MOLECULAR COMPOUNDS

UNIT 1

When solution of two or more simple stable salts are mixed together in simple molecular proportion (or stoichiometric amounts) and the solution thus obtained is allowed to evaporate, crystals of a new compound are obtained. This new compound is called addition or molecular compound. The formation of some addition compounds has been shown below:

Simple compounds ***Addition compounds***

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$$

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow \underset{\text{Mohr's salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

Types of Addition Compounds:

Double Salts and Coordination (or complex) Compounds

1. **Double salts :** These compounds lose their identity in solution. These compounds are stable in the solid state but give their constituent ions when dissolved in water or in any other ionic solvent. In these compounds the individual properties of the constituent ions are not lost.

   Example : $\underset{\text{Double salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O} \longrightarrow \underset{\text{constituent ions}}{Fe^{2+}, SO_4^{2-}, NH_4^+}$

2. **Coordination (or complex) compounds :** These compounds donot give all their constituent ions when dissolved in water. In these compounds the individual properties of some constituent ions are lost and some are retains.

$$CuSO_4 \cdot 4NH_3 \rightleftharpoons \underset{\substack{\downarrow \\ \text{retain their identity}}}{[Cu(NH_3)_4]^{2+}} + SO_4^{2-}$$

Thus $CuSO_4 \cdot 4NH_3$ is formulated as $[Cu(NH_3)_4]SO_4$.

A neutral complex compound like $[Ni^0(CO)_4]$ $[Ni^{2+}(dmg)_2]^0$, $[Pt^{2+}(NH_3)_2Cl_2]^0$ etc., does not undergo ionisation and hence does not give any ions in aqueous solution.

Coordination chemistry.

The branch of inorganic chemistry that deals with the study of coordination compounds is called coordination chemistry.

Complex ion

Complex ion is a positively or negatively charged species which contains a central metal cation/atom and a suitable number of ligands surrounding the central metal cation/atom. The central metal atom may be in zero, positive or negative oxidation state. The ligands may be either neutral molecules or anions (generally) or a combination of the neutral molecules and anions.

Depending on the nature of the charge on the complex ion ,complex ion may be cationic complex ion or anionic complex ion. Cationic complex ion has positive charge on it while anionic complex ion has negative charge. Thus $[Co^{3+}(NH_3)_6]^{3+}$ and $[Co^{3+}(NH_3)_5Cl]^{2+}$ are cationic complex ions and $[Ni^0(CN)_4]^{4-}$ and $[Fe^{2+}(CN)_6]^{4-}$ are anionic complex ions.

Neutral Complex:

A complex which has no charge on it is called neutral complex. lt is a non electrolyte, does not undergo ionisation and hence does not give any ions in aqueous solution. Examples of neutral complexes are $[Co^{3+}(NH_3)_3Cl_3]^0$, $[Ni^0(CO)_4]^0$, $[Pt^{2+}(NH_3)_2Cl_2]^0$, $[Ni^{2+}(dmg)_2]^0$ etc.

Coordination Sphere and Ionisation Sphere

While writing the structural formula of a given complex compound the central metal atom and the ligands attached with it are always written in a square bracket, [ ]. This square bracket is called coordination (or inner) sphere. The portion outside the coordination sphere is called ionisation (or outer) sphere. Thus in $[Co(NH_3)_5Cl]Cl_2$, the square bracket which contains the central metal ion (Co^{3+} ion) and the ligands (five NH_3 molecules and one Cl^- ion) is coordination sphere and the portion that contains two Cl^- ions is ionisation sphere.

The species written in ionisation sphere are ionisable and hence can be precipitated by means of a suitable precipitating agent while those given in the coordination sphere (i.e., metallic atom and ligands) are non-ionisable and hence cannot be precipitated. This is shown below for $[Co(NH_3)_5Cl]Cl_2$.

$$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

Two Cl^- ions present in ionisation sphere can be precipitated as AgCl (white ppt) by adding $AgNO_3$ solution.

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

Cl^- ion written in coordination sphere is not ionisable and can therefore, not be precipitated.

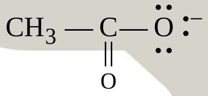
Classification of Ligands

Depending on the number of donor a toms of a ligand coordinated to the central metallic atom, the ligands have been classified in two classes.

1. **Monodentate or unidentate ligands.** The ligands which have only one donor atom or are co-ordinated through one electron pair are called monodentate or unidentate ligands. Such ligands are coordinated to the central metal ion at one site or by one metal-ligand bond only.

