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COMPLEXOMETRIC TITRATION

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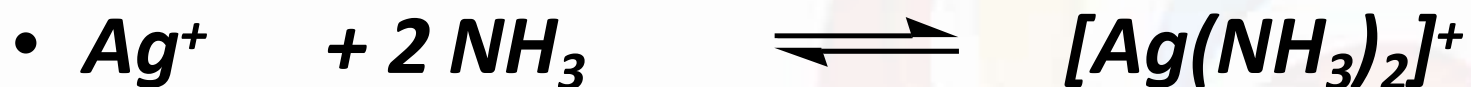
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- **Complexometric titration** is a form of volumetric titration in which the formation of a colored complex is used to indicate the end point of a titration.
- The complexes are formed by the reaction of a metal ion (an acceptor, a central atom or a cation) with an anion, a neutral molecule or very rarely a positive ion.

- Complexometric titrations are particularly useful for the determination of a mixture of different **metal ions** in solution.
- An indicator capable of producing an distinct color change is usually used to detect the end point of the titration.

- **Complexometry** : is the type of volumetric analysis involving the formation of complexes which are slightly ionized in solution, like weak electrolyte and sparingly soluble salt.
- **Complex** is formed by the reaction of metal ion (M^{n+}) with either an anion e.g. $[Ag(CN)_2]^-$ or neutral molecule e.g. $[Ag(NH_3)_2]^+$
- **The metal ion** is known as **Central metal atom**.
- **The anion or neutral molecule** is known as **Ligand (L)**

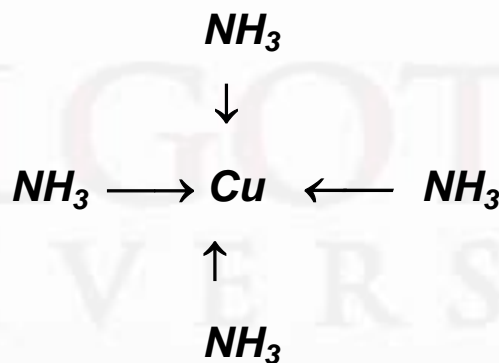


- **Central metal atom** = acts as Lewis acid (electron acceptor)

- **Ligand** = acts as Lewis base (electron donor)

- **Coordinate bond (dative)** = The bond formed between central metal atom (ion) (**acceptor**) and the Ligand (**donor**)

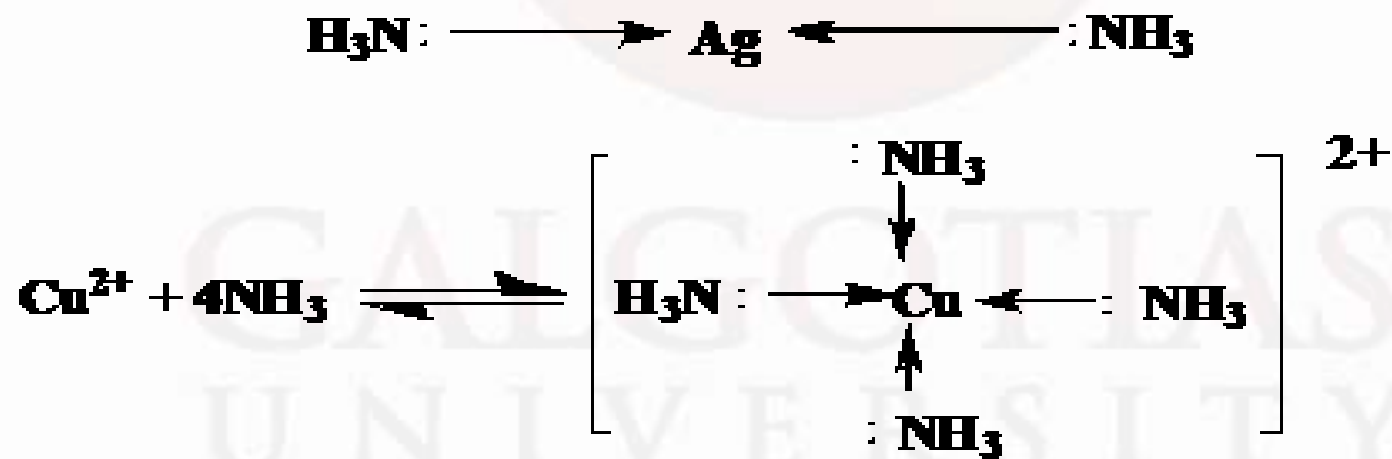
- Dative bond is similar to covalent bond (formed of two electrons) **But** in dative bond the electrons pair are donated from one atom to the other. The atom gives electron pair is known as donor, while the atom accept electron pair is known as acceptor. The bond is represented by an arrow (\longrightarrow) from donor to acceptor.



