CHAPTER-2

MOLECULAR COMPOUNDS

Molecular Compounds

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***

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{Carnallite}}{KCl \cdot MgCl_2 \cdot 6H_2O}$$

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

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

$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{Tetrammine copper sulphate}}{CuSO_4 \cdot 4NH_3}$$

$$Fe(CN)_2 + 4KCN \longrightarrow \underset{\text{Potassium ferrocyanide}}{Fe(CN)_2 \cdot 4KCN}$$

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. For example when carnallite $KCl{\cdot}MgCl_2{\cdot}6H_2O$ which is a double salt gives its constituent ions namely K^+ Mg^{2+} and Cl^- ions when dissolved in water and hence the aqueous solution of $KCl{\cdot}MgCl_2{\cdot}6H_2O$ gives the tests of K^+, Mg^{2+} and Cl^- ions.

2. **Coordination (or complex) compounds :** These compounds retain their identity in solution. These compounds donot give all their constituent ions when dissolved in water. ln these compounds the individual properties of some constituent ions are lost. For example $CuSO_4{\cdot}4NH_3$ which is a complex compound does not give all its constituent ions *viz.* Cu^{2+} and SO_4^{2-} in solution. lt gives only SO_4^{2-} ion and Cu^{2+} ion is obtained as $[Cu(NH_3)_4]^{2+}$ ion which is called *complex ion.*

$$CuSO_4 \cdot 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Thus $CuSO_4{\cdot}4NH_3$ is formulated as $[Cu(NH_3)_4]SO_4$. lt follows from this discussion that $CuSO_4{\cdot}4NH_3$ gives the tests of SO_4^{2-} only and not show the tests of Cu^{2+} ions. $[Cu(NH_3)_4]SO_4$ is called complex (or coordination) compound. A complex compound compose of simple cation and complex anion as shown below :

$$K_3[Fe(CN)_6] \rightleftharpoons \underset{\text{Simple cation}}{3K^+} + \underset{\text{Complex anion}}{[Fe(CN)_6]^{3-}}$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons \underset{\text{Complex cation}}{[Co(NH_3)_6]^{3+}} + \underset{\text{Simple anion}}{3Cl^-}$$

$$[Pt(NH_3)_4][PtCl_4] \rightleftharpoons \underset{\text{Complex cation}}{[Pt(NH_3)_4]^{2+}} + \underset{\text{Complex anion}}{[PtCl_4]^{2-}}$$

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. Examples of complex ions are $[Co^{3+}(NH_3)_6]^{3+}$, $[Ni^0(CN)_4]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Co^{3+}(NH_3)_5Cl]^{2+}$ etc.

It may be seen that, 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. It 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.

Ligands or Coordinating groups and central metallic atom

The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called ligands or co-ordinating groups. In Lewis sense in most of the complex compounds the ligands act as Lewis bases (electron pair donors)and the central metal ion acts as a Lewis acid (electron pair acceptor), i.e., in most of the complex compounds the ligands donate one or more electron pairs to the central metal ion.

$$\underset{\substack{\text{Central metal ion}\\\text{(Lewis acid or electron}\\\text{pair acceptor)}}}{M^{n+}} + \underset{\substack{\text{Ligand}\\\text{(Lewis base or electron}\\\text{pair donor)}}}{x\,L} \longrightarrow \underset{\substack{\text{Complex}\\\text{compound}}}{[ML_x]^{n+}}$$

In some complex compounds the ligand acts as donor and acceptor. For example, in metallic carbonyls, CO molecules which act as ligands act both as donor and acceptor ($M \rightleftarrows CO$). In a ligand the atom which actually donates the electron pair to the central metal ion is called donor or coordinating atom. The ligands are attached with the central metal ion through their donor atom (or atoms).

The metallic atom with which the ligands are attached through co-ordinating bonds is called central metallic atom .

This metallic atom may be in zero, positive or negative oxidation state.

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.

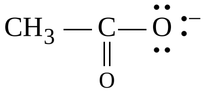
Classification of Ligands

Depending on the number of donor atoms of a ligand coordinated to the central metallic atom, the ligands have been classified as monodentate (or unidentate) and polydentate (or multidentate) ligands.