2. **Polydentate or multidentate ligands.** These may be bidentate, tridentate, tetradentate, pentadentate and hexadentate, if the number of donor atoms present in one molecule of the ligand attached with the central metallic atom is 2, 3, 4, 5 and 6 respectively. Thus one molecule of these ligands is coordinated to the central metallic atom at 2, 3, 4, 5 and 6 sites respectively.

Table : Examples of Monodentate Ligands

(a) Neutral ligands name					
$(C_2H_5)_3N$	.....	Triethyl amine	$(C_6H_5)_3P$	.....	Triphenyl phosphine
$NH_2–NH_2$ or N_2H_4	.....	Hydrazine	CH_3CN	.....	Acetonitrile
CH_3NH_2	.....	Methyl amine	O_2 or $:\ddot{O}=\ddot{O}:$	.....	Dioxygen
NH_2OH	.....	hydroxylamine	N_2 or $:N\equiv N:$	.....	Dinitrogen
$(CH_3)_2NH$	.....	Dimethylamine	PF_3	.....	Phosphorus trifluoride
C_5H_5N or py	.....	Pyridine	$(C_2H_5)_3P$	.....	Triethyl phosphine
(b) Neutral ligands					
CO	.....	Carbonyl	NO	.....	Nitrosyl
CS	.....	Thiocarbonyl	NS	.....	Thionitrosyl
H_2O	.....	Aqua	NH_3	.....	Ammine
(c) Anionic (negative) ligands. The names of negative ligands end in *o*. Examples are given below:					
F^-	.....	Fluoro (fluorido)	Cl^-	.....	Chloro (Chlorido)
Br^-	.....	Bromo (bromido)	I^-	.....	Iodo (Iodido)
H^-	.....	Hydrido	 $CH_3-\underset{\underset{O}{\parallel}}{C}-\ddot{\underset{\cdot\cdot}{O}}:^-$	.....	Acetato
NH_2^-	.....	Amido	NH^{2-}	.....	Imido
			OH^-	.....	Hydroxo
O^{2-}	.....	Oxo (Oxido)			
O_2^{2-} or $^-:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^-$	.....	Peroxo	O_2^-	.....	Superoxo
HS^-	.....	Mercapto	S^{2-}	.....	Sulphido
SO_3^{2-}	.....	Sulphito	SO_4^{2-}	.....	Sulphato
CO_3^{2-}	.....	Carbonato	CN^-	.....	Cyno (coordination through C-atom)
NC^-	.....	Iso-cyano (coordination through N-atom)			
CH_3O^-	.....	Methoxo			

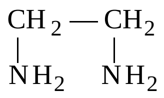
N_3^-	.....	Azido	NO_2^-	.....	Nitro (coordination through N-atom
ONO^-	.....	Nitrito (coordination through O-atom	SCN^-	.....	Thiocyanato
NCS^-	.....	Iso-thiocyanto	NO_3^-	.....	Nitrato

Polydentate ligands are further classified as:

Bidentate Ligands

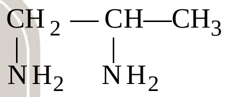
Bidentate ligands may be neutral molecules or anions. For example

Ethylene diamine (*en*)



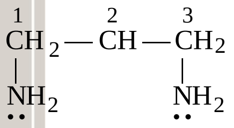
$\underset{NH_2}{CH_2}-\underset{NH_2}{CH_2}$

Propylene diamine or 1, 2-diamino propane (*pn*)



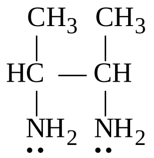
$\underset{NH_2}{CH_2}-\underset{NH_2}{CH}-CH_3$

1, 3-diamino propane or trimethylene diamine (*tn*)



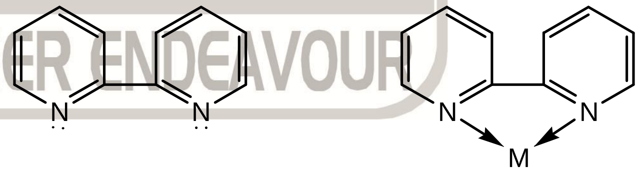
$\underset{\ddot{N}H_2}{\overset{1}{CH_2}}-\overset{2}{CH}-\underset{\ddot{N}H_2}{\overset{3}{CH_2}}$

Buthylene diamine (*bn*)



$\underset{\ddot{N}H_2}{\overset{CH_3}{HC}}-\underset{\ddot{N}H_2}{\overset{CH_3}{CH}}$

