DEFINITIONS OF SOME IMPORTANT TERMS PERTAINING TO COORDINATION COMPOUNDS

Addition Compounds

They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Addition Compounds

Double Salts Compounds (Complexes)

Molecular/Addition Compound

Molecular/Addition compounds are formed when stoichiometric amounts of two or more simple compounds join together. Molecular/ Addition compounds are of two types.

Double Salts

Those which retain their identity in solutions are called double salts.

For example:

$$\underset{\text{carnallite}}{KCl + MgCl_2 + 6H_2O \rightarrow KCl.MgCl_2.\ 6H_2O}$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \rightarrow \underset{\text{potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Complex Compounds

Those which lose their identity in solution (complexes).

For example:

$$CuSO_4 + 4\ NH_3 \rightarrow \underset{\text{tetramine copper (II) sulphate}}{CuSO_4.4\ NH_3 \text{ or } [Cu(NH_3)_4]SO_4}$$

$$Fe(CN_2) + 4\ KCN \rightarrow \underset{\text{potassium ferrocyanide}}{Fe\ (CN_2).\ 4KCN \text{ or } K_4[Fe(CN)_6]}$$

Upon dissolving crystals of carnallite in water, the resulting solution exhibits characteristics of K^+, Mg^{2+} and Cl^- ions. Likewise, a solution of potassium alum displays properties of K^+, Al^{3+} and $SO_4{}^{2-}$ ions. These are instances of double salts, which are solely present in their crystalline form. In contrast, when the other two coordination compounds are dissolved, they do not produce simple ions (Cu^{2+}/ Fe^{2+} and CN^-); instead, they form complex ions.

Representation of Complex Ion

$$[ML_x]^{n\pm}$$

where M = Central Metal atom /ion (usually of d-block)

L = Ligand

x = No. of ligands

n± = charge on coordination

Outside region apart from coordination sphere is called ionisation sphere.

Coordination Entity

A coordination compound is composed of a central metal atom or ion that is bonded to a specific number of ions or molecules through coordinate bonds. For instance, in the coordination sphere (entity) of $[CoCl_3(NH_3)_3]$, the cobalt ion (Co^{3+}) is surrounded by three ammonia molecules and three chloride ions, forming coordinate bonds with each of them.

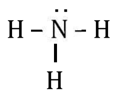
Central Atom/Ion, Ligands

Central Atom/Ion

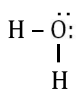
The central ion serves as a receptor (Lewis's acid) and is required to accept electron pairs donated by the donor atom of the ligand, necessitating the presence of vacant orbitals. This clarifies why transition metals with available d-orbitals readily create coordination compounds.
For instance, in the complexes $[Ni\ (NH_3)_6]^{2+}$ and $[Fe\ (CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} serve as the central metal ions, respectively.

Ligands

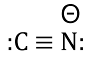
Entities that are directly connected to the central metal atom/ion in a complex ion are referred to as ligands. These ligands are bound to the central metal atom/ion through a coordinate or dative bond, and free ligands typically possess at least one lone pair.



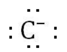
$H-\ddot{N}-H$ with H below N



$H-\ddot{O}:$ with H below O



$:C\equiv N:^{\ominus}$



$:\ddot{\underset{\cdot\cdot}{C}}^{-}:$

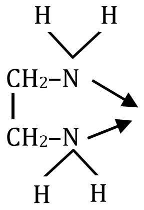
Therefore, the ligands function as Lewis bases, while the central metal ions/atoms act as Lewis's acids. Ligands can be classified into different types based on the number of donor atoms they contain:

(i) Mono / Unidentate Ligands

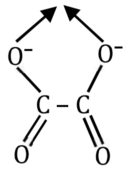
They have one donor atom, i.e., they can donate only one electron pair to the central metal atom /ion eg., F^-, Cl^-, Br^-, H_2O, NH_3, CN^-, NO_2^-, OH^-, CO etc.

(ii) Bidentate Ligands

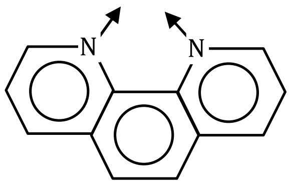
Ligands which have two donor atoms and have the ability to link with the central metal atom /ion at two positions are called bidentate ligands e.g.



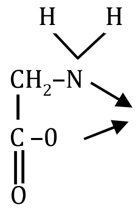
Ethylenediamine (en)



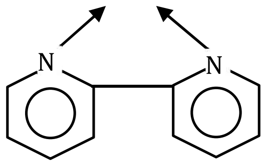
Oxalate (ox)



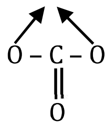
1,10–phenanthroline (phen)



Glycinate (Gly)



2,2–dipyridine (dipy)

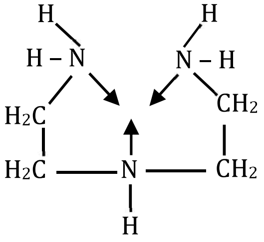


carbonate

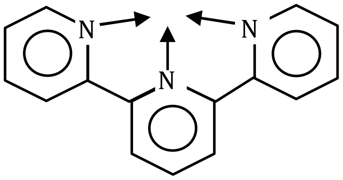
(iii) Tridentate Ligands

Ligands having three donor atoms are called tridentate ligands.