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)

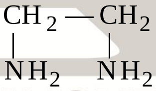
H^-	.....	Hydrido	CH_3COO^- or  $CH_3-\underset{\underset{O}{\Vert}}{C}-\ddot{\underset{\cdot\cdot}{O}}:^-$	.....	Acetato
NH_2^-	.....	Amido	NH^{2-}	.....	Imido
$[(CH_3)_2N]^-$	.....	Dimethyl amido	OH^-	.....	Hydroxo
O^{2-}	.....	Oxo (Oxido)	HO_2^-	.....	Perhydroxo
O_2^{2-} or $^-:\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}:^-$	.....	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)	$S_2O_3^{2-}$	.....	Thiosulphato
CH_3O^-	.....	Methoxo	$C_2H_5O^-$	.....	Ethoxo
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

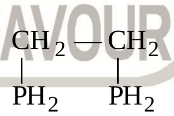
Bidentate ligands may be neutral molecules or anions. For example

Ethylene diamine (*en*)



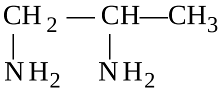
$$\underset{NH_2}{\underset{|}{CH_2}}-\underset{NH_2}{\underset{|}{CH_2}}$$

Ethylene diphosphine (*diphos*)



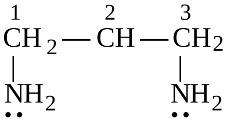
$$\underset{PH_2}{\underset{|}{CH_2}}-\underset{PH_2}{\underset{|}{CH_2}}$$

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



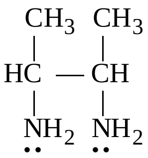
$$\underset{NH_2}{\underset{|}{CH_2}}-\underset{NH_2}{\underset{|}{CH}}-CH_3$$

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



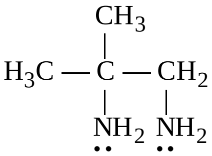
$$\underset{\underset{\cdot\cdot}{NH_2}}{\underset{|}{\overset{1}{CH_2}}}-\overset{2}{CH}-\underset{\underset{\cdot\cdot}{NH_2}}{\underset{|}{\overset{3}{CH_2}}}$$

Buthylene diamine (*bn*)



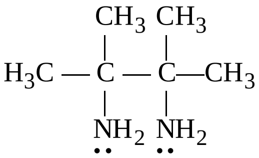
$$\underset{\underset{\cdot\cdot}{NH_2}}{\underset{|}{\overset{CH_3}{\overset{|}{HC}}}}-\underset{\underset{\cdot\cdot}{NH_2}}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}$$

Isobutylene diamine (*i-bn*)



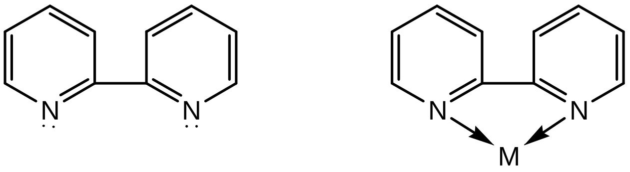
$$H_3C-\underset{\underset{\ddot{N}H_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{\ddot{N}H_2}{|}}{CH_2}$$

Tetramethyl ethylene diamine (*tetrameen*)



$$H_3C-\underset{\underset{\ddot{N}H_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{\ddot{N}H_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

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

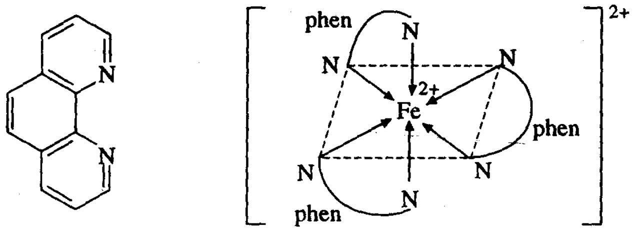


(a) **(b)**

o-phenylene bis dimethyl arsine (diars)

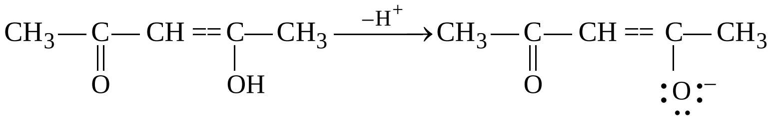
Some important bidentate ligands are as follows:

(i) **o-phenanthroline or 1, 10-phenanthroline (o-phen or phen) :** When it gets attached with a metal atom, it is denoted as $\left.\begin{matrix}N\\N\end{matrix}\right)\text{phen}$ and its attachment to a metal atom, *M* is indicated as $M\begin{matrix}\swarrow N\\ \nwarrow N\end{matrix}\Big)\text{phen}$. For example this ligand gets attached with Fe^{2+} ion and give $[Fe(phen)_3]^{2+}$ complex ion.