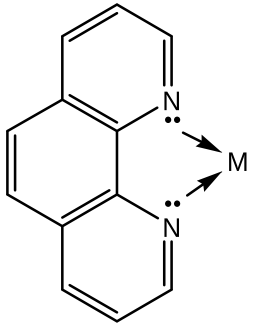
2, 2-bipyridine (bpy) (or bipyridyl)



(a) **(b)**

Some important bidentate ligands are as follows:

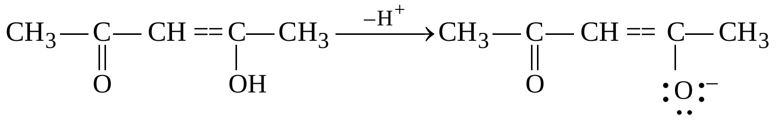
(i) o-phenanthroline or 1, 10-phenanthroline (o-phen or phen) :



Example : $[Fe(Phen)_3]^{2+}$

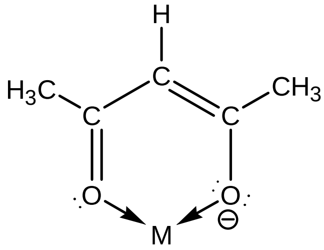
Bidentate

(ii) Acetylacetonato ion (acac$^-$) : This ion is obtained when one molecule of the enol form of acetyl acetone (Hacac) loses a proton. H$^+$

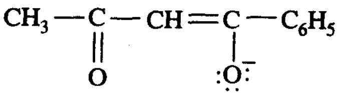


$$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{-H^+} CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{:\ddot{O}:^-}{|}}{C}-CH_3$$

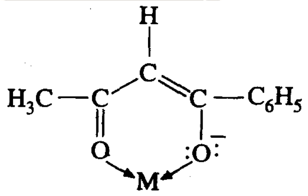
This ligand gets attached with the central metal atom through its two O-atoms and forms a chelated complex having one 6-membered ring.



(iii) Benzoyl acetonato ion :

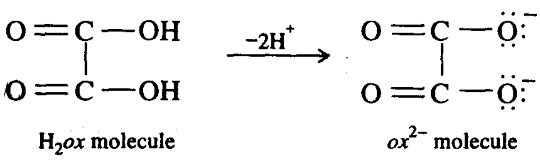


(*a*)

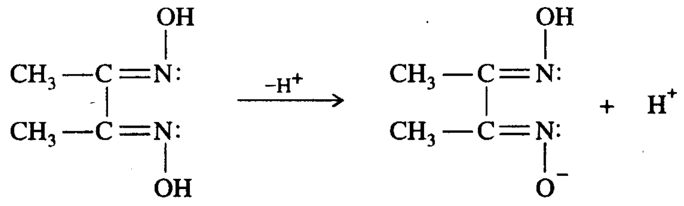


(*b*)

(iv) Oxalato ion, $C_2O_4^{2-}(ox^{2-})$ **:** This ion can be obtained when one molecule of oxalic acid ($H_2C_2O_4$) loses two protons.



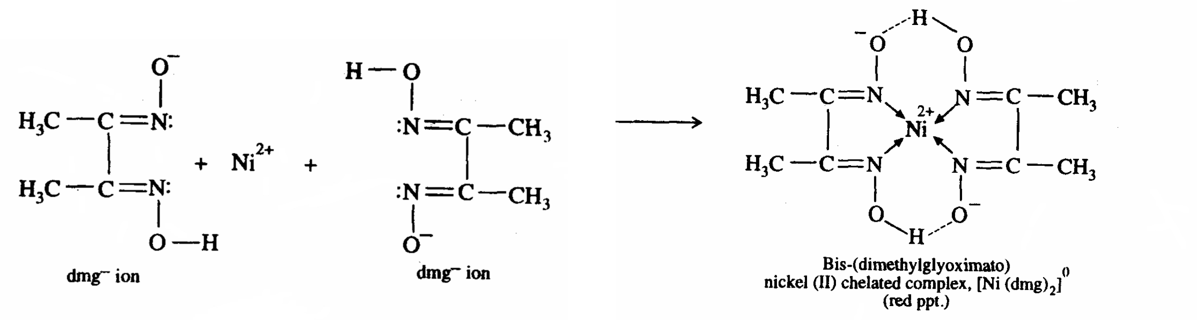
(v) Dimethyl glycoximato ion (dmg$^-$ or DMG$^-$) : This ion is obtained when one OH group attached with N atom in Hdmg molecule loses a proton.