- * **Coordination number** = The no. of coordinate bonds formed to a metal ion by its ligands.
- * **Characters of coordination number** *
- 1- It is even number: **2** e.g. Ag^+ , **4** e.g. Ni^{2+} , Cu^{2+} , **6** e.g. Fe^{3+} , Cr^{3+}
- 2- It is usually double the charge of the metal.
- The charge of a complex is the algebraic sum of the charges of the central ion and ligand .. e.g.
- $[Ag(CN)_2]^- \longrightarrow Ag^+ + 2 CN^-$
- $1 (+ve) + 2 (-ve) = 1 (-ve)$
- e.g. $[Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + 6 CN^-$
- $3 (+ve) + 6 (-ve) = 3 (-ve)$
- The higher the valence of metal ion the more stable the complex e.g. Ferricyanide is more stable than Ferrocyanide

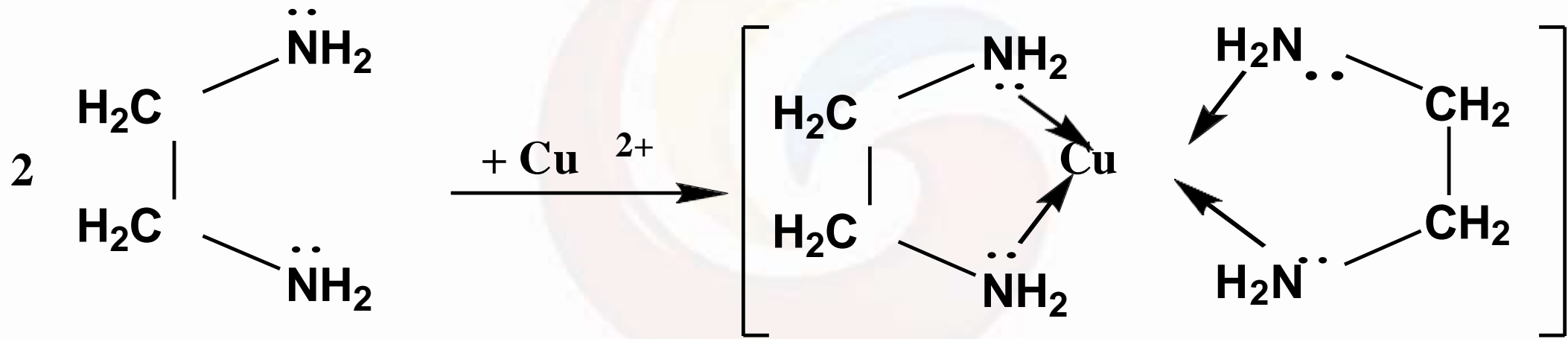
Types of complexing agents ((Classification of ligands according to the no. of sites of attachment to the metal ion))

- **Unidentate (Monodentate) Ligand or "Simple Ligand"**
- The ligand attached to metal at one site e.g. H_2O , NH_3 , CN^- , Cl^- , I^- , Br^- , (i.e. forming one coordinate bond, or capable of donating one unshared pair of electrons)



- **Bidentate Ligand**

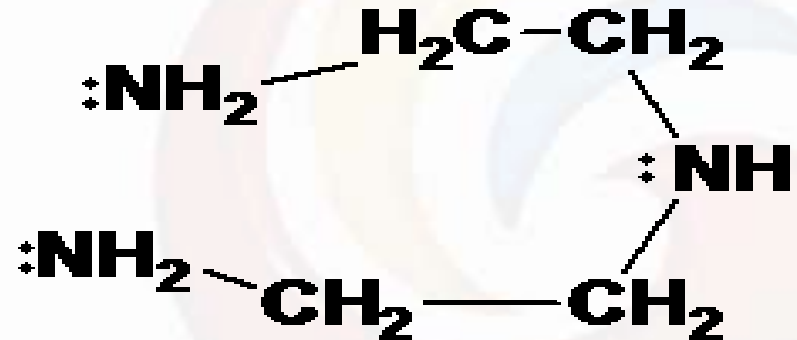
The ligand attached to metal at two sites.



