# CHAPTER III : *Complexes*

## 1. Definition

A complex is a polyatomic chemical species $\mathbf{ML_n}$ soluble in water. It consists of a central metal atom or cation **M**, surrounded by **n** molecules or ions **L**, called ligands.

### 1.1. The central element (M)

The central element is a metallic atom or cation, which can be a transition metal cation from the d-block (e.g., $Fe^{2+}$, $Fe^{3+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) or a cation from the alkali or alkaline earth metals in the s-block (e.g., $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$). The metal center, characterized by electron deficiencies, functions as a Lewis acid, meaning it can accept at least one pair of electrons.

### 1.2. Ligands (L)

Ligands are species that have at least one lone pair of electrons on an atom that is either formally or partially negatively charged, making them Lewis bases. Ligands can be classified into two categories :

- **Anionic ligands :** These carry a negative charge when not coordinated to the metal (e.g., $Br^-$, $HO^-$, etc.).
- **Neutral ligands :** These have no net charge (e.g., $H_2O$, $NH_3$, etc.).

## 2. Complex Formula

The formula of a complex is written inside square brackets, beginning with the central atom (**M**), followed by the **anionic ligands**, and concluding with the **neutral ligands**.

$$[M(L)_n]^{x+}$$

**Where**

**M** represents the central metal atom or ion.

**L** represents the ligands bound to the metal.

**n** is the number of ligands coordinated to the metal.

**x** indicates the overall charge of the complex, which depends on the charges of the central metal and the ligands.

### Example

| | | | | |
|---|---|---|---|---|
| $Fe^{2+}$ | + | $6CN^-$ | → | $[Fe(CN)_6]^{4-}$ |
| $Cu^{2+}$ | + | $4NH_3$ | → | $[Cu(NH_3)_4]^{2+}$ |
| Central cation | | Ligand | | Complex |

## 3. Nomenclature of Complexes

### 3.1.Rules

- The name of the complex is written as a single word.
- If the complex [**ML**] is not neutral (anion or cation), it is preceded by the word "**ion**."
- Ligands (**L**) are listed in alphabetical order, followed by the central element (**M**).
- The number of monodentate ligands is indicated by prefixes such as **di-**, **tri-**, **tetra-**, **penta-**, **hexa-**, etc.
- The number of polydentate ligands is indicated by prefixes such as **bis-**, **tris-**, **tetrakis-**, **pentakis-**, etc.
- For anionic complexes, the metal's name ends with the suffix "**-ate**."
- The oxidation state of the central element is indicated in Roman numerals at the end of the complex name.

***Prefix-Ligand Names + Metal Name + (Oxidation State)***

### 3.2. Names of Ligands

The name is derived from the name of the molecule or ion.

***3.2.1. Anionic Ligands*** **:** The suffix "**o**" is added.

**Examples**

**Monodentate Anionic Ligands**

- $Cl^-$ : chloro
- $I^-$ : iodo
- $F^-$ : fluoro
- $H^-$ : hydride
- $CN^-$ : cyano
- $OH^-$ : hydroxo
- $SO_4^{2-}$ : sulfate
- $SCN^-$ : thiocyanato
- $NO_2^-$ : nitrito

**Polydentate Anionic Ligands**

- $S_2O_3^{2-}$ : thiosulfato
- $C_2O_4^{2-}$ : oxalato
- $C_6H_4(COO)_2$ : phthalato

### *3.2.2. Neutral (Molecular) Ligands*

**Examples**

**Monodentate Neutral Ligands**

- $H_2O$ : aqua
- $NH_3$ : ammine
- CO : carbonyl
- NO : nitrosyl
- $CH_3NH_2$ : methylamine

**Polydentate Neutral Ligands**

- en : ethylenediamine

## 3.3. Names of Complexes

Complexes can either be neutral (no overall charge), cationic (positively charged), or anionic (negatively charged), depending on the metal's charge and the nature of the ligands involved.

***3.3.1. Neutral complexes :*** These complexes do not carry a net charge. The total charge is balanced between the central metal ion and the ligands ($[Ni(CO)_4]$).

