# **Classification of ligands**

Depending on the number of sites at which one molecule of a ligand is coordinated to the central metallic atom, the ligands have been classified as mono dentate (or uni dentate) and poly dentate (or multi dentate) ligands.

## 1- Mono dentate ligands

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

These ligands may be neutral molecules or in anionic form.

# (a) Neutral ligands which are named as such.

$(C_2H_5)_3N$		Triethyl amine	$(C_6H_5)_3P$		Triphenyl phosphine
CH <sub>3</sub> NH <sub>2</sub>	•••	Methyl amine	CH₃CN		Acetonitrile
NH <sub>2</sub> OH		Hydroxylamine	PF <sub>3</sub>	***	Phosphorus trifluoride
(CH <sub>3</sub> ) <sub>2</sub> NH	***	Dimethylamine	$(C_2H_5)_3P$	***	Triethyl phosphine
C.H.N or py	•••	Pyridine			

# (b) Neutral ligands which are given special names, e.g.

CO		•••	Carbonyl	NO	•••	Nitrosyl
CS		•••	Thiocarbonyl	NS	•••	Thionitrosyl
H <sub>2</sub> O	16	•••	Aquo or aqua	NH <sub>3</sub>	***	Ammine

According to latest system of nomenclature, the word "aqua" is used for H2O molecule.

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#### **Coordination Chemistry**

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Anionic (negative) ligands. The names of negative ligands end in o

F ..... Fluoro Cl ..... Chloro

Br ..... Bromo I ..... Iodo

H ..... Hydro or Hydrido CH<sub>3</sub>COO ..... Acetato

NH<sub>2</sub> ..... Amido OH ..... Hydroxo or hydroxyl

 $N^{3-}$  ..... Nitrido  $N_3^{-}$  ..... Azido

O<sup>2</sup> ..... Oxo HS ..... Mercapto

S<sup>2</sup> ..... Sulphido or thio CN ..... Cyano(coordination

through C-atom)

NC ..... Iso-cyano(coordination CH<sub>3</sub>O ..... Methoxo

through N-atom)

 $C_2H_5O^2$  ..... Ethoxo  $NO_2^2$  ..... Nitro (coordination

through N-atom)

ONO ..... Nitrito (coordination SCN Thiocyanato

Through O-atom)

NCS ..... Iso-thiocyanato

## 2- Poly-dentate ligands

These may be bi-dentate, tri-dentate, tetra-dentate, penta-dentate and hexa-dentate, 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.

(one molecule of these ligands makes 2, 3, 4, 5 and 6 metal-ligand coordinated bonds respectively.

Bi-dentate ligands may be neutral molecules or anions.

## **Examples of bi-dentate ligands**

Ethylene diamine (en) 
$$CH_2$$
— $CH_2$ 
 $NH_2$   $NH_2$ 

Ethylene diphosphine  $CH_2$ — $CH_2$ 
 $CH_2$ 
 $PH_2$   $PH_3$ 

\*2,2-bipyridine (bipy)

\*Hydrazine

\*o-phenanthroline or 1,10-phenanthroline (0-phen or phen or phenan)

\*Acetylacetonato ion (acac)

$$\begin{array}{c|cccc} CH_3-C-CH=C-CH_3 & \xrightarrow{-H^+} & CH_3-C-CH=C-CH_3 \\ \parallel & \mid & \parallel & \mid & \parallel & \mid \\ O & OH & O & :O: \end{array}$$

Mode of attachment of acetylacetanato ion to the metal atom, M.

\*Oxalato ion  $C_2O_4^{2-}(ox^{2-})$ 

 $[Pt^{2+}(ox)_2]^{2-}$ 

$$\begin{bmatrix}
O = C - O & O - C = O \\
O = C - O & O - C = O
\end{bmatrix}$$

$$O = C - O & O - C = O$$

$$O = C - O & O - C = O$$

$$O = C - O & O - C = O$$

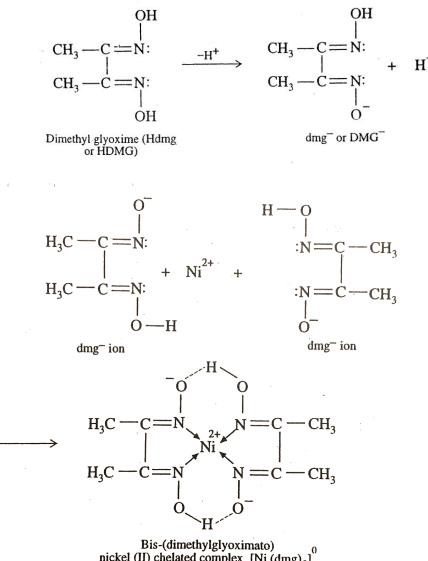
$$O = C - O & O - C = O$$

$$O = C - O & O - C = O$$

\* 8- hydroxyl quinolinato ion (oxine)

