

Chapter-21**Coordination Chemistry (Introduction)**

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In coordination compounds there is a 3rd bracket. The space within the 3rd bracket is to be treated as coordination sphere contains metal and non metals (ligands). The space outside the 3rd bracket treated as ionization sphere contains ions. Non metallic part (Lewis base) donates electrons and metallic part (Lewis acid) accepts those electrons in their vacant s, p and d orbitals. In this way, non metallic part ligated to the metallic part through coordinate bond. Thus, non metallic part within the coordination sphere is to be treated as ligand.

So, shortly we can say, *coordination complex* is the product of a Lewis acid-Lewis base reaction in which neutral molecules or ions (ligands) bond to a central metal atom (or ion) through coordinate covalent bonds.

Coordination compounds are those molecular compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituents.

Examples are $K_4[Fe(CN)_6]$; $[Ni(CN)_4]^{2-}$ etc.

Ligand:

The atom, ions or molecules which are capable of donating at least a pair of electrons to the central metal atom or ion are called ligands.

Classification of Ligands:**i) Classification based on charge of ligands:**

a. Neutral ligands contain no charge, e.g. NH_3 , H_2O , CO , ethylenediamine (en), pyridine (py), α -picoline (α -pic), 1,3-diamino propane (tn), 1,2-diamino propane (pn) etc.

b. Anionic ligands contain negative charge, e.g. OH^- , CN^- , NO_2^- , X^- (Cl^- , Br^- , I^- , F^-), oxalate ion ($C_2O_4^{2-}$) etc.

c. Positive ligands contain positive charge, e.g. NO^+ , $NH_2 - NH_3^+$, etc.

ii) Classification based on denticity of ligands:

Denticity of the ligand: Denticity refers to the number of donor atom/atoms or groups in a single ligand. The ligand containing one, two or more donor atoms are called unidentate, bidentate and polydentate or multidentate ligands respectively. Monodentate ligands are attached to the metal or metal ion via only a single donor atom. Ligands can, however, be bidentate, tridentate, or, in

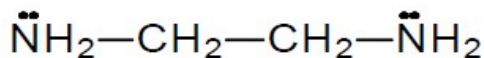
general, multidentate indicating that they are attached to the metal at two, three, or several donor sites, respectively.

a. Monodentate ligands contain one donor atom attached with metal or metal ion. They are attached to the metal or metal ion via only a single donor atom.

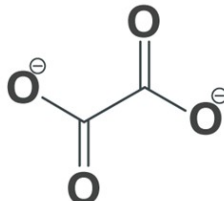
e.g. F^- , Cl^- , Br^- , I^- , NO_2^- , H_2O , NH_3 , py , CO , OH^- etc.

b. Bidentate ligands contain two donor atoms attached with metal or metal ion.

e.g. $C_2O_4^{2-}$ (oxalate ion), en (ethylenediamine), 1,3-diamino propane (tn), 1,2-diamino propane (pn) etc. In amines each nitrogen atom has a lone pair that can be shared with a metal ion.



Ethylenediamine (en)



Oxalate ion ($C_2O_4^{2-}$)

c. Tridentate ligands contain three donor atoms attached with metal or metal ion.

e.g. $NH_2CH_2CH_2NHCH_2CH_2NH_2$ (diethylenetriamine) etc.

d. Tetradentate ligands contain four donor atoms attached with metal or metal ion.

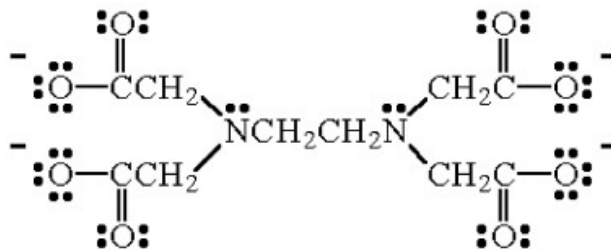
e.g. $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ (triethylenetetramine) etc.

e. Pentadentate ligands contain five donor atoms attached with metal or metal ion.

e.g. $(-OOCCH_2)_2NCH_2CH_2NH(CH_2COO^-)$ (ethylenediaminetriacetate ion) etc.

f. Hexadentate ligands contain six donor atoms attached with metal or metal ion.

e.g. $(-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$ (**ethylenediaminetetraacetate ion, $EDTA^{4-}$**) etc.



Structure of $EDTA^{4-}$

Chelating ligands and metal chelate complex:

A metal-containing ring shown below is called a chelate ring. Multidentate or polydentate ligands are chelating agents, and complexes that contain polydentate ligands are called chelate complexes.

When ligands coordinates to a metal ion by more than one donor site, then a ring type closed structure is obtained. Such ligands are called chelating ligands, the resulting complex is called *metal chelate*.

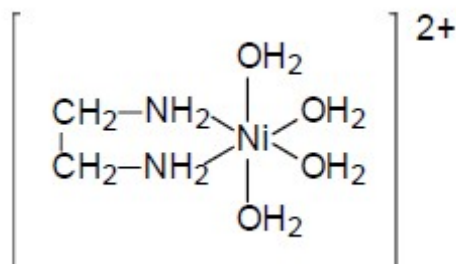
Chelate Effect (Stability of Coordination complexes):

It is observed that coordination complexes of multidentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the chelate effect. With increasing denticity of ligands chelate effect increases (stability increases).

