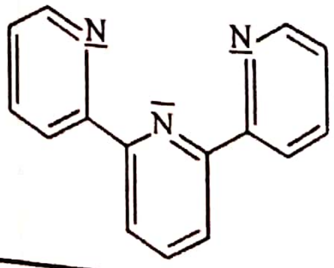


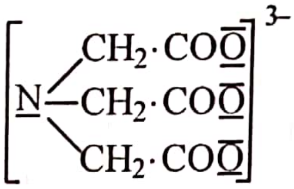
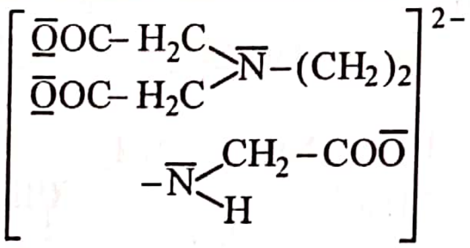
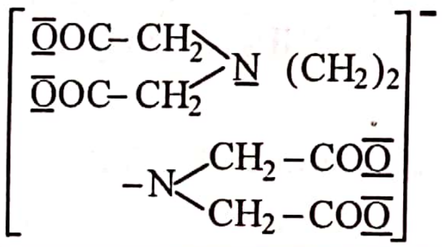
Examples of bridge ligands are : OH^-, F^-, Cl^-, NH_2, CO, O_2^-, SO_4^{-2} etc.

Symmetrical and unsymmetrical bidentate ligands : Bidentate ligands may be symmetrical or unsymmetrical. In symmetrical bidentate ligands both coordinating atoms are same, while in unsymmetrical bidentate ligands, both coordinating atoms (donor atoms) are different.

Some of the comon polydentate ligands are given below : (The underlined atom represent coordinating donor atoms.)

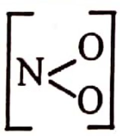
Type of ligand	Name of ligand	Abbreviation	Structure
Bidentate	Carbonato	CO_3^{-2}	 $\left[\bar{O}=\underset{\underset{O}{\|}}{C}-\bar{O}\right]^{-2}$
Bidentate	Acetylacetonato	$(acac)^-$	 $\left[H_3C-\underset{\underset{\underline{O}^-}{\vert}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3\right]^-$
Bidentate	2,2'–Dipyridyl or 2,2'–dipyridine	dipy	
Bidentate	Oxalato	$(ox)^{-2}$	 $\left[\bar{O}-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-O^-\right]^{-2}$
Bidentate	Dimethyl glyoximato	$(dmg)^-$	 $\left[H_3C-\underset{\underset{\underset{O^-}{\vert}}{\underline{N}}}{\underset{\|}{C}}-\underset{\underset{\underset{OH}{\vert}}{\underline{N}}}{\underset{\|}{C}}-CH_3\right]^-$
Bidentate	Ethylene diamine	en	$H_2\underline{N}CH_2CH_2\underline{N}H_2$
Bidentate	Propylene diamine or 1,2–diamino propane	pn	 $\underset{\underset{\underline{N}H_2}{\vert}}{\overset{1}{C}H_2}-\underset{\underset{\underline{N}H_2}{\vert}}{\overset{2}{C}H}-\overset{3}{C}H_3$
Bidentate	Isobutylene diamine	i-bn	 $H_2\underline{N}-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-\underline{N}H_2$
Bidentate	Butylene diamine	bn	 $H_2N-\underset{\underset{CH_3}{\vert}}{CH}-\underset{\underset{CH_3}{\vert}}{CH}-NH_2$ **OR**  $CH_3\,\underset{\underset{\underline{N}H_2}{\vert}}{CH}-\underset{\underset{\underline{N}H_2}{\vert}}{CH}-CH_3$

Bidentate	Tetra methyl ethylene diamine	tetrameen	 $CH_3-\overset{CH_3}{\underset{\underline{N}H_2}{C}}-\overset{CH_3}{\underset{\underline{N}H_2}{C}}-CH_3$
Bidentate	8–hydroxyquinolinato (8HQ)	(oxin)⁻ or (oxinate)⁻	
,,	1,10-phenathroline or o-phenathroline	o-phen	
,,	o–phenylene dimethyl arsine	diars or D	
,,	Glycinato	(gly)⁻	 $[H_2\underline{N}-CH_2-\overset{O}{\overset{\|}{C}}-\underline{\overline{O}}]^-$
,,	Biguanido	(Big)⁻	 $[\underline{N}H_2-\overset{NH}{\overset{\|}{C}}-NH-\overset{\overline{N}^-}{\overset{\|}{C}}-NH_2]^-$
Tri dentate	Diethylene triamine	dien	$H_2\underline{N}-(CH_2)_2-\underline{N}H-(CH_2)_2-\underline{N}H_2$
	Imino–di–acetato	$(IDA)^{2-}$	$[\overline{O}OC-H_2C-\underline{N}H-CH_2-CO\overline{O}]^{2-}$
	2,2',2"-terpyridine	terpy	

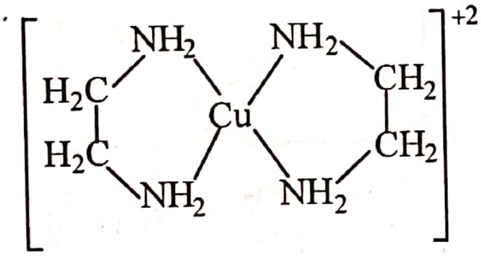
Tetra dentate	Triethylene tetramine	trien	$H_2\underline{N}-(CH_2)_2\underline{N}-(CH_2)_2-\underline{N}H$ $-(CH_2)_2-\underline{N}H_2$
	Nitrilo triacetato	[N $^{-3}$	
Penta– dentate	Ethylene diamine triacetato	–	
Hexa– dentate	Ethylene diamine tetracetato	$(EDTA)^{4-}$ or Y^{4-}	

Ambidentate ligands : The ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal ion at a given time is known as ambidentate ligands. Some examples are given below :

Make a Table

Ligand	**Name**
 ion	Nitro ($M-NO_2$) Nitrito ($M-ON=O$)
CN^- ion	Cyano (MCN) Isocyano (MNC)
NCS^- ion	Thiocaynate (MSCN) Isothiocyanate (MNCS)
NCO^- ion	MOCN, MNCO
$SeCN^-$ ion	MSeCN, MNCSe
R_2SO	S–bonded or O-bonded
$S_2O_2^{2-}$ ion	Thiosulphato–S ($MSSO_3$) Thiosulphato–O ($MOSO_2S$)

Chelation : When a multidentate (polydentate) ligand uses more than one of its coordinating atom to form two or more coordinate bonds with the same central metal atom, the resulting complex containing closed rings is called chelate compound. The process is known as chelation. The increase in the stability of complexes containing chelated ligands is called chelate effect. As chelate compounds are formed by multidentate ligands, the multidentate ligands are known as chelating ligands. It should be noted that every multidentate ligand is not necessary to be a chelating ligand. The coordinated atoms of the ligand may be so arranged that they cannot be coordinated to the same metal atom to produce a ring structure. Thus $\underline{N}H_2CH_2CH_2\underline{N}H_2$ is a chelating ligand.