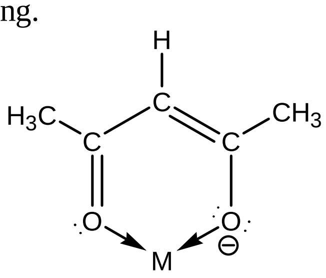
(*a*) (*b*)

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

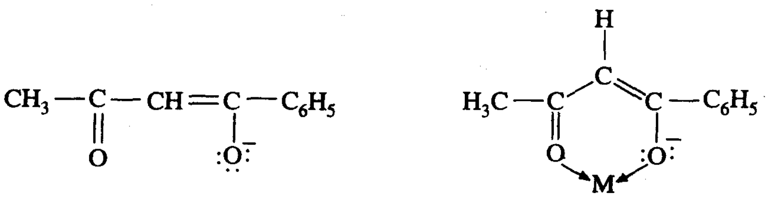


$$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3\xrightarrow{-H^+}CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{:\ddot{O}:^-}{|}}{C}-CH_3$$

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

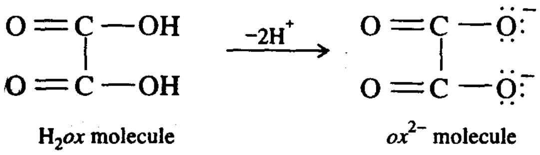


(iii) Benzoyl acetonato ion :

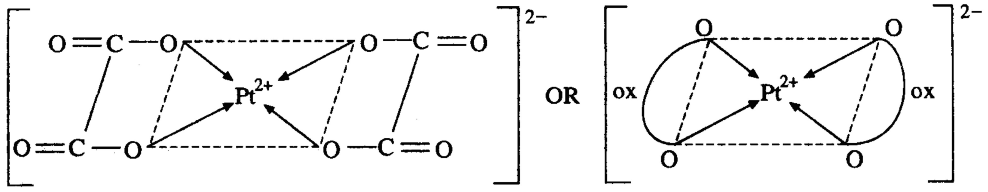


(*a*) (*b*)

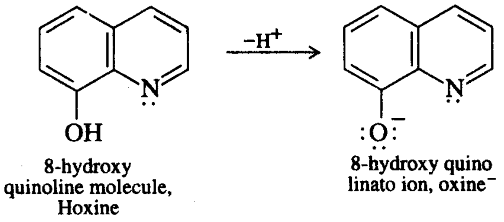
(iv) Oxalato ion, $C_2O_4^{2-}(ox^{2-})$ **:** This ion can be obtained when one molecule of oxalic acid ($H_2C_2O_4$) loses two protons.



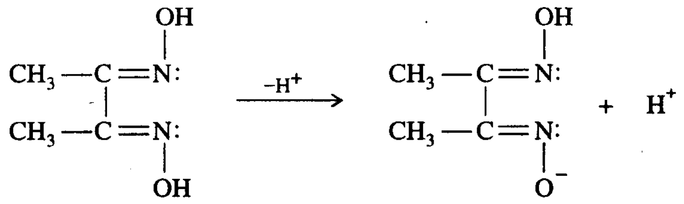
$C_2O_4^{2-}(ox^{2-})$ is a bidentate dibasic ligand and its coordination to the central metal atom occurs through its both negatively charged O-atom (acidic donor atoms), forming 5-membered chelated complex.



(v) 8-hydroxyl quinolinato ion : This ion is obtained when OH group attached with the ring of 8-hydroxyl quinoline molecule, loses a proton (H^+).



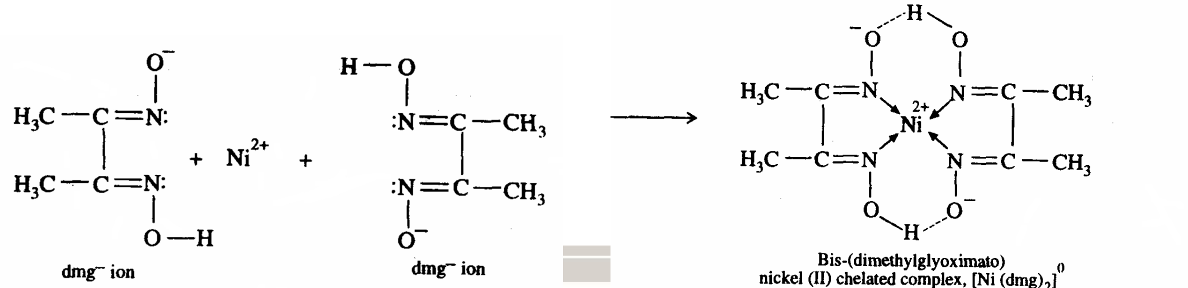
(vi) Dimethyl glycoximato ion (dmg⁻ or DMG⁻) : This ion is obtained when one OH group attached with N atom in Hdmg molecule loses a proton.



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.

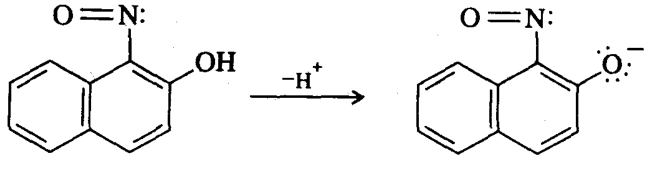


dmg⁻ ion

dmg⁻ ion

Bis-(dimethylglyoximato) nickel (II) chelated complex, $[Ni(dmg)_2]^0$ (red ppt.)