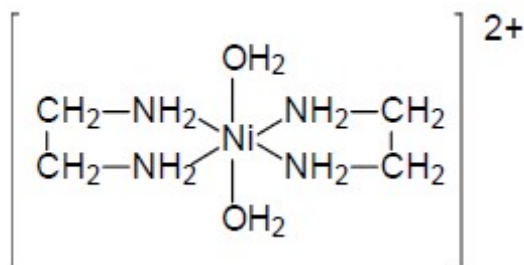
Chelate complexes are more stable than the analogous complexes with monodentate ligands. The stability of a chelate complex depends on the size of the chelate rings. For ligands with a elastic organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings.

For example, the complex of nickel (II) with three ethylenediamine ligands $[\text{Ni}(\text{en})_3]^{2+}$ is about 363,000 times more stable than the corresponding nickel (II) complex with trimethylenediamine $[\text{Ni}(\text{tn})_3]^{2+}$. So, shortly we can say when denticity be same then with increasing chain length of ligands ring strain increases thus stability decreases.

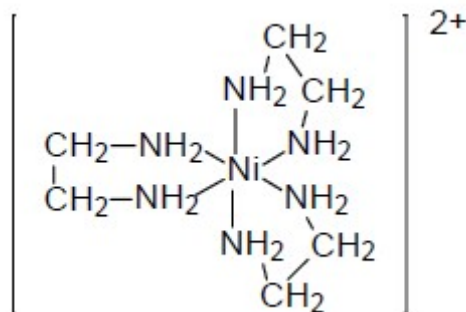
e.g., **Chelate with one ethylenediamine (en) ligand**



Chelate with two ethylenediamine (en) ligands



Chelate with three ethylenediamine (en) ligands



Ambidentate ligand:

Such ligands have **two or more donor atoms** but only one donor atom is attached to the metal during complex formation.

e.g., NO_2^- group has two donor atoms N and O. Only one donor atom (N or O) is linked to metal as $\text{M}^{n+} \leftarrow \text{ONO}$ or $\text{M}^{n+} \leftarrow \text{NO}_2$.

SCN^- can attach to the central metal atom M from two different sites either from S or from N as $\text{M} \leftarrow \text{SCN}$ or $\text{M} \leftarrow \text{NCS}$.

In the same way, CN^- can link itself to the central atom either from C or N. If the ion is linked from C, it would look like $\text{M} \leftarrow \text{CN}$ and if it is linked from N, it would look like $\text{M} \leftarrow \text{NC}$.

Coordination number:

The total number of donor atoms within the 3rd bracket (coordination sphere) attached to the central metal ion is known as the coordination number of that metal ion.

Werner's theory of coordination compounds:

Alfred Werner (12 December 1866 – 15 November 1919), **father of modern coordination chemistry won the Nobel Prize in Chemistry in 1913 as a first inorganic chemist.**

According to his theory

1. Metal possess two types of valencies.

(i) **Primary valencies (oxidation state of the metal or metal ion)** are those which a metal normally exhibit in the formation of its simple salts. These are satisfied by only anions. **These are represented by dotted lines** between central metal atom or anion.

(ii) **Secondary valencies (coordination number of the metal or metal ion)** are those which a metal cation exercises towards a neutral molecule or negative group in the formation of its complex ions. These are satisfied by electron pair donors, the ions or the neutral species. **These are represented by thick lines.**

2. Each metal has a fixed number of secondary valencies which are also referred as coordination number.

3. The ions attached to primary valencies possess ionizing nature whereas the ions attached to secondary valencies do not ionize when the complex is dissolved in a solvent.

4. The secondary valencies are directed in space about the central metal ion. The primary valencies are non-directional. The presence of secondary valencies give rise to stereoisomerism in complexes.

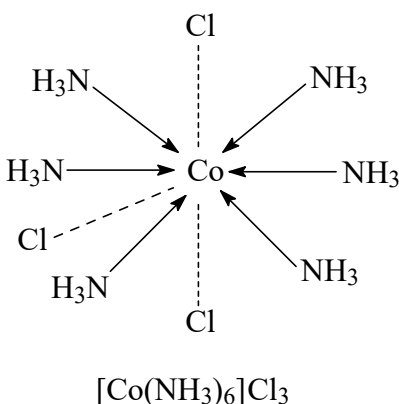


Fig.1. Primary and Secondary valency of hexamminecobalt(III) chloride $\text{CoCl}_3 \cdot 6\text{NH}_3$

Related Questions:

Q.1. What is *Werner's theory*?

Q.2. Predict primary and secondary valencies of metal ions from the following list of coordination compounds



Q.3. Arrange $\text{K}_2[\text{Ni}(\text{EDTA})]$, $[\text{Ni}(\text{en})_3]\text{Cl}_2$, $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, $[\text{Ni}(\text{tn})_3]\text{Cl}_2$ in order of decreasing stability.

Reference Books:

1. *Introduction to Coordination Chemistry*, Geoffrey A. Lawrance
 2. *Coordination chemistry*, Joan Ribas Gispert
 3. *Coordination Chemistry, 20: Invited Lectures Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979*, D. Banerjea
 4. *Comprehensive Coordination Chemistry III*, Gerard Parkin, Edwin C Constable, Lawrence Que
 5. [https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_\(Inorganic_Chemistry\)/Coordination_Chemistry/Complex_Ion_Equilibria/Stability_of_Metal_Complexes_and_Chelation](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Equilibria/Stability_of_Metal_Complexes_and_Chelation)
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