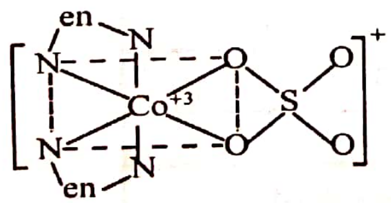


Bis (ethylene diamine) copper(II) ion

Chelate effect : The difference in stability between metal chelate and the analogous simple complex is called as chelate effect.

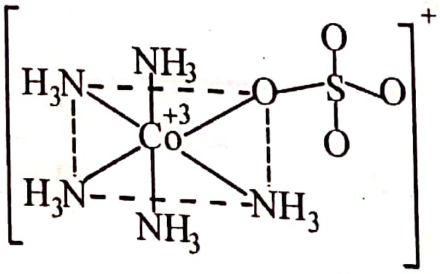
Flexidentate character of polydentate ligands : Polydentate ligands have flexidentate character, it means, it may not use all its donor atoms to get coordinated to the metal ion. e.g. EDTA acts as a hexadentate ligand, function as a pentadentate ligand in $[Cr^{III}(OH)\ (HEDA)]^{-2}$ and $[Co^{III}(Br)(HEDTA)]^{-2}$ and tetradentate ligand in $[Pd^{II}\ (H_2EDTA)]^{o}$.

In $[Co^{III}\ (NH_3)_5SO_4]^+$ and $[Co^{III}\ (en)_2\ SO_4]^+$ complex sulphate group acts as a mono dentate and bidentate ligand respectively and give six and eight absorption bands due to S – O vibrations respectively. In Fig. (a) Sulphate group acts as a bindentate group. In Fig. (b) oxygen atom of the sulphate group is covalently bonded to Co^{+3}. Thus Fig. (a) and (b) showing flexidentate character of SO_4^{-2} ion.



(a)

$[Co^{III}(en)_2SO_4]^+$ ion



(b)

$[Co^{III}(NH_3)_5SO_4]^+$ ion

Classification of chelates :

The polydentate ligands may be attached to the central metal ion through two types of functional groups like acidic group and coordinating group to form covalent bond and coordinate bond respectively. The classification of chelates follows the number and type of bond by ligand with metal ion. The covalent bonds are formed by replacement of one or more H – atoms from acidic groups present in the ligand by the metal atom. The common acidic groups are – COOH, – SO_3H, – OH and = NOH (oxime). Coordinating bond formed by the donation of an electron pair from the ligand without replacement of H – atom. e.g. $-NH_2$, –NH, $-\overset{|}{\underset{|}{N}}:$, =NOH (oxime), –OH, C=O and –S–O–(thio ether). Chelates have application in day to day life to medical science.

Uses of chelates :

(i) In analytical chemistry : Some ions quantitatively identified by the formation of stable and coloured chelates e.g. Al^{+3}, Ni^{+2}, Mg^{+2} ete. Chelate agents are used for the titration of certain metal ions.

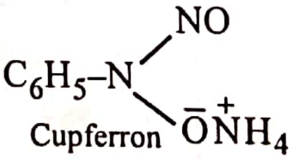
(ii) In water softening

Due to hardness of water (Ca^{+2} and Mg^{+2} ions), soap form sticky precipitation and wasted. But by complexing the metal ions, we can prevent, the precipitation of soap with Ca^{+2} and Mg^{+2} ions. So excess complexing agents such as polyphoshates and poly dentate amino acids present in hard water can prevent the precipitation. Thus hard water is effectively softened.

Sequestration : The suppression of the precipitation reaction of Ca^{+2} and Mg^{+2} ions, which are responsible for the hardness of water is known as sequestration.

(iii) In the elimination (to remove) of harmfull radioactive metals from the body : EDTA (ethylene diamine tetraacetic acid) is the best chelating agent, therefore, it is used in the elimination of harmfull radioactive metals from the body.

(iv) In solvent extraction : Some neutral chelate have low solubility in water but they have considerable solubility in organic solvents.

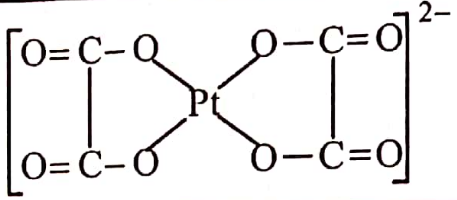
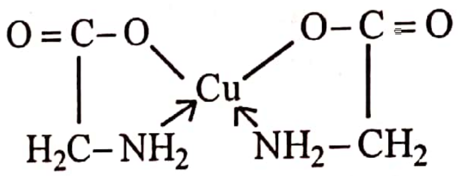
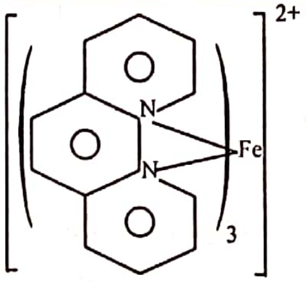
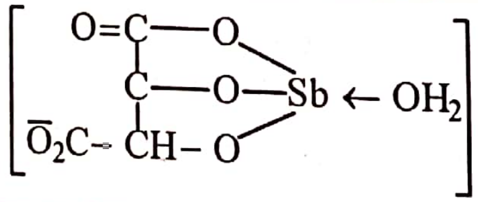
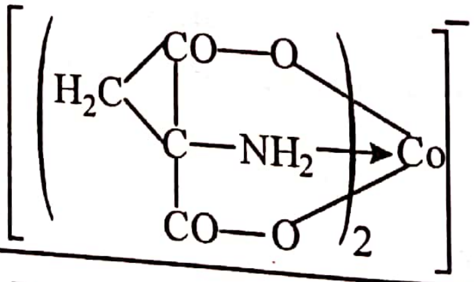
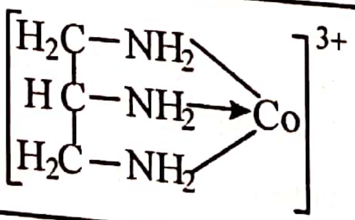
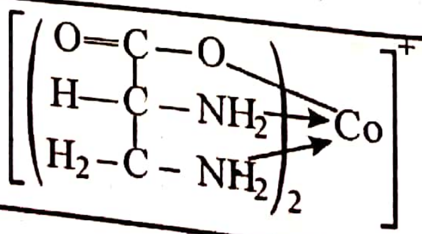