Dimethyl glyoxime (Hdmg or HDMG)

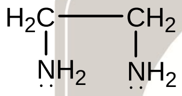
dmg$^-$ or DMG$^-$

Two dmg$^-$ ions react with Ni^{2+} or Pd^{2+} ion in ammoniacal solution and form an insoluble neutral red chelated complex. $[M(dmg)_2]^0$ (M = Ni^{2+}, Pd^{2+}) which has two 5-membered and two 6-membered ring.

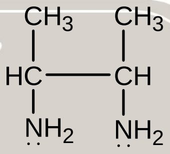


Symmetric and Unsymmetric Bidentate Ligands:

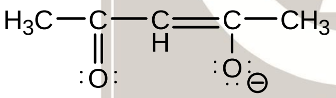
Symmetrical bidentate ligands are those in which the two donor atoms are the same while unsymmetrical bidentate ligands are those in which the two donor atoms are different. Thus a symmetrical bidentate ligand is denoted by (*AA*) in which two *A*'s are two similar donor atoms while an unsymmetrical bidentate ligand is denoted as (*AB*) in which *A* and *B* are two different donor atoms. Example of symmetrical bidentate ligands are given below.



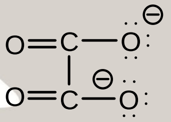
Ethylene diamine, en
(N, N)



Butylene diamine, bn
(N, N)



Acetylacetonato, acac⁻
(O, O⁻)



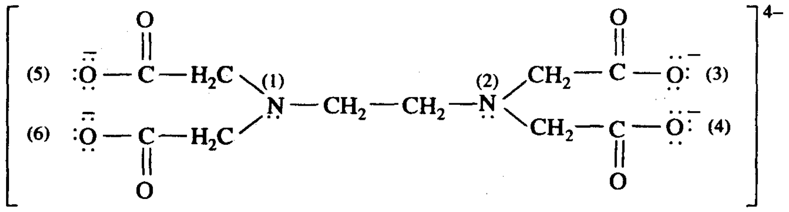
or $C_2O_4^{2-}$

Oxalato, OX^{2-}
(O, O⁻)

Hexadentate Ligand

Six donor atoms are present in these ligands.

Example : Ethylene diamine tetracetate ion (edta^{-4} or EDTA^{-4}) is an important example of hexadentate ligand.



It has two neutral N-atoms (numbered as 1 and 2) and four negatively-charged O-atoms numbered as 3, 4, 5 and 6) as its donor atoms. Thus it is tetrabasic hexadentate ligand. The co-ordination of this ligand to the metal atom takes place through two N-atoms and four O-atoms, forming five 6-membered rings.

Ambidentate Ligands and Linkage Isomerism:

These ligands have two or more different donor atoms. Such ligands can coordinate to the metal atom through any of their atoms at a time and hence are given different names corresponding to the nature of donor atoms linked to the metal atom. Amidentate ligands show linkage isomerism. Linkage isomerism arises due to the tendency of the ambidentate ligand to link to the metal atom in different ways through its two different donor atoms.

1. NO_2^- ion:

(a) When NO_2^- ion gets coordinated to the metal atom through a lone pair of electron on N-site, it is called nitro ligand. The complexes containing nitro ligand are called nitro complexes. For example $[Co^{3+}(NH_3)_5(NO_2)]Cl_2$ (yellow brown) is called pentammine nitro cobalt (III) chloride.

(b) When NO_2^- ion gets coordinated to the metal atom through a lone a pair of electrons on O-site. It is called nitrito ligand which is written as $ON\bar{O}$. The complexes containing nitrito ligand are called nitrito complexes. For example $[Co^{3+}(NH_3)_5(ONO)]Cl_2$ (red) is called pentammine nitrito cobalt (III) chloride.

Both nitro and nitrito complex compounds mentioned above are called linkage isomers and the isomerism shown by them is called linkage isomerism.

2. SCN^- ion:

(a) When SCN^- ion gets coordinated to the metal atom through the lone pair on negatively-charged S-atom $[M \leftarrow \bar{S}CN]$, it is called thiocyanto ligand. The complexes containing thiocyanato ligand are called thiocyanato complexes.

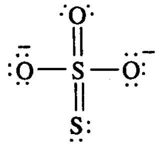
(b) When the coordination of $SC\bar{N}$ ion to the metal atom takes place through N-atom $[M \leftarrow \bar{N}CS]$, this ion is called isothiocyanato ligand. The complex compounds having $\bar{N}CS$ ion as a monodentate ligand are called isothiocyanato complexes.