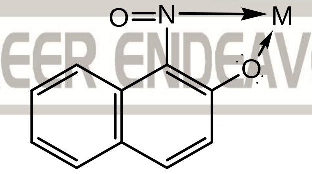
(vii) **α-nitroso β-naphthol anion:** This anion is obtained when α-nitroso β-naphthol molecule loses a proton (H^+) from OH group.



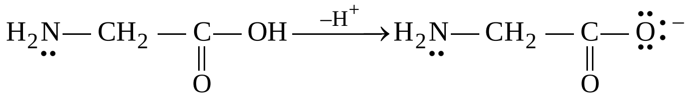
α-nitroso β-naphthol

α-nitroso β-naphthol ion

This ion gets linked with metal atom, M through its N-atom of NO group and negatively charged O-atom. A 5-membered ring is fomed at M atom.



(viii) **Glycinato ion (gly⁻):** This ion is derived by removing one proton from one molecule of glycine (amino acetic acid), $H_2N—CH_2—COOH$ (Hgly).

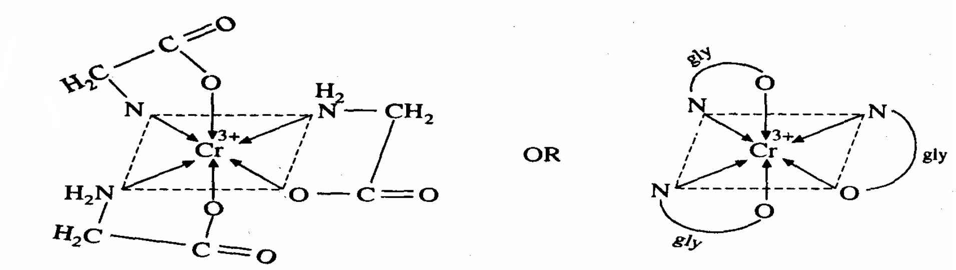


$$H_2\ddot{N}—CH_2—\underset{\underset{O}{\|}}{C}—OH \xrightarrow{-H^+} H_2\ddot{N}—CH_2—\underset{\underset{O}{\|}}{C}—\ddot{\underset{\cdot\cdot}{O}}{:}^-$$

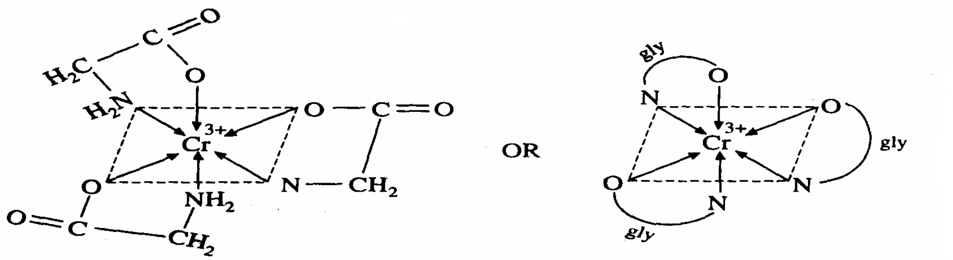
Glycine molecule (Hgly) Glycinato ion (gly⁻)

Glycinato ion (gly⁻) is a bidentate monobasic ligand and its co-ordination to the metal ion occurs through neutral N-atom (neutral donor atom) and negatively-charged O-atom (acidic donor atom), forming a 5-membered ring.

Note: CO_3^{2-}, NO_3^-, SO_4^{2-} ligands act as monodentate and bidentate ligands both.



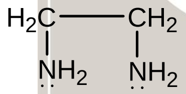
cis-isomer



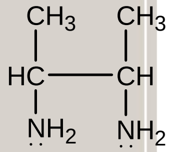
trans-isomer

Symmetric and Unsymmetric Bidentate Ligands:

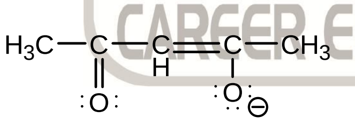
Symmetrical bidentate ligands are those in which the two donor atoms are the same while unsymmetrical bidentate ligands are those in which the two donor atoms are different. Thus a symmetrical bidentate ligand is denoted by (*AA*) in which two *A*’s are two similar donor atoms while an unsymmetrical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



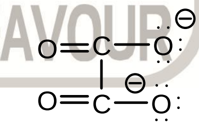
Ethylene diamine, en
(N, N)



Butylene diamine, bn
(N, N)

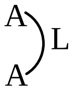


Acetylacetonato, acac$^-$
(O, O$^-$)