Cupferron

Thus, in presence of ligands that are capable to form inner complexes, many metals like Zr and Hf can be extracted into water – immiscible organic phase. e.g. Trifluoroacetylacetone is very important organic solvent for extraction of Zr and Hf metals. Also cupferron used in refinement of a number of metals.

(v) In food preservation : Fruit, fruit juices, food stuffs etc. are preserved with the help of some chelating compounds.

Types of Chetates

Type of Chelates	Type of Linkages	Example of Chelates
1. Bidentate	Two covalent linkages	
	One covalent and one co–ordinate linkage	 Cu–glycinate
	Two coordinating linkages	 Ferrous orthophenothroline complex ion
2. Tridentate	Three covalent linkages	
	Two covalent and one coordinate linkage	
	Three coordinating linkages	
	One covalent and two coordinating linkages	

Coordination number and stereochemistry of complexes :

Every metal has a characteristic coordination number. The coordinate bonds to the ligands are directed in space, so, as to give a definite geometrical arrangement.

(1) Coordination number (C.N.) 2 : Only metal ions with d^{10} configuration forms complex (Cu^+ have C. N. 2). Thus Cu^+, Ag^+, Au^+ and Hg^{+2} ions form such complexes. The geometry for this C.N. is linear so, such geometry have minimum ligand repulsion. e.g. $Cu(CN)_2^-$, $Cu(NH_3)_2^+$, $Ag(NH_3)_2^+$, $Ag(CN)_2^-$, $Au(CN)_2^-$, $Hg(NH_3)_2^{+2}$ and $Hg(CN)_2$.

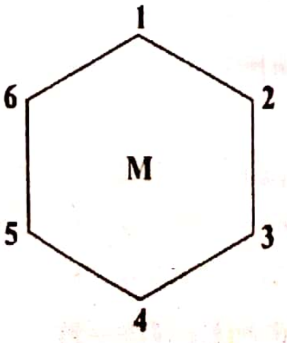
(2) Coordination number (C.N.) 3 : This coordination number is rare. If complexes have C.N. 3 then it shows two possible geometries like (i) equilateral triangular and (ii) trigonal pyramidal $[HgI_3]^-$ in which I^- ions are arranged at the corners of a slightly distorted equilateral triangle and Hg^{+2} present in its centre. Thus, $[HgI_3]^-$ complex has distorted equilateral triangle geometry. $[H_3O]^+$ has trigonal pyramidal geometry.

(3) Coordination number 4 : Complexes with C.N. 4 may be tetrahedral or square planar in geometry e.g. $ZnCl_4^{-2}$, $ZnBr_4^{-2}$, $Zn(CN)_4^{-2}$, $Zn(NH_3)_4^{-2}$, $Cu(CN)_4^{-2}$, CuX_4^{-2} ($X = Cl^-$, Br^-, I^-, CNS^-), $Hg(CN)_4^{-2}$, $\left[Ni(CO)_4\right]^0$, $FeCl_4^-$ are tetrahedral. Some oxyanions such as VO_4^{-3}, CrO_4^{-2}, FeO_4^{-2} and MnO_4^- are also tetrahedral.

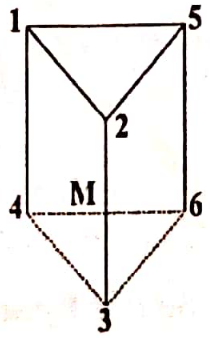
Square planar geometry is formed in complexes of Cu^{+2}, Ni^{+2}, Pt^{+2}, Pd^{+2}, Au^{+3} etc. ions. e.g. $[Cu(en)_2]^{+2}$, $Cu(NH_3)_4^{+2}$, $Ni(NH_3)_4^{+2}$, $Ni(CN)_4^{-2}$, $[Ni(dmg)_2]^0$, $Pt(NH_3)_4^{+2}$, $PdCl_4^{-2}$, $AuCl_4^-$ etc.

(4) Coordination number 5 : This coordination number is very rare. Two different geometries are possible for C.N. 5. Trigonal bipyramidal and square pyramidal. e.g. $Fe(CO)_5$, $Fe(CO)_4R_3P$, $Fe(CO)_3(R_3P)_2$, $[Mn(CO)_5]^-$, $CuCl_5^{-3}$, $SnCl_5^-$, $[Cu(dipy)_2\,I]$ etc, have trigonal bipyramidal geometry while $[VO(acac)_2]$, $NiBr_3[(C_2H_5)_3P]_2$ have square pyramidal structure.

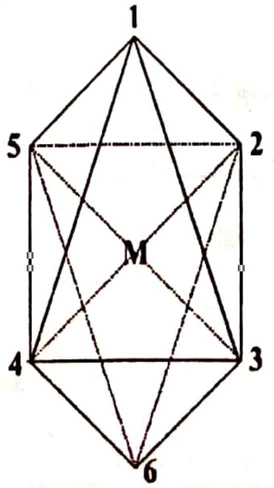
(5) Coordination number 6 : This coordination number is most comon. The geometrical arrangement of ligands around the central metal ion are possible (i) Hexagonal planar (ii) Trigonal prism (iii) Octahedral (regular octahedral).