3. Cyanide ion, CN^-

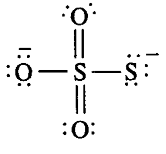
(a) When this ion gets linked to the metal atom as a monodentate ligand through C-atom [M ← CN], this ion is called cyano ligand.

(b) When this ion is linked to the metal atom as a monodentate ligand through N-atom (M ← NC), this ion is called isocyano ligand.

4. Thiosulphate ion, $S_2O_3^{2-}$: This ion can have any of the following two structures:



[Thiosulphato – O ion, OSO_2S^{2-}]

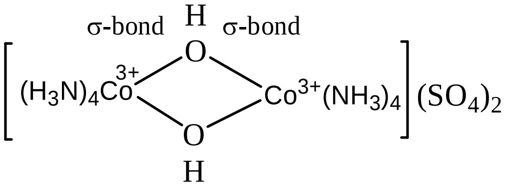


[Thiosulphato – S ion, SSO_3^{2-}]

Bridging Ligands and Bridged Complexes

In coordination chemistry a bridging ligand is a ligand that connects two or more atoms. e.g. N_2 , N_2H_4 , OH^-, NH_2^-, NH^{2-}, Cl^-, F^- , O^{2-}, O_2^{2-}, O_2^-, SO_4^{2-}, NO_2^-, CO etc. are monodentate ligands, they also act as bidentate ligands when they are attached with two separate metals atoms, making a bridge between them. Such ligands are called bridging ligands and the complexes thus formed are called bridged (or polynuclear or multinuclear) complexes.

Example :



Bridging complex

Flexidentate Ligands

There are several ligands which has two or more donor atoms. There ligands can coordinate with metal atom or ion either through one donor atoms forming non-chelated complex or two donor atom forming a chelate. These ligands are called Flexidentate ligands.

e.g. SO_4^{2-}, CO_3^{2-}, NH_2NH_2, N_2 etc.

SOLVED PROBLEM

1. Choose the correct formula of Mohr's salt

(a) $FeSO_4.(NH_4)SO_4.6H_2O$ (b) $FeSO_4.(NH_4)_3SO_4.24H_2O$

(c) $Fe(NH_4)_2SO_4.24H_2O$ (d) $FeSO_4.(NH_4)_2SO_4.6H_2O$

Soln. $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)

Correct answer is (d)

2. Which of the following are correct

(i) CH_3NH_2, NH_2OH, CS are neutral ligands

(ii) CO, H_2O, pyridine, N_2H_4 are neutral ligands

(iii) CS, , SCN, are anionic ligands

(iv) ethylenediamine, ethylene diphosphine, bipyridyl and isobutylene diamine are bidentate ligands

(a) (iv) (b) (i), (ii), (iv)

(c) (iii), (i) (d) All of the above

Soln.

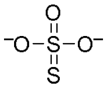
Neutral ligands	Anionic ligands	Bidentate ligands
CH_3NH_2	N_3^-	Ethylene diamine
NH_2OH	SCN^-	Ethylenediphosphine,
CS		Bipyridyl
CO		Isobutylene diamine
H_2O		
Pyridine		
NH_2NH_2		

Correct answer is (b)

3. Which of the following is ambidentate ligands

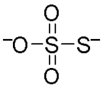
(a) $S_2O_3^{2-}$ (b) $C_2O_4^{2-}$ (c) DMG (d) gly

Soln. $S_2O_3^{2-}$



$^{-}O-\overset{O}{\underset{S}{S}}-O^{-}$

(Thiosulphato - O ion)



$^{-}O-\overset{O}{\underset{O}{S}}-S^{-}$

(Thiosulphato - S ion)

Correct answer is (a)

4. Mohr's salt is a/an **[JNU-2010]**

(a) simple salt (b) coordination compound

(c) organometallic compound (d) double salt

Soln. Double salts are salts containing more than one cation or anion and are obtained by combination of two different salts.

Example : Mohr's salt $[(NH_4)_2Fe(SO_4)_2.6H_2O]$

Correct option is (d)

5. Coordinate covalent compounds are formed by **[JNU-2012]**

(a) transfer of electrons only (b) sharing of electrons only

(c) donation of electrons (d) transfer and sharing of electrons

Soln. The covalent bond that forms when both electrons are donated by the same atom is called coordinate covalent bonds.

Correct option is (c)