Examples are:



Diethylene triamine (dien)

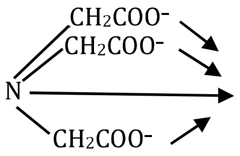


2,2’2”–terpyridine (terpy)

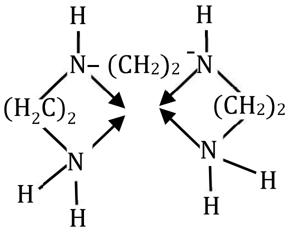
(iv) Tetradentate Ligands

These ligands possess four donor atoms.

Examples are:



Nitriloacetate

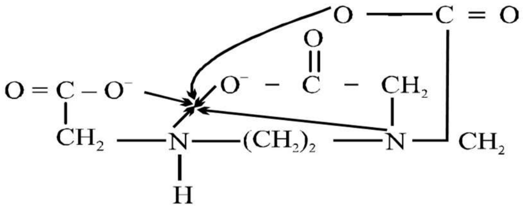


Tri ethylene tetramine (trien)

(v) Pentadentate Ligands

They have five donor atoms.

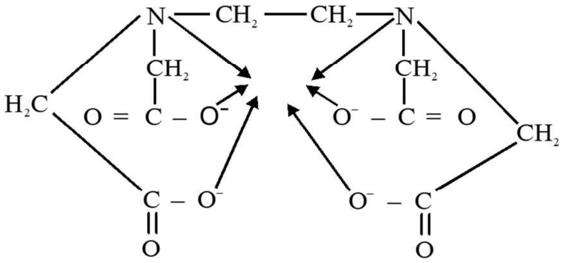
For example, ethylenediamine triacetate ion.



ethylendiamine triacetate ion

(vi) Hexadentate Ligands

They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



ethylenediamine tetraacetate (EDTA)

(vii) Ambidentate ligands

Certain ligands possess multiple donor atoms, yet when they form complexes, only one donor atom becomes attached to the metal/ion. These ligands are referred to as ambidentate ligands. Examples of such ligands include:

$M \leftarrow NO_2^-$ nitrite – N $\quad$ $M \leftarrow ONO^-$ nitrite –O

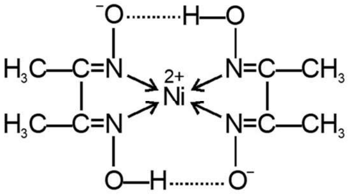
$M \leftarrow CN^-$ cyanide $\quad$ $M \leftarrow NC^-$ isocyanide

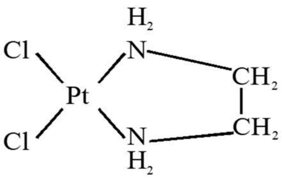
$M \leftarrow SCN^-$ thiocyanide $\quad$ $M \leftarrow NCS^-$ isothiocyanide

(viii) Ligands with more than two donor atoms are termed polydentate or multidentate ligands. Multidentate ligands, known as chelating ligands, give rise to the creation of a stable cyclic ring, which leads to the formation of complexes referred to as chelates. Typically, chelating ligands are organic compounds.

(ix) Chelate ligand

A chelate ligand is a di- or polydentate ligand that employs two or more donor atoms to bind to a single metal ion, creating a ring structure. The resulting complex is termed a chelate complex, and the process of forming such chelates is known as chelation. The number of these ligating groups on the ligand is referred to as its denticity. Chelate rings may consist of various numbers of atoms, with the most common ones containing five or six atoms, including the metal ion. Smaller rings exhibit smaller angles and distances, leading to strain, while larger rings often lead to crowding both within the ring and between adjacent ligands. Some ligands have the ability to form multiple rings; for example, ethylene diamine tetraacetate (EDTA) can form five rings by utilizing its four carboxylate groups and two amine nitrogen's, as depicted in the structures.





The chelate complexes exhibit higher stability when compared to complexes containing unidentate ligands with similar characteristics. This enhanced stability of chelate complexes, in contrast to regular complexes, is referred to as the chelate effect.

For example,

$$Ni^{2+}\,(aq) + 6\,NH_3\,(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}\,(aq) \qquad K_{formation} = 10^8$$

$$Ni^{2+}\,(aq) + 3\,NH_2CH_2CH_2NH_2(aq) \rightleftharpoons [Ni(en)_3]^{2+}\,(aq)K_{formation} = 10^{18}$$

The five and six membered rings are more stable.