Hexagonal planar

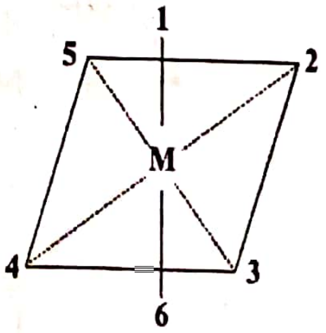


Trigonal prismatic

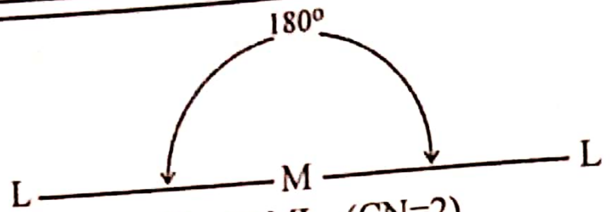


Regular octahedral

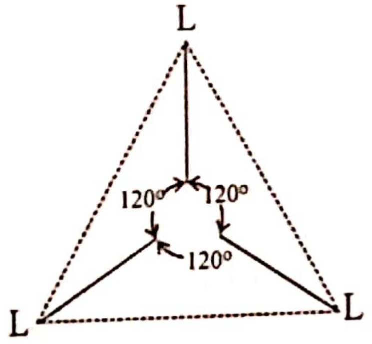
OR



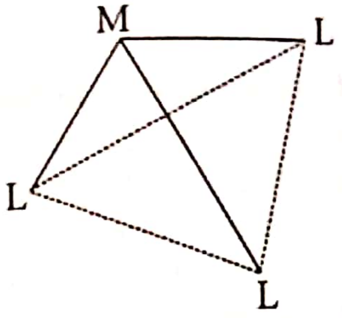
Octahedral



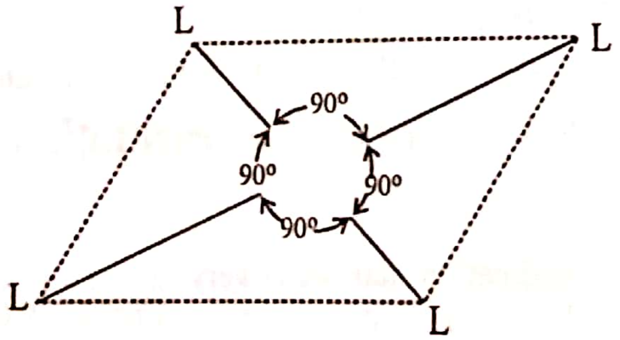
Linear ML_2 (CN=2)



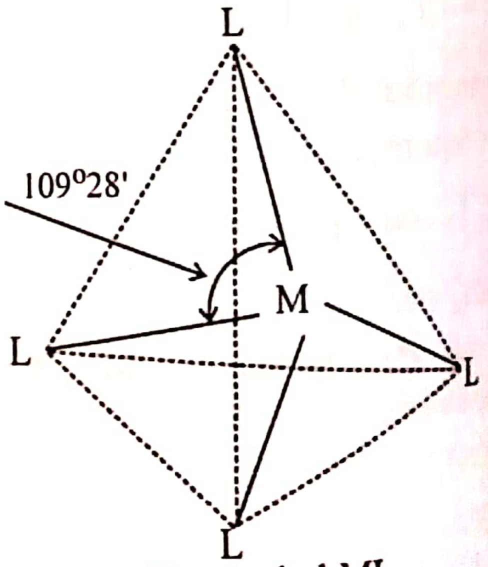
Equilateral triangular ML_3 (CN=3)



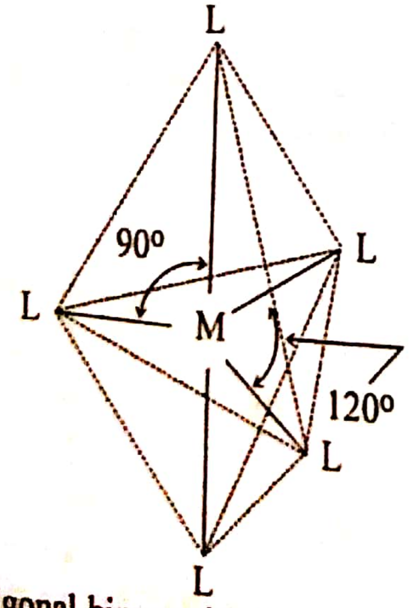
Trigonal Pyramidal ML_3 (CN=3)



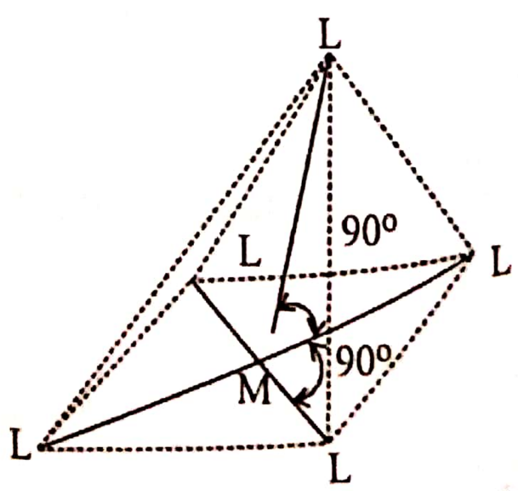
Square planar ML_4 (CN=4)



Tetrahedral ML_4 (CN=4)



Trigonal bipyramidal ML_5 (CN=5)



Square Pyramidal ML_5 (CN=5)

Complexes with such coordination number are mostly formed by transition metal ions. The six ligands in complexes may be arranged around the central metal ion, M, either at the corners of hexagonal plane or at the center of a regullar octahedron. These arrangements with numbers designating substitution positions may be represented as shown in above figures. The study of the geometrical and optical isomers of complexes with C. N. 6 indicate that arrangement of six ligands in complex is always octahedral and other possible geometries like hexagonal planar and trigonal prismatic (prism) are of historical interest only and are not preferred geometries for 6–coordination complex. Werner find out the theoretical number of geomtrical isomers for the complexes like ML_6, ML_5L', $ML_4L'_2$, $ML_3L'_3$. The complexes $ML_4L'_2$ have only two geometrical isomers like hexagonal planar and trigonal prism. Three isomers of hexagonal planar geometry are possible. This is like the structure of disubstituted benzene (1,2; 1,3; 1,4) like ortho, meta and para. Only two isomers for regular octahedral geometry are known like (1, 2) and (1, 6) similarly for $ML_3L'_3$ complexes have two geometrical isomers and have only octahedral geometry.