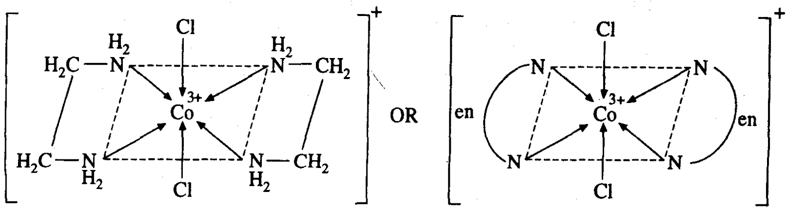


or $C_2O_4^{2-}$

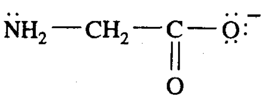
Oxalato, OX^{2-}
(O, O$^-$)

The attachment of a symmetrical bidentate ligand to the central metal atom is shown by a curve  where *L* is the abbreviation of the symmetrical bidentate ligand and two *A*’s are two (similar) donor atoms.

For example the attachment of two molecules of ethylene diamine, NH_2—CH_2—CH_2—NH_2 (en) to Co^{3+} ion to form *trans*-isomer of $[Co(en)_2Cl_2]^+$ ion (octahedral ion) is shown below.

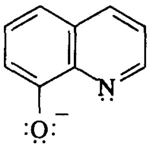


Examples of unsymmetrical bidentate ligands.

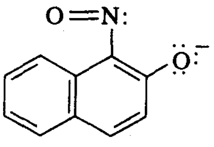


$NH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - \ddot{O}:^-$

Glycinato ion, *gly*⁻
(N, O⁻)



8-hydroxy quinolinato ion
(N, O⁻)

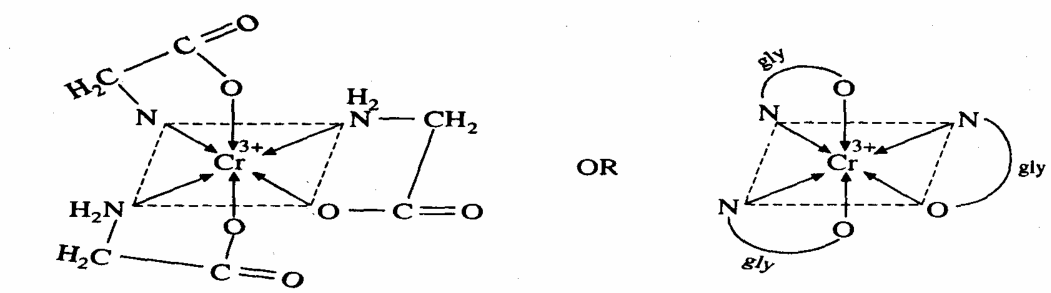


α-nitroso β-naphthol ion
(N, O⁻)

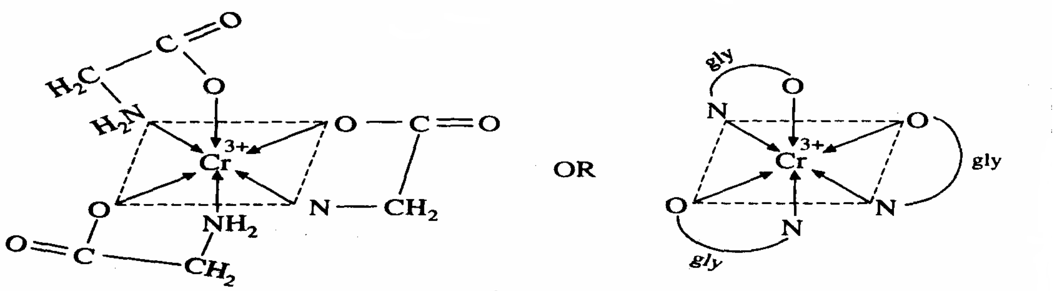
The attachment of an unsymmetrical bidentate ligand to the central metal atom is shown by a curve

A
$\big)$L where *L* is the abbreviation of the ligand and *A* and *B* are two (different) donor atoms. For
B

example, the attachment of three glycinate ions, $NH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - O^-(gly^-)$ to Cr^{3+} ion to form *cis*-and *trans*-isomers of octahedral $[Cr(gly)_3]^0$ is shown below:



cis-isomer

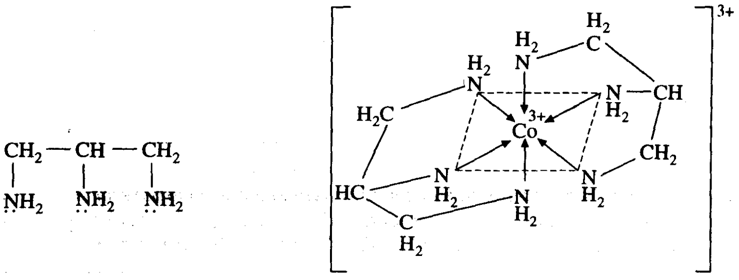


trans-isomer

Tridentate Ligands

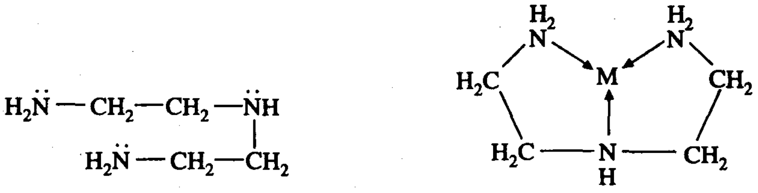
Three donor atoms are present in these ligands.
Example:

1. **Triaminopropane:** The coordination of this ligand to the central metal atom takes place through its three N-atoms (donor atoms), leading to the formation of two 5-membered rings.



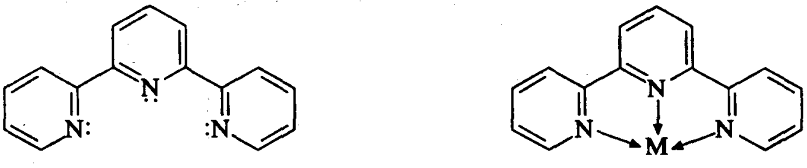
(a) (b)

2. **Diethylene triamine (dien):** This ligand gets attached with the central metal atom through its three N-atom (donor atoms) and forms a chelate which contain two 5-membered.



(a) (b)

3. **2, 2', 2''-terpyridine or terpyridyl (terpy):**

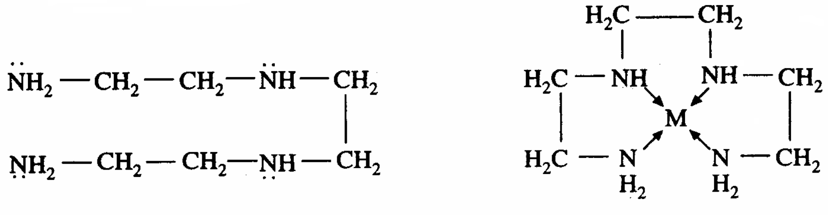


(a) (b)

Tetradentate ligands

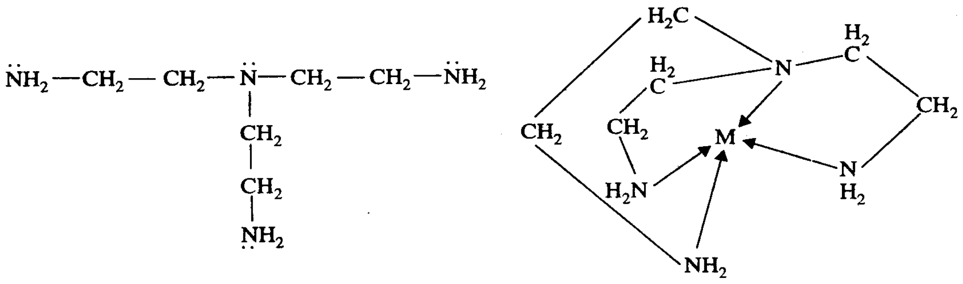
Four donor atoms are present in these ligands.
Example:

1. **Triethylene tetramine (trien):** Coordination of this ligand to the metal ion takes place through four N-atoms, forming a chelated complex containing three 5-membered rings.



(a) (b)

2. **Triaminotriethylamine (tren), N(CH$_2$—CH$_2$—NH$_2$)$_3$:** The attachment of this ligand to the central metal atom, M in its complexes takes place through its four N-atoms, resulting in the formation of chelated complex having three 5-membered rings.



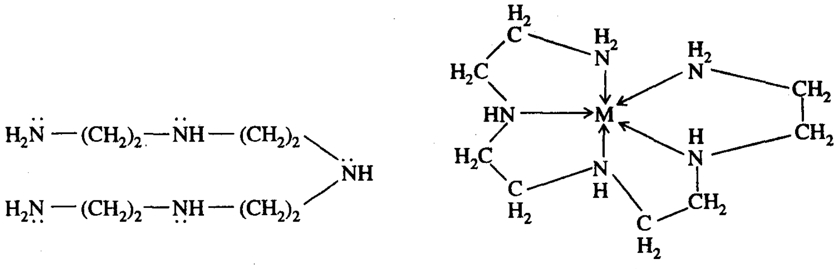
(a) (b)

Pentadentate Ligands

Five donor atoms are present in these ligands.

