Classification of ligands

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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.

Triethyl amine $(C_6H_5)_3P$ Triphenyl phosphine $(C_2H_5)_3N$ Methyl amine CH₃CN Acetonitrile CH₃NH₂ Hydroxylamine PF₃ Phosphorus trifluoride NH₂OH Dimethylamine $(C_2H_5)_3P$ Triethyl phosphine (CH₃)₂NH Pyridine C₅H₅N or py

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

CO ... Carbonyl NO ... Nitrosyl
CS ... Thiocarbonyl NS ... Thionitrosyl
H₂O ... Aquo or aqua NH₃ ... Ammine

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

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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 CH₃COO Acetato

NH₂ Amido OH Hydroxo or hydroxyl

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

 O^{2-} Oxo HS^{-} Mercapto

S² Sulphido or thio CN Cyano(coordination

through C-atom)

NC Iso-cyano(coordination CH₃O 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.

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(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.

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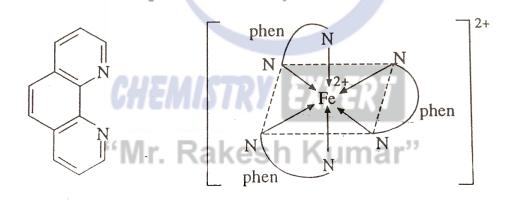
Examples of bi-dentate ligands

*2,2-bipyridine (bipy)

*Hydrazine

$$H_2N$$
 H_2N

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



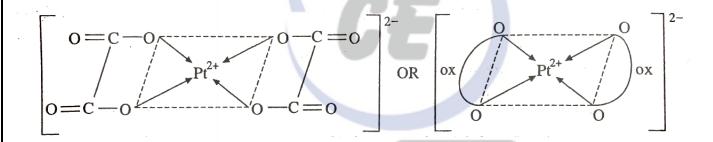
*Acetylacetonato ion (acac)

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

*Oxalato ion $C_2O_4^{2-}$ (ox²⁻)

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



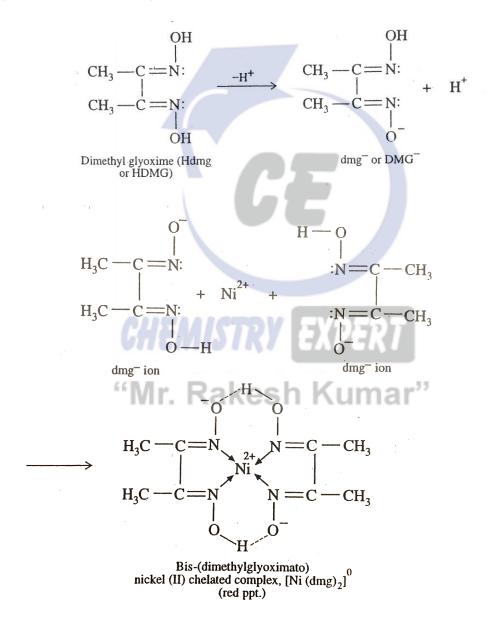
* 8- hydroxyl quinolinato ion (oxine)

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

$$O \rightarrow M$$

*Dimethyl glyoximato ion (dmg or DMG)



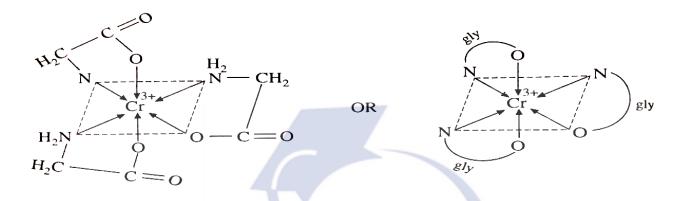
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*Glycinato ion (gly)

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

Glycine molecule (Hgly)

Glycinato ion (gly⁻)



*Carbonato CO₃², nitrato NO₃ and sulphato SO₄²

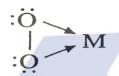
The structure of these ions and the way in which they are coordinated to the metal atom are shown blow:

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* Peroxo, O₂²-

$$H \longrightarrow O \longrightarrow H$$
 $\xrightarrow{-2H^+}$ $\vdots \stackrel{\overline{}}{\circ} \longrightarrow \stackrel{\overline{}}{\circ} \vdots$
Hydrogen peroxide molecule, H_2O_2 Peroxo group $(O_2^{2^-})$

 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_2 H_2 H_2 H_2 H_2 H_2 H_2 H_2 H_3 H_4 H_4

b- 2,2⁻,2⁻-terpyridine or terpyridyl (terpy)

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Example of tetra-dentate ligand

Triethylene tetraamine (trien)

$$H_2C$$
 — CH_2
 H_2C — NH — NH — CH_2
 H_2C — N — N — CH_2
 H_2 — H_2 — H_2

Example of penta-dentate ligand

Tetraethylene pentaamine (tetraen)

$$H_2\ddot{N} - (CH_2)_2 - \ddot{N}H - (CH_2)_2$$
 $\ddot{N}H$
 $H_2\ddot{N} - (CH_2)_2 - \ddot{N}H - (CH_2)_2$

Example of hexa-dentate ligand

Ethylene diamine tetraacetate ion (edta⁴⁻ or EDTA⁴⁻ or Y⁴⁻)

Bridging Ligand and Bridged Complexes

Although the ligands like OH⁻ (hydroxo), NH₂⁻ (amido or amino), NH²⁻ (imido), Cl⁻, F, SO_4^{2-} , NO₂⁻, 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 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, teranuclear etc.

$$\left[(NH_3)_4 Co^{3+} \underbrace{OH}_{OH} Co^{3+} (NH_3)_4 \right] (SO_4)_2$$

$$\begin{bmatrix}
NH_{3} \\
(NH_{3})_{4} & Co^{3+} \\
OH \\
OH
\end{bmatrix}$$

$$\begin{bmatrix}
NH_{3} \\
OH \\
OH
\end{bmatrix}$$

$$Co^{3+} \\
OH
\end{bmatrix}$$

$$NH_{3}$$

$$OH$$

$$OH$$

$$NH_{3}$$