Further, the hexagonal and trigonal prism geometries do not predict any optical isomers for the complex like $[M(AA)_3]$, where (AA) is a symmetrical bidentate ligand. But octahedral shape predicts two isomers like mirror – image isomers. Hence, Werner concluded that 6–coordinate complex have octahedral geometry is the preferred geometry. The distortion is important for an octahedral complex like $[Cu(NH_3)_4(H_2O)_2]^{+2}$ and it becomes tetragonal which arises due to the elongation of the ligands along Z–axis.

Nomenclature of coordination compounds :

The fundamental rules of nomenclature was first suggested by Werner. These rules have been modified by committee of the IUPAC. Trivial names for certain coordination compounds is still in use, e.g. $[Fe^{II}(CN)_6]^{-4}$ and $[Fe^{III}(CN)_6]^{-3}$ are called ferrocyanide and ferricyanide respectively instead of hexacyanoferrate (II) and hexacyanoferrate (III) ions respectively as given by IUPAC system. The complexes are classified on the basis of nature of the cation and anion.

(i) Cationic complexes, e.g. $[Cr(H_2O)_4Cl_2]^+$, $[Cu(NH_3)_4]^{+2}$, $[Ni(en)_2Cl_2]^{+2}$ etc.

(ii) Anionic complexes, e.g. $[Cr(en)I_4]^-$, $[Pt(NH_3)Cl_5]^-$, $[Fe(CN)_6]^{-4}$, $[Fe(CN)_6]^{-3}$ etc.

(iii) Ionic complexes : These contains simple complex cation and simple or complex anion. e.g.

$$K_2^+[PtCl_6]^{-2},\ [Pt(NH_3)_4Br_2]^{+2}Br_2^-,\ \left[Pt(py)_4\right]^{+2},\ \left[PtCl_4\right]^{-2}$$

(iv) Neutral complexes : These are non–ionic or molecular complexes, i.e. $[Ni(CO)_4]^o$, $[Co(NO_2)_3(NH_3)_3]^o$

Following rules are consider for naming all types of complexes mentioned above.

(i) The cation is given name first. It is followed by anion.

(ii) In naming the complex, the names of ligands are written first in the order (a) anionic ligand (b) neutral ligand and (c) cationic ligands. After the name of ligands, the name of central atom is written.

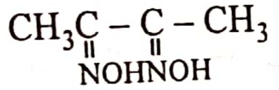
(iii) There is no characteristic endings in the name of cationic and neutral complexes. The names of anionic complexes ends in "ate".

(iv) The oxidation state (oxidation number) of the central atom is indicated by Roman number in parantheses.

(v) If the complex contain various types of ligands then ligands are named in alphabetical order. The prefixes di, tri etc. are not to be considered. e.g. $[Co(NH_3)_4(NO)_2 Cl]^{+2}$ ion is named as tetraminechloronitro cobalt (III) ion.

(vi) Name of ligands are given as shown below :

(a) The name of anionic ligands or anion name ends in –O. In general, if the name of anion ends in –ide, –ite or ate, the final –e is replaced by –O, giving –ido, –ito and –ato respectively e.g. SO_3^{-2} (Sulphito), SO_4^{-2} (Sulphato), CH_3COO^- (acetato), S^{-2} (Sulphido or thio), NO_3^- (nitrato), NH^{-2} (Imido), NH_2^- (amino or amine), N_3^- (azido), NHOH (hydroxylamido),



$CH_3\underset{NOH}{\underset{\|}{C}} - \underset{NOH}{\underset{\|}{C}} - CH_3$ (Dimethyl glyoximato).

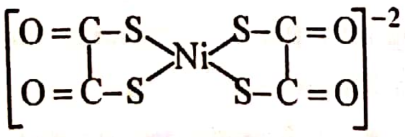
Following are the exceptions :

F^- (fluoro), Cl^- (chloro), CN^- (cyano), O^{-2} (oxo), OH^- (hydroxo), O_2^{-2} (peroxo), O_2H^- (perhydroxo), H^- (hydro), Br^- (bromo), S^- (thio), $C_2O_4^{-2}$ (oxalato).

(b) The neutral ligands are given name as the name of molecule. Exceptions are given below : H_2O (aquo), NH_3 (amine), CO (carbonyl), NO (nitrosyl), CS (thiocarbonyl), NS (thionitrosyl).

(c) Positive ligands have suffix (end) –ium, e.g. $NH_2NH_3^+$ (hydrazinium) and NO^+ (nitrosylium).

(d) To indicate the number of identical ligands, the prefixes di, tri, tetra, penta etc. are used before the name of ligands. If the name of ligand itself contains prefixes like di, tri, tetra, penta etc., the prefixes are bis, tris, tetrakis, pentakis etc. are used before the name of ligands. e.g.



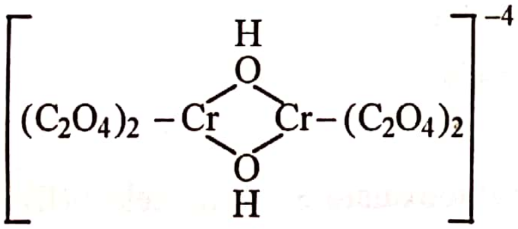
The simple ligands such as Cl^-, CH_3COO^-, $C_2H_4^{-2}$ etc. is indicated by using before them the Greek prefixes like di, tri, tetra, penta, etc. In case of chelating ligands like ethylene diamine (en), trialkyl phosphine the prefixes (like bis, tris, tetrakis, pentakis etc.) are placed in bracket. e.g.

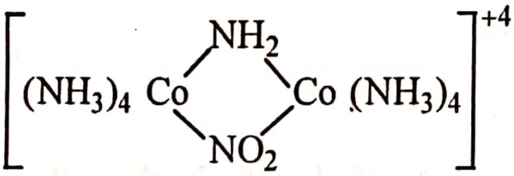
$[Co^{III}(NH_3)_2(en)_2]Cl_3$ → diamine bis(ethylene diamine)cobalt (III) chloride.