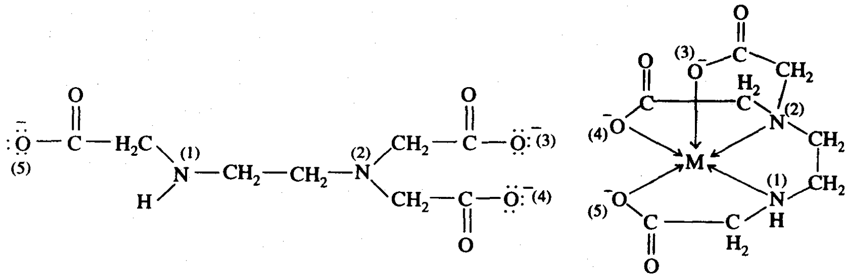
Example:

1. **Tetraethylene pentamine (tetraen):** This ligand coordinates to the metal atom through five N-atoms and forms four 5-membered rings.



(a) (b)

2. **Ethylene diamine triacetate ion :** It is an anionic ligand. It has three negative charges and five donor atoms viz two N-atoms (numbered as 1 and 2) and three negatively charged O-atoms (numbered as 3, 4 and 5). Its coordination to the metal atom occurs through two N-atoms (neutral donor atoms, and three negatively charged O-atoms (acidic donor atoms) of COO$^-$ groups, forming four 5-membered rings.

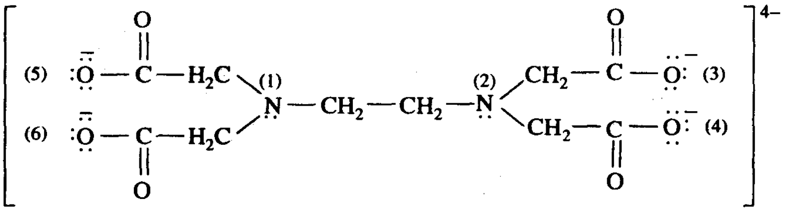


(a) (b)

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. Such ligands are called ambidetate or ambident ligands**.** When an ambidentate ligand having two different donor atoms coordinates to the metal atom through either of its two donor atoms, two different complex compounds are obtained. These compounds are different because they have different structure. Such compounds are called linkage isomers and the phenomenon is called 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 $\overset{-}{N}[O_2\overset{-}{N} \rightarrow M]$, it is called nitro ligand and is written as NO_2^-, 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, since the coordination of Co^{3+} ion to NO_2^- ion occurs through N-atom.

(b) When NO_2^- ion gets coordinated to the metal atom through a lone a pair of electrons on $\overset{-}{O}[M \leftarrow \overset{-}{O}NO]$, it is called nitrito ligand which is written as $ON\overset{-}{O}$. 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, because the coordination of NO_2^- ion to Co^{3+} ion takes place through O-atom.

Sometimes ambidentate ligands are distinguished by putting the symbol of the atom through which the coordination of the ligand to the central metal atom takes place. For example $[Co^{3+}(NH_3)_5(NO_2)]Cl_2$ (yellow-brown) is called pentammine nitrito (N) cobalt (III) chloride and $[Co^{3+}(NH_3)_5(ONO)]Cl_2$ (red) is called pentammine nitrito (O) 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 $[M \leftarrow \overset{-}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}—C \equiv N\colon \text{ or } M \leftarrow \overset{-}{S}CN]$, it is called thiocyanto ligand red is written as $\overset{-}{S}CN$. The complexes containing thiocyanato ligand are called thiocyanato complexes.

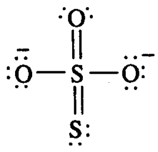
(b) When the coordination of $SC\overset{-}{N}$ ion to the metal atom takes place through N-atom $(M \leftarrow \overset{-}{\underset{\cdot\cdot}{N}}{=}C{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}} \text{ or } M \leftarrow \overset{-}{N}CS)$, this ion is called isothiocyanato ligand and is written as $\overset{-}{N}CS$. The complex compounds having $\overset{-}{N}CS$ ion as a monodentate ligand are called isothiocyanato complexes.

3. Cyanide ion, CN^-

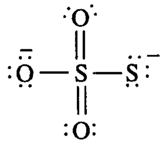
(a) When this ion gets linked to the metal atom as a monodentate ligand through C-atom [M ← CN], this ion is called cyano ligand which is written as CN^-

(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-}]

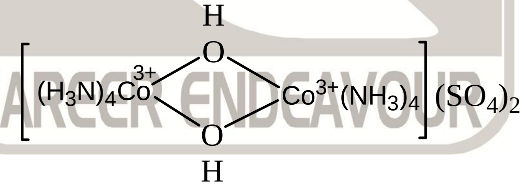


[Thiosulphato – S ion, SSO_3^{2-}]