Ethylenediamine

- **Tridentate Ligand:**

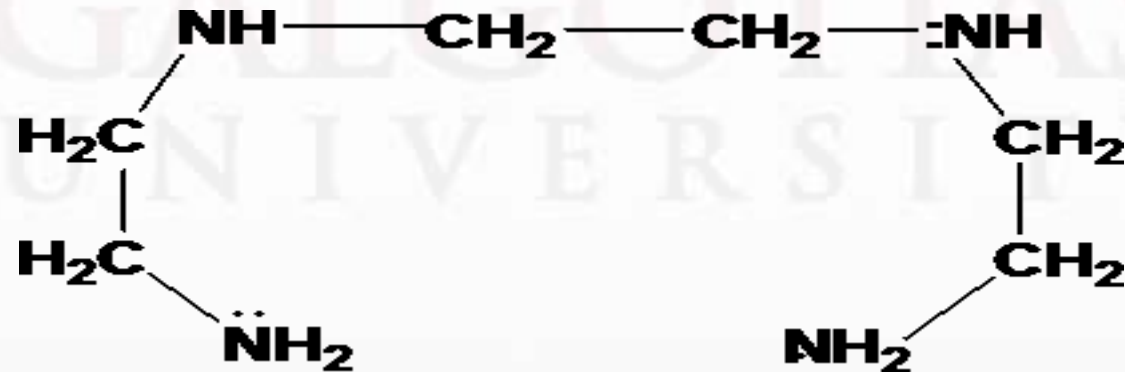
The Ligand attached to metal at 3 sites



Diethylene triamine

- **Tetradentate Ligand:**

The Ligand attached to metal at 4 sites



Triethylene tetramine

Chelation

- **Chelate** : It is a complex formed between the ligand containing two or more donor groups and metal to form ring structure. (heterocyclic rings or chelate rings).
- **Chelating agents**: organic molecules containing two or more donor groups which combine with metal to form complex having ring structure.
- **Chelates are** usually insoluble in water but soluble in organic solvent.
- **Sequestering agent** : Ligands which form water soluble chelates e.g. EDTA.

Classification of Complexometric Titrations

- 1) Direct Titration**
- 2) Back titration**
- 3) Replacement Titration**
- 4) Alkalimetric titration of metals**

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Direct Titration

In this type of titrations, the sample solution of metal ion, in the presence of a suitable buffer, is titrated against standard disodium edetate solution.

- ***M-EDTA*** complex must be more stable than ***M- Ind.*** complex in buffered medium.
- The compound to be determined is water soluble.
- The reaction between ***EDTA*** and metal must be rapid. If the reaction is slow it must be catalyzed.
- ***Mⁿ⁺*** should not be ppt. at the pH of titration. If ***Mⁿ⁺*** is ppt. as ***MOH***, auxiliary reagent must be added to prevent pptn. of ***Mⁿ⁺***.

- **Direct determination of water hardness**
- Water hardness is due to the presence of **Ca^{2+} & Mg^{2+}** salts.
- ***EDTA*** forms complex with **Ca^{2+} & Mg^{2+}** , ***Ca-EDTA*** complex is more stable than ***Mg-EDTA*** complex.
- At pH 12 ***EDTA*** forms complex with **Ca^{2+}** only.
- **Total Ca^{2+} & Mg^{2+} :**
- Total **Ca^{2+}** and **Mg^{2+}** determined by titration with ***EDTA*** at pH 10 using ammonia buffer and ***EBT*** (Eriochrome Black T) as ind.
- Upon titration with ***EDTA***, **Ca^{2+}** will be chelated first, then **Mg^{2+}** .
- **For Ca^{2+} only:**
- Direct titration with ***EDTA*** at pH 12 using 8% ***NaOH*** and Murexide.
- **Mg^{2+}** is pptd. as **$Mg(OH)_2$** leaving **Ca^{2+}** which is titrated with ***EDTA***
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- **For Mg^{2+} :**
- **Total – Ca^{2+} = Mg^{2+}**

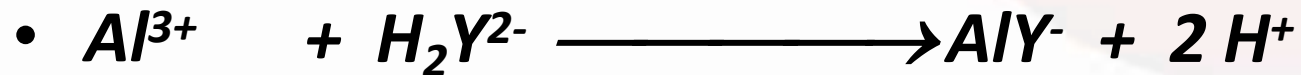
Back Titration

- Addition of known excess of st. **EDTA** to the sample
- The medium is buffered.
- Exss. **EDTA** is titrated with standard soln. of another metal ion e.g. Mg^{2+} or Zn^{2+}
- ***It is used in the following cases:***
- Insoluble substances e.g. BaSO_4 , $\text{Ca}(\text{C}_2\text{O}_4)_2$, PbSO_4 , $\text{Mg}_3(\text{PO}_4)_2$... etc.
Usually soluble in hot **EDTA**.
- The reaction between M^{n+} & **EDTA** is slow (incomplete) e.g. Fe^{3+} , Al^{3+} , Cr^{3+} , Th^{4+} , ... etc.
- The M^{n+} is pptd. at the pH suitable for titration e.g. $\text{Al}(\text{OH})_3$.
- The colour change at the end point :
 - **From free ind. colour** \longrightarrow to ***M-Ind.* complex**
(opposite that direct titration)