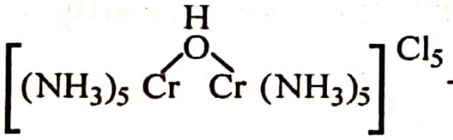
$[Co^{III}(en)_3]_2(SO_4)_2$ → tris (ethylene diamine) cobalt (III) sulphate

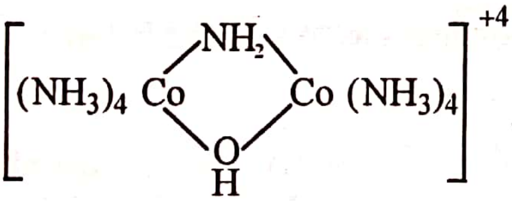
$[Fe^{II}(CN)_2(CH_3NC)_4]$ → dicyano tetrakis (methylisocyanide) iron (II).

(vii) In polynuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens and by adding the prefix 'μ' before its name. The Greek letter 'μ' should be repeated before the name of each different bridging group. If two or more bridging groups of the same kind are their then they are indicated by di–μ, tri–μ etc. e.g.

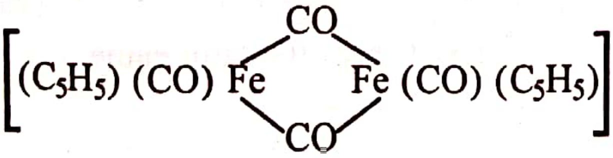

→ di–μ–hydroxotetraoxalato dichromate (III) ion.


→ μ–amido–μ–nitro octaamine dicobalt (III) ion.


→ μ–hydroxy–bis {pentaamine chromium(III)} chloride.


→ μ–amino–μ–hydroxo octa amine dicobalt (III) ion.

$[(CO)_3Fe(CO)_3Fe(CO)_3]$ → Tri–μ–carbonyl – bis (tricarbonyl iron).


→ Di–μ–carbonyl – bis (carbonyl cyclopentadienyl iron)

If a bridging group, bridge by more than two metal ions, then μ_3, μ_4 etc, should be used to indicate the number of central atoms. e.g.

$[Be_4O(CH_3COO)_6]$ is called μ_4 – oxo–hexa – μ–acetatotetraberyllium (II). The comon name of this compound is basic beryllium acetate.

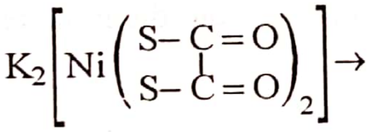
(vii) (viii) In case of ambidentate ligands (the ligands which can be coordinated to central metal ion through either of two donor atoms are **called ambidentate ligands**) such as –SCN (thiocyanate), –NCS (isothiocyanate), $-NO_2$ (nitro) and – ONO (nitrito), the symbol of the element coordinated with the metal ion is written after the name of the ligand. e.g. thiooxalate–S for a thio–oxalate group coordinated to metal ion through sulphur atom and similarly thio–oxalato–O coordniated through oxygen atom. e.g.

$[Co(NH_3)_5-ONO]Cl_2$ → Nitro–O (or Nitrito) complex

$[Co(NH_3)_5-NO_2]Cl_2$ → Nitro–N (or Nitrato) complex

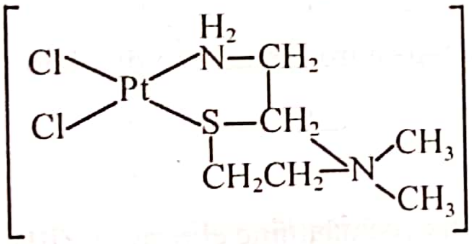
$[Pd(diph)(SCN)_2]$ → Thiocynate – S complex

$[Pd(diph)(NCS)_2]$ → Thiocynate – N complex



$$K_2\left[Ni\left(\begin{array}{l} S-C=O \\ \quad\;\, | \\ S-C=O \end{array}\right)_2\right]$$

→ Potassium bis (dithiooxalato S, S') nickelate (II)



→ Dichloro (N, N–dimethylamino ethylamino ethyl sulphide–N', S)platinum(II)

Naming the central metal ion and mononuclear complexes :

Different rules are used for naming different complexes as mentioned below :

(i) For anionic complexes :

Ligands are named first and then the central metal ion. The suffix "ate" is attached to the name of central metal ion and after that (without a space) write the oxidation state of the metal ion by Roman numeral (like I, II, III, IV etc.) in the parantheses. Put (0) for an oxidation state of zero. If negative oxidation state, the negative sign (–) is placed before the Roman numeral. In some cases, the metal name is derived from the latin name, e.g.

Ag → Argentate, Au → Aurate, Cu → Cuprate

Fe → Ferrate, Pb → plumbate

e.g. $[Cr^{III}(en)I_4]^-$ → Tetra iodo (ethylene diamine) chromate (III) ion.

(ii) For cationic and neutral complexes :

For cationic and neutral complexes, the ligands are named first and then its oxidation state by a Roman numeral in parentheses followed by central metal ion to indicate its oxidation state. The suffix "ate" is not attached to the name of the metal ion. e.g.

$[Cr^{III}(H_2O)_4Cl_2]^+$ → Dichlorotetraaquochromium (III) ion.

The neutral and cationic ligands are placed in the order of H_2O, NH_3, other inorganic ligand and then organic ligands in alphabetical order. e.g.

$[Cr^{III}Cl(H_2O)(en)_2]^{+2}$ → Chloroaquobis (ethylene diamine) chromium (III) ion.

(iii) For ionic Complexes :

In ionic complexes, the cation is named first and then the anion as we did in naming a simple salt like NaCl. The rules for naming the anionic and cationic parts of ionic complexes are the same as mentioned above in (i) and (ii) respectively. e.g.