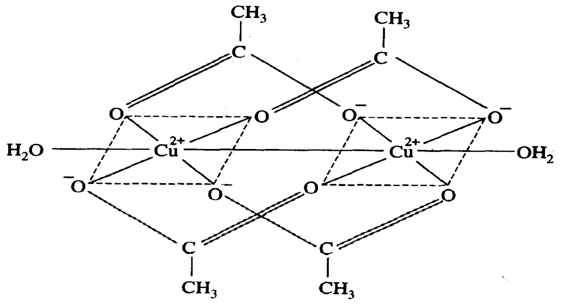
Bridging Ligands and Bridged Complexes

Although the ligands like N_2 or $:N\equiv N:$ (dinitrogen), NH_2—NH_2 or N_2H_4 (hydrazine), OH^- (hydroxo), NH_2^- (amido or amino), NH^{2-} (imido), Cl^-, F^- O^{2-}(oxo), O_2^{2-} or $:\ddot{\bar{O}}-\ddot{\bar{O}}:$ (peroxo), O_2^- or $:\ddot{O}\dot{-}\dot{-}\ddot{O}:^-$ (superoxo), 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. Each bridging ligand makes two σ-bonds with two metal atoms. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two metal atoms. The polynuclear complex may be dinuclear, trinuclear, tetranuclear etc.

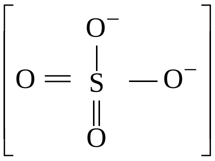
Example :

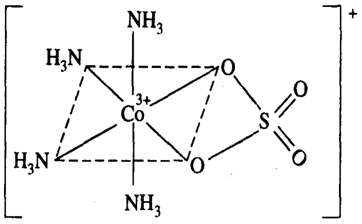


Flexidentate Ligands

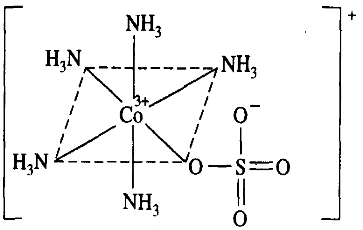


There are many ligands which have more than one donor atoms (polydentate ligands). Examples of such ligands are SO_4^{2-} (both negatively-charged O-atoms are donor atoms). CO_3^{2-} (both negatively-charged O-atoms are donor atoms). N_2 (both N-atoms are donor atoms), NH_2—NH (both N-atoms are donor atoms) etc. All these ligands have two donor atoms. When these ligands get coordinated to the metal atom/ion, they give rise to the formation of two types of complex compounds. In one type they get linked to the metal atom through one donor atom only while in the formation of another type of the complex compound, they get coordinated to the metal atom through both of its donor atoms.

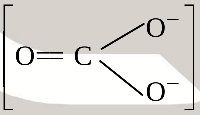
Example : Sulphate (SO_4^{2-}) and carbonate (CO_3^{2-}) ions, SO_4^{2-} ion  $\left[O = \overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{S}} - O^-\right]$ has two negatively-charge O-atoms as its donor atoms and hence behaves as a bidentate ligands complex ions like $[Co^{3+}(NH_3)_4(SO_4)]^+$ (I). This ion uses only one of its two negatively-charged O-atoms as donor atom in formation of complex ions like $[Co^{3+}(NH_3)_5(SO_4)]^+$ (II). Thus in this complex ion SO_4^{2-} ion behaves as a monodentate ligand. Note that in both the complex ions given above coordination number of Co^{3+} ion in six. In (I) this coordination number is satisfied by four NH_3 and one SO_4^{2-} ion (bidentate ligand) while in (II) this number is satisfied by five NH_3 molecules and one SO_4^{2-} ion (monodentate ligand).



Structure of $[Co^{3+}(NH_3)_4(SO_4)]^+$ ion (I)



Structure of $[Co^{3+}(NH_3)_5(SO_4)]^+$ ion. (II)

In the formation of $[Co^{3+}(NH_3)_4CO_3]^+$ ion CO_3^{2-} ion  $\left[O{=}C\genfrac{}{}{0pt}{}{\diagup O^-}{\diagdown O^-}\right]$ acts as a bidentate ligand while in $[Co^{3+}(NH_3)_5CO_3]^+$ ion this ion acts as a monodentate ligand. In the formation of $[Co^{3+}(NH_3)_3Cl_2CO_3]^-$ ion also, CO_3^{2-} ion acts as a monodentate ligands.

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.

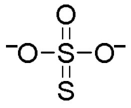
Neutral ligands	**Anionic ligands**	**Bidentate ligands**
CH_3NH_2	N_3^-	Ethylene diamine
NH_2OH	SCN^-	Ethylenediphosphine,
CS		Bipyridyl
CO		Isobutylene diamine
H_2O		
Pyridine		
NH_2NH_2		

Correct answer is (b)

3. Which of the following is ambidentate ligands

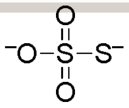
(a) $S_2O_3^{2-}$ (b) $C_2O_4^{2-}$ (c) DMG (d) gly

Soln. $S_2O_3^{2-}$



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

(Thiosulphato - O ion)



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

(Thiosulphato - S ion)

Correct answer is (a)