Attachment of oxine ion to a metal atom (M) in complex compounds

\*Dimethyl glyoximato ion (dmg or DMG )

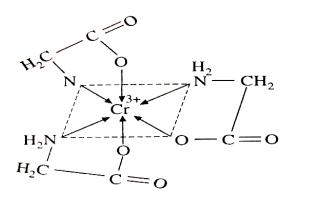


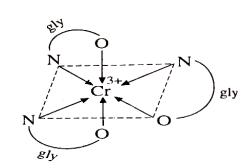
 $\begin{array}{c} \text{Bis-(dimethylglyoximato)} \\ \text{nickel (II) chelated complex, [Ni (dmg)_2]}^0 \\ \text{(red ppt.)} \end{array}$ 

\*Glycinato ion (gly)

$$\begin{array}{c} H_2N - CH_2 - C - OH \xrightarrow{-H^+} H_2N - CH_2 - C - O \\ \parallel & \parallel & \parallel \\ O & O \end{array}$$

Glycine molecule (Hgly)





\*Carbonato  $CO_3^{2-}$ , nitrato  $NO_3^{-}$  and sulphato  $SO_4^{2-}$ 

The structure of these ions and the way in which they are coordinated to the metal atom are shown blow:

OR

$$O = C$$

$$O = M$$

$$O = N$$

$$O =$$

\* Peroxo, O<sub>2</sub><sup>2</sup>-

 $O_2^{2-}$  group gets coordinated to the central metal ion as:

# **Examples of tridentate ligands**

a- Diethylene triamine (dien)

$$H_{2}\ddot{N} - CH_{2} - CH_{2} - \ddot{N}H$$
 $H_{2}\ddot{N} - CH_{2} - CH_{2}$ 

$$H_2C$$
 $M$ 
 $CH_2$ 
 $H_2C$ 
 $N$ 
 $CH_2$ 
 $H_2C$ 
 $N$ 
 $CH_2$ 

b- 2,2<sup>-</sup>,2<sup>--</sup>-terpyridine or terpyridyl (terpy)

# **Example of tetra-dentate ligand**

Triethylene tetraamine (trien)

$$\frac{\ddot{N}H_{2}-CH_{2}-CH_{2}-\ddot{N}H-CH_{2}}{\ddot{N}H_{2}-CH_{2}-CH_{2}-\ddot{N}H-CH_{2}}$$

$$H_{2}C \longrightarrow CH_{2}$$
 $H_{2}C \longrightarrow NH$ 
 $NH \longrightarrow CH_{2}$ 
 $H_{2}C \longrightarrow N$ 
 $N \longrightarrow CH_{2}$ 
 $H_{2}C \longrightarrow N$ 
 $H_{2}$ 
 $H_{2}C \longrightarrow N$ 
 $N \longrightarrow CH_{2}$ 

## **Example of penta-dentate ligand**

Tetraethylene pentaamine (tetraen)

$$H_2N - (CH_2)_2 - NH - (CH_2)_2$$
 $NH$ 
 $H_2N - (CH_2)_2 - NH - (CH_2)_2$ 
 $NH$ 

$$\begin{array}{c} H_{2} \\ C \\ H_{2}C \\ HN \\ \longrightarrow M \\ H_{2}C \\ C \\ H_{2} \\ \end{array} \begin{array}{c} H_{2} \\ N \\ \longrightarrow M \\ CH_{2} \\ CH_{2} \\ H_{2} \\ \end{array}$$

#### **Example of hexa-dentate ligand**

Ethylene diamine tetraacetate ion (edta<sup>4-</sup> or EDTA<sup>4-</sup> or Y<sup>4-</sup>)

## **Bridging Ligand and Bridged Complexes**

Although the ligands like OH (hydroxo), NH<sub>2</sub> (amido or amino), NH<sup>2</sup> (imido), Cl , F ,  $SO_4^{2-}$ , NO<sub>2</sub> , CO etc. are mono-dentate ligands, they also act as bi-dentate ligands when they 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 ligands or multinuclear) complexes. Each ligand makes two  $\sigma$ -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, teranuclear etc.

$$\left[ (NH_3)_4 Co^{3+} \left\langle \begin{array}{c} OH \\ OH \end{array} \right\rangle Co^{3+} (NH_3)_4 \right] (SO_4)_2$$

$$\begin{bmatrix} NH_{3} & NH_{3} & OH \\ NH_{3} & OH & Co \\ OH & OH & OH \\ NH_{3} & OH \end{bmatrix}^{5+}$$