$K_2[Pt^{IV}Cl_6]$ → Potassium hexachloro platinate (IV)

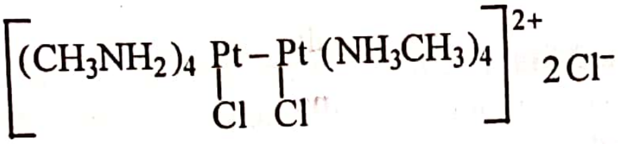
The names of some mononuclear ionic complex compounds are given below :

Composition	**Cation and anion type**	**Name**
$K_2[Pt^{IV}Cl_6]$	Simple cation, K^+ and complex anion $[Pt^{IV}Cl_6]^{2-}$	Potassium hexa chloro platinate (IV)
$NH_4[Cr^{III}(SCN)_4(NH_3)_2]$	Simple cation, NH_4^+ and complex anion. $[Cr^{III}(SCN)_4(NH_3)_2]^-$	Ammonium tetrathiocyanato diammine chromate (III)
$[Pt^{II}(Py)]_4[Pt^{II}Cl_4]$	Complex cation, $[Pt^{II}(Py)_4]^{2+}$ and complex anion $[Pt^{II}Cl_4]^{2-}$	Tetrapyridine platinum (II) tetrachloroplatinate (II)
$[Co^{III}(NH_3)_6]Cr^{III}(C_2O_4)_3]$	Complex cation $[Co^{III}(NH_3)_6]^{3+}$ and complex anion $[Cr^{III}(C_2O_4)_3]^{3-}$	Hexammine cobalt (III) trioxalato chromate (III)
$[Pt^{IV}(NH_3)_4Br_2]Br_2$	Complex cation, $[Pt^{IV}(NH_3)_4Br_2]^{3+}$ and Simple anion Br^-	Dibromo tetrammine platinum (IV) bromide
$[Fe^{III}(H_2O)_4(C_2O_4)]_2SO_4$	Complex cation, $[Fe^{III}(H_2O)_4C_2O_4)]^+$ and simple anion SO_4^{2-}	Oxalato - tetra aquoiron (III) sulphate

It should be noted that the names of cation and anion are separated by a space and the number of each type of ion is not indicated.

3. Metal – to metal bonding

For complexes containing metal – to metal bonds, the prefix bi–is used before the name of the metals forming a metal – to metal bond e.g. the name of the complex having the formula,

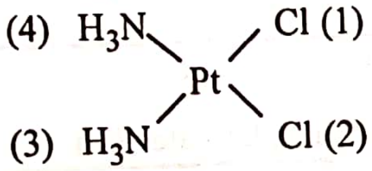


$$\left[(CH_3NH_2)_4\underset{Cl}{Pt}-\underset{Cl}{Pt}(NH_3CH_3)_4\right]^{2+} 2Cl^-$$

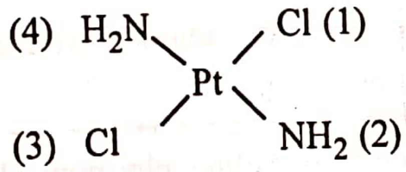
is syn–dichloro octakis (methyl–amine) bi–platinum (II) chloride.

Geometrical isomers :

Geometrical isomers are named either by using the prefix cis for adjacent positions and trans for opposite positions before the name of the ligands or by numbering system.



Cis – diammine dichloro platinum (II) or 1,2–dichloro diamine platinum (II)



trans – diammine dichloro platinum (II) or diammine–1, 2 dischloro platinum (II)

Lets have some practice for writing IUPAC name of different type of complexes.

Anionic complexes :

$[Cr^{III}(en)Br_4]^-$ → Tetrabromo (ethylene diamine)chromate (III) ion
$[Pt^{IV}(NH_3)Cl_5]^-$ → Pentachloro mono – ammine platinate (IV) ion
$[Zn^{II}(OH)_4]^{-2}$ → Tetrahydroxo zincate (II) ion
$[Ag^{I}Cl_2]^-$ → Dichloro argentate (I) ion
$[Fe^{II}(CN)_6]^{-4}$ → Hexacyano ferrate (II) ion (ferrocyanide ion)
$[Fe^{III}(CN)_6]^{-3}$ ⇒ Hexacyanoferrate (III)ion (ferrocyanide ion)
$[Ni(CN)_4]^{-4}$ → Tetracyanonicklate (0) ion
$[Co^{-I}(CO)_4]^-$ → Tetracarbonylcobaltate (–I) ion
$[BrF_4]^-$ → Tetrafluorobromate (III) ion
$[Cr^{III}(C_2O_4)_3]^{-3}$ → Trioxalatochromate (III) ion
$[Ag^{I}(SCN)_2]^-$ → Dithiocyanatoargentate (I) ion
$[Co(CN)(CO)_2NO]^{-2}$ → Cyanodicarbonylnitrosylcobaltate (0) ion

Cationic Complexes :

$[Cr^{III}(H_2O)_6]^{+3}$ → Hexaaquochromium (III) ion

$[Ag^{I}(NH_3)_2]^{+}$ → Diammine silver (I) ion

$[Cu^{II}(NH_3)_4]^{+2}$ → Tetra – ammine copper (I) ion

$[Al^{III}(OH)(H_2O)_5]^{+2}$ → Hydroxopentaaquoaluminium (III) ion

$[Ni^{IV}(en)_2Cl_2]^{+2}$ → Dichioro bis(ethylene diammine) nickel (IV) ion

$[Co^{III}(NH_3)_6]^{+3}$ → Hexaamnine cobalt (III) ion

$[Co^{III}Br(H_2O)(NH_3)_4]^{+2}$ → Bromoaquotetrammine cobalt (III) ion

$[Co^{II}(NH_3)_2(en)_2]^{+2}$ → Diamnine bis(ethylenediamine) cobalt (II) ion

$[Pt^{II}Cl(en)NH_3NH_2]^{+2}$ → Chloro(ethylenediammine) hydrazinium platinum (II) ion

Neutral Complexes :

$[Ni(CO)_4]^{o}$ → Tetracarbonyl nickel(0)

$[Co^{III}(NO_2)_3(NH_3)_3]^{0}$ → Trinitrotriammine cobalt (III)

$[Co^{III}Cl_3(NH_3)_3]$ → Trichlorotriammine cobalt (III)

$[CoCl_2(CH_3NH_2)_2]$ → Dichloro bis(methylamine) cobalt (II)

$[CoCl_3(NH_3)_2(CH_3)_2NH]$ → Trichlorodiamnine(dimethylamine) cobalt (III)

$[Fe(C_5H_5)_2]$ → bis(cyclopentadienyl)iron (II)

$[Cu(acac)_2]$ → bis(acetylacetonate)copper (II)

Cis – $[PtCl_2(NH_3)_2]$ → Cis–dichlorodiamnine platinum (II)

trans – $[PtCl_2(NH_3)_2]$ → trans–dichlorodiamnine platinum (II)