(x) Flex dentate Ligand

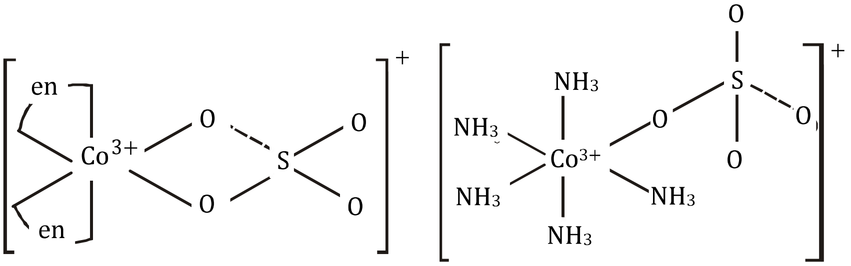
It's important to understand that not all of the donor atoms within polydentate ligands need to establish coordinate bonds with the central metal atom or ion. In other words, when a polydentate ligand exhibits varying denticity in different coordination compounds, it is termed a flex dentate ligand. It's worth noting that within a specific complex, the denticity of a given ligand remains fixed and cannot change.

For instance, EDTA has the capability to function as a hexa-, penta-, or tetra-dentate ligand.

EDTA usually acts as hexadentate ligand but in $[Cr\ (III)(OH)(EDTA)]^{2-}$ and $[Co\ (III)Br\ (EDTA)]^{2-}$ as pentadentate and in $[Pd\ (II)H_2(EDTA)]^0$ as a tetradentate ligand.

Sulphate ion, SO_4^{2-} can also be mono or bi dentate ligand.

For example:



Coordination Number

The coordination number is a parameter that defines the count of coordinate bonds established between the central atom or ion and the ligands surrounding it within a coordination complex.

For instance, in coordination entities such as $[Ag(CN)_2]^-$, $[Cu(NH_3)_4]^{2+}$, and $[Cr(H_2O)_6]^{3+}$, the coordination numbers for Ag, Cu, and Cr are 2, 4, and 6, respectively. This elucidates the number of ligands directly bonded to the central metal atom or ion within the complex.

Likewise, in compounds like $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, both Fe and Co exhibit a coordination number of 6. This is because each $C_2O_4^{2-}$ (oxalate) and en (ethylene-1,2-diamine) forms two coordinate bonds with the central metal atom or ion. This exemplifies how the coordination number reflects the quantity of coordinated ligands surrounding the central atom or ion in a coordination complex, offering insight into its structural arrangement and bonding characteristics.

Coordination Polyhedron

The arrangement of ligands in space around a central metal atom or ion is referred to as the coordination polyhedron. This term describes the geometric shape formed by the ligands as they surround the central metal entity. Among the various coordination polyhedral that exist, the most commonly encountered ones include:

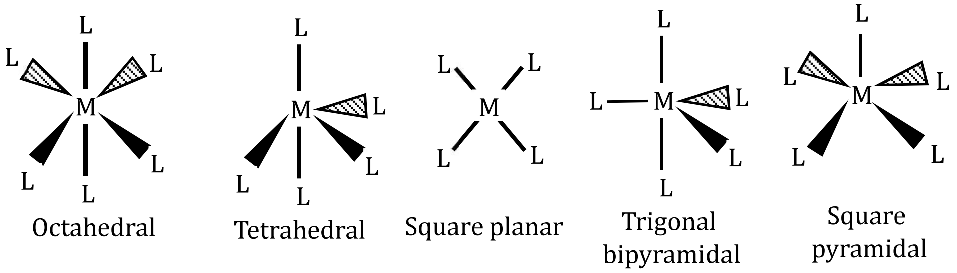


Fig.: Shapes of different coordination polyhedral. M represents the central atom/ion and L, a unidentate ligand

Oxidation Number

The oxidation number of the central metal atom or ion within a complex indicates the charge it would possess if all the ligands were removed along with the electron pairs shared with the central atom. This value is often denoted by Roman numerals in parentheses following the name of the central atom.
For instance, in complexes such as $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, and $[Ni(CO)_4]$, the oxidation numbers for Co, Fe, and Ni are +3, +2, and 0, respectively. These are represented as Co(III), Fe(II), and Ni(0). This notation provides insight into the oxidation state of the central metal atom or ion within the complex, accounting for its electronic configuration and valence electron distribution.

Homoleptic and Heteroleptic Complexes

Complexes that contain only a single type of ligand are termed homoleptic, as exemplified by $[Co(NH_3)_6]^{3+}$. Conversely, complexes featuring more than one type of ligand are referred to as heteroleptic, illustrated by $[Co(NH_3)_4Cl_2]^+$ complexes.

HSAB Principle

Certain metals or ions exhibit a specific propensity to form complexes with particular ligands, a phenomenon elucidated by the HSAB principle, which stands for Hard and Soft Acid and Base theory. According to this principle, metals or their ions can be categorized into two main groups:

(1) Soft acids
(2) Hard acids

Similarly, ligands can also be classified into two categories:

(1) Soft bases
(2) Hard bases

Note: Soft metals have a preference for binding with soft bases, while hard metals tend to favor hard bases.

Soft acids - Li^+, Be^{+2}, Sc^{+3}, La^{+3}, Ce^{+4}, Ti^{+4}, Mn^{+7}, Fe^{+3}, Co^{+3}
Hard acids- Pd^{+2}, Pt^{+2}, Pt^{+4}, Cu^+, Ag^+, Au^+, Ca^{+2}
Soft bases- NH_3, $R\text{-}NH_2$, H_2O, OH^-, O^{-2}
Hard bases- H^-, R^-, C_2H_4, R_2S, CO, CN^-