***3.3.2. Non-neutral Complexes :*** These complexes carry a net charge, which can either be positive (**cationic**) or negative (**anionic**), depending on the charges of the metal ion and the ligands ($[Cu(H_2O)_6]^{2+}$), ($[Fe(CN)_6]^{4-}$ ).

**Example**

Let's consider the complex $[Cu(NH_3)_4]^{2+}$

**Name of the Ligands** : The ligand is **ammine**, since $NH_3$ is a neutral ligand.

**Name of the Metal** : The metal is **copper** (Cu).

**Oxidation State of the Metal** : The oxidation state of copper in this complex is $^{+2}$, so it is written as **copper(II)**.

**All Together** : The name of the complex is **tetraamminecopper(II) ion**.

*3.3.3. Case of a complex salt :* The name of the complex salt follows the general rule of naming salts : the anion is named first, followed by the cation.

**Example**

$K_3[Fe(CN)_6]$ : Potassium hexacyanoferrate(III)

**Cation** : $K^+$, The potassium ions are named first as "potassium" since they are outside the coordination sphere.

**Anionic Complex** : $[Fe(CN)_6]^{3-}$

**Ligands** : Cyanide (**$CN^-$**) ligand with the prefix **hexa-** for six ligands → **Hexacyano**.

**Metal** : Iron (Fe) is part of an anionic complex, so the name changes to **ferrate**.

**Oxidation State** : Iron is in the +III

So the complete Name is **Potassium hexacyanoferrate(III)**

$[Cr(NH_3)_4]Cl_3$ : Tetramminechromium(III) chloride

***3.3.4. Case of Multiple Ligands :*** When a complex contains multiple ligands, the nomenclature follows specific rules to ensure clarity and consistency.

- The central metal is named after all the ligands have been listed.
- If the complex is an anion, the metal name will end with "**ate**" (e.g., **ferrate** for iron).
- The oxidation state of the metal is written in Roman numerals in parentheses after the metal name (e.g., **Cu(II)**).

**Example**

$[Cu(CO)_2Cl_2]$: dicarbonyldichlorocopper(II)

$[Co(H_2O)_3I_3]$ : tris(aqua)triiodocobalt(III)

**Note**

For anionic complexes, the **metal's name is modified to end with "-ate"** and for some metals, the **Latin-derived name** is used :

- Iron → Ferrate
- Copper → Cuprate
- Silver → Argentate
- Gold → Aurate

## 3. Formation of a complex

The formation of a complex involves the process where a central metal ion forms bonds with ligands (molecules or ions) through coordination interactions

### 3.1. Formation Constant

The overall formation constant is the equilibrium constant associated with the formation equilibrium of the complex MLn. This equilibrium constant is denoted as βn.

For the complex **$[Ag(NH_3)_2]^+$**, its formation equilibrium is written as:

$$Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$$

Therefore : $K_f = \frac{[Ag(NO_3)_2]^+}{[Ag^+][NH_3]^2}$

**$K_f$** is called the overall formation constant or stability constant ; it is denoted as **β** or **$K_f$**. It characterizes the formation equilibrium of the complex.

***$K_f$ ↗ The more stable complex***

**Note :** The formation of the complex is complete if : **$K_f \geq 10^4$**

## 3.2. Dissociation Constant

This is the equilibrium constant associated with the dissociation equilibrium of the complex. This equilibrium constant is denoted as **$K_d$**.

$$K_d = \frac{1}{K_f} = \frac{[Ag^+][NH_3]^2}{[Ag(NO_3)_2]^+}$$

It is also observed that : $pK_d = -\log K_d = \log K_f$

**Note :** The complex is more stable when **$K_f$** is larger and **$K_d$** is smaller.

**Example**

$$\mathrm{Fe}^{2+} + 6\mathrm{CN}^- \leftrightarrow [\mathrm{Fe(CN)}_6]^{4-}, \quad K_f = 10^{24}, \quad K_d = 10^{-24}$$

$$\mathrm{Ag}^+ + 2\mathrm{NH}_3 \leftrightarrow [\mathrm{Ag(NH_3)_2}]^+, \quad K_f = 10^{7.1}, \quad K_d = 10^{-7.1}$$

The complex **$[Fe(CN)_6]^{4-}$** is more stable than **$[Ag(NH_3)_2]^+$**, because $K_f$ for **$[Fe(CN)_6]^{4-}$** is greater than $K_f$ for **$[Ag(NH_3)_2]^+$**.