Ionic Complexes :

$[Co^{III}(en)_3]_2(SO_4)_3$ → tris(ethylenediamine) cobalt (III) Sulphate

$[Pt^{IV}ClNO_2(NH_3)_2(en)]SO_4$ → Chloronitrodiammine (ethylenediamine)platinum (IV) sulphate

$K_2[pt^{IV}Cl_6]$ → potassium hexachloro platinate (IV)

$NH_4[Cr^{III}(SCN)_4(NH_3)_2]$ → Ammoniumtetrathiocyanatodiammine chromate (III)

$[pt^{II}(py)_4[Pt^{II}Cl_4]$ → Tetrapyridine platinum (II) tetrachloroplatinate (II)

$[Co^{III}(NH_3)_6][Cr^{III}(C_2O_4)_3]$ → Hexaammine cobalt (III) trioxalatochromate (III)

$[Pt^{IV}(NH_3)_4Br_2]Br_2$ → Dibromo–tetraammine platinum (IV) bromide.

$[Fe^{III}(H_2O)_4(C_2O_4)]_2SO_4$ → Oxalatotetraaquo iron (III) sulphate.

$[CoBr(H_2O)(NH_3)_4](NO_3)_2$ → Bromoaquotetrammine cobalt (III) nitrate.

$K[CrOF_4]$ → Potassium oxotetrafluoro chromate (V)

$K[SbCl_5(C_6H_5)]$ → Potassium pentachloro (phenyl) antimonate (V)

$H_2\ [PtCl_6]$ → haxachloroplatinic (IV) acid

$Na_2\ [Fe(CN)_5NO]$ → Sodium pentacyanonitrosyl ferrate (III)

$[Co(NH_3)_6]\ [CO(CN)_6]$ → Hexaammine cobalt (III) hexacyano cobaltate (III)

$[Ptpy_4]\ [PtCl_4]$ → tetrakis (pyridine) platinum (II) tetrachloroplatinate (II)

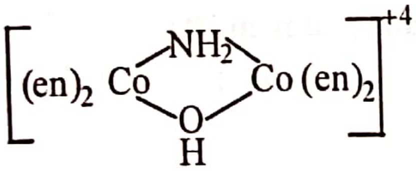
$[(CO)_3\ Fe\ (CO)_3\ Fe\ (CO)_3]$ → Tri–μ–Carbonyl–bis (tricanbonyl iron)

$[Co(NH_3)_4(NO_2)Cl]^+$ → Chloro tetrammine nitro cobalt (III) ion

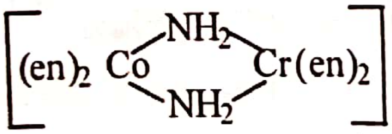
$[Co^{III}(NH_3)_2(en)_3]Cl_3$ → diammine tris (ethylenediamine) cobalt (III) chloride

Difference between Coordination or complex compound and double salt.

Coordination compound	Double salt (lattice compound)
(i) They may or may not contain salt in stochiometric amount.	(i) They contain salt in stochiometric amount.
(ii) They do not exibit (positive test) properties of individual components.	(ii) They exibit properties of individual components.
(iii) Out of two ions (cation and anion), one or both ion may be complex ion.	(iii) They dissociate into simple cations and anions.

1. 

Bis (ethylenediamine) Cobalt (III)–μ–~~imido~~amino–μ–hydroxo bis (ethylenediamine) cobalt (III) ion.

2. 

Bis (ethylene diamine) cobalt (III) di–μ–amino – bis (ethylenediamine) chromium (III) ion

3. $[PtCl_2(NH_3)_4]Br_2$ Dichlorotetra ammine platinum (IV) bromide
4. $Na_3\ [Fe\ (CN)_6]$ Sodium hexacyanoferrate (III)
5. $Na_2\ [Co(NO_2)_6]$ Sodium hexanitritocobaltate (III)
6. $[Co(NO_2)\ (NH_3)_5]\ SO_4$ Nitro penta ammine cobalt (III) sulphate
7. $[Al(H_2O)_6]^{+3}$ Hexaquoaluminium (III) ion
8. $[Ag\ (CN)_2]^-$ Dicyano argentate (I) ion.

Numerically coordination number represents the total number of the chemical bonds formed between the central metal atom and the donor atoms of the ligand.

(j) **Ambidentate ligand :** The ligands which can be coordinated to the central metal ion through either of the two donor atoms are called ambidentate ligand.

For example, $[Co(NH_3)_5\ NO_2)]\ Cl_2$ exists in two linkage isomers $[Co(NH_3)_5\ ONO]Cl_2$ (nitrite isomer) and $[Co(NH_3)_5\ NO_2]\ Cl_2$ (nitro isomer).

(k) **Co-ordination sphere :** The central metal ion and the ligands that are directly attached to it are enclosed in a square bracket which is called Co-ordination sphere or first sphere of attraction. The anion being outside the square bracket forms the second sphere of attraction.

(l) **Molecular or addition compounds :** When solutions containing two or more salts in stoichiometric (i.e. simple molecular) proportion are allowed to evaporate, gives crystals of compounds known as molecular or addition compounds.

There are two types of molecular or addition compounds depending upon their behaviour in aqueous solution. They are (i) Double Salt or Lattice compound and (ii) co-ordination (or complex) compounds.

(m) **Lattice compound (Double Salt) :** The addition compounds having the following characteristics are called double salt or lattice compound.

(a) They exist as such in crystalline state.

(b) When dissolved in water, these dissociate into ions in the same way in which the individual components of double salts do.

$$FeSO_4(NH_4)_2\ SO_4\ 6H_2O \rightarrow Fe^{+2}_{(aq)} + 2NH^{+}_{4(aq)} + 2SO^{2-}_{4(aq)} + 6H_2O$$

Mohr's salt

$$K_2SO_4Al_2(SO_4)_3 24H_2O \rightarrow 2K^{+}_{(aq)} + 2Al^{+3}_{(aq)} + 4SO_4^{2-}(aq) + 24\,H_2O$$

Potash alum.

(n) **Polynuclear complex (Bridging complexes) :** The complexes having two or more metal atoms are called Polynuclear complex (Bridging complexes).

In this complex the bridging group is indicated in the formula of the complex by hyphens and by adding the prefix μ before its name