## 3.3. Successive Formation Constants of Complexes

Successive formation constants (also called **stability constants**) are equilibrium constants that describe the stepwise formation of metal-ligand complexes. They are denoted as $K_1$, $K_2$, $K_3$,…, representing each step where an additional ligand binds to the central metal ion. When a metal ion $M^{n+}$ forms a complex with a ligand L, the reaction can be described step by step.

**First step**

$$M + L \leftrightarrow ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \leftrightarrow ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \leftrightarrow ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

The equilibrium constants can further be extended for the attack of n number of ligands as given bellow.

$$ML_{n-1} + L \leftrightarrow ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where $K_1$, $K_2$, $K_3$…… $K_n$ are the equilibrium constants for different steps.

Typically, the successive constants decrease in magnitude : $K_1 > K_2 > K_3$. This reflects the fact that adding more ligands becomes less favorable as the complex becomes more saturated.

The **overall formation constant** ($\beta_n$) for a complex $[ML_n]$ is the product of the successive constants : $\beta_n = K_1 \cdot K_2 \cdot K_3 \cdots K_n$

### Example

For the complex $[Cu(NH_3)_4]^{2+}$, the successive formation constants might be:

$K_1 = 4.5\times10^3$, $K_2 = 2.8\times10^3$, $K_3 = 1.5\times10^3$, $K_4 = 7.9\times10^2$

### Exercice 5

## 4. Effect of pH on Complexes

The **pH** of a solution plays a critical role in determining the availability of ligands with ionizable functional groups (**$OH^-$**, **$NH_2$**) for coordination to a metal center.

- **At low pH :** Protonation of ligands reduces the availability of lone pairs, decreasing complex stability or preventing complexation.
- **At high pH :** Deprotonation enhances ligand basicity, making them stronger donors and increasing complex stability.

### Example

**Glycine ($NH_2CH_2COOH$)**

**At low pH,** Glycine exists in the form $NH_3^+$. Both the amino group ($NH_2$) and carboxylic group (COOH) are protonated, so glycine cannot coordinate to a metal ion.

**At neutral pH**, Glycine exists in the form $NH_3^+CH_2COO^-$. The amino group ($NH_2$) is protonated to $NH_3^+$, while the carboxylic group (COOH) is deprotonated to $COO^-$, so partial coordination is possible via the $COO^-$ group.

**At high pH**, Glycine exists in the form $NH_2CH_2COO^-$. Both the amino group ($NH_2$) and carboxylic group ($COO^-$) are deprotonated. Complete coordination is possible via both $NH_2$ and $COO^-$, allowing glycine to act as a bidentate ligand.

## 5. Some application of complexes

Complexes play a crucial role in various scientific, industrial, and biological fields due to their unique properties. Here are some examples of the applications of complexes in different domains:

### 5.1. Analytical Chemistry

***5.1.1. Complexometric Titration :*** Determination of $Ca^{2+}$ and $Mg^{2+}$ in hard water using EDTA complex with metal ions are used to accurately measure the concentrations of metals in solutions.

***5.1.2. Metal Indicators :*** as Eriochrome Black T as an indicator for alkaline earth metals.

### 5.2. Biology and Medicine

***5.2.1. Metalloenzymes:*** Many essential enzymes contain metal complexes , such as Hemoglobin ($Fe^{2+}$) transports oxygen in blood.

***5.2.2. Medical Treatments:*** Some complexes are used as drugs, such as Cisplatin $[PtCl_2(NH_3)_2]$ a complex used in cancer therapy.

### 5.3. Agriculture

Complexes are used as Fertilizers**,** as Iron-EDDHA complexes are used to treat iron deficiency (chlorosis) in plants.

### 5.4. Environment

***5.4.1. Water Treatment :*** Complexes, such as those formed by chelating agents, are used to remove heavy metals from wastewater, example: EDTA is used to remove $Pb^{2+}$, $Hg^{2+}$, etc.

***5.4.2. Pollution Reduction :*** Catalytic complexes are used in catalytic converters to reduce vehicle exhaust emissions such as the Rhodium and platinum complexes.