- **Det. of Aluminium salts:**

- Sample of Al^{3+} is heated with known xss. of st. **EDTA** at pH 7-8.
- The soln. is then adjusted to pH=10 using ammonia buffer.
- The residual **EDTA** is titrated against st. Zn^{2+} using EBT (Eriochrome Black T) indicator.
- The colour change from blue to wine red.

pH 7-8



- Boil



Replacement Titration

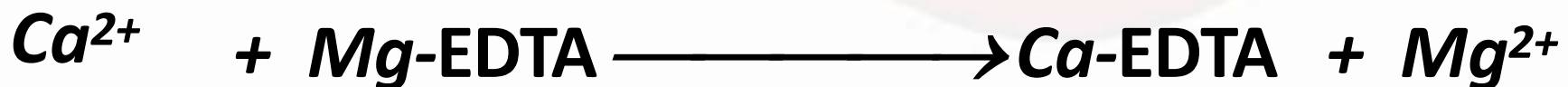
When both back titration and direct titration is not possible due to the end point not being sharp enough. Then the replacement titration is a method of choice.

In this method of titration determination of metal ion is done by displacing magnesium or zinc ions from EDTA complex with an equivalent amount of metal ion and liberated Mg or Zn ions are then titrated with standard EDTA solution.

Mordant black used as indicator.

Calcium salt is determined in this way. In this, add standard volume of Mg-EDTA solution to Ca salt in the presence of buffer.

Calcium displaces Mg ion and forms a stable complex with EDTA as Ca-EDTA complex. The displaced and liberated Mg ions are then titrated Standard EDTA solution using Mordant black as indicator.



Cadmium, Lead and Mercury can also be determined by this titration.

Alkalimetric titration of metals

- Metal-EDTA complex formation reaction explains that protons are liberated from disodium edetate leading to formation of acid.



The acid that is formed can be titrated against a standard alkali but in an unbuffered solution. End point detection can be done by using acid base visual indicator or potentiometric method of detecting end point.

- **Masking and demasking agent**

- **Masking agents:** are reagents which prevent interfering ion from reaction without physical separation.
- These reagents form complexes with interfering ions which are more stable than complexes formed with ind. & **EDTA**.

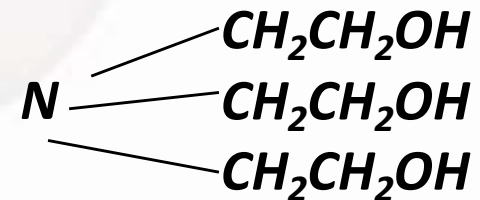
- **Examples of masking agent:**

- **(A)- KCN**

- It is used as masking agent for **Ag^+ , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , ... etc.**



- **(B)- Triethanolamine :**



- - It is used as masking agent for **Fe^{3+} , Al^{3+} and Sn^{2+}**

- **(C) Fluoride (e.g. NH_4F):**

- - It is used as masking agent for **Fe^{3+} and Al^{3+}** to give hexafluoro complex **$[FeF_6]^{3-}$ and $[AlF_6]^{3-}$**

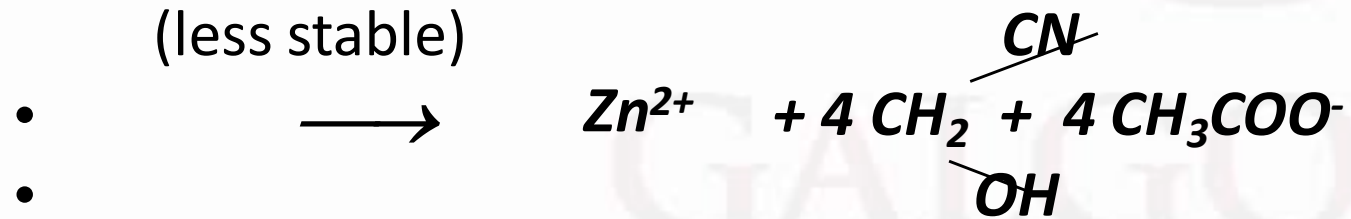
- **(D)- Iodide (KI):**

- - It is used as masking agent for **Hg^{2+}** to give tetraiodo complex (**HgI_4**)

- **Demasking agent** : is the process in which masking substance reverses back to its ability to take part in the reaction.
 - are reagents which regain the ability of masked ion to enter the reaction with ind. and **EDTA**.
- **Example:**
 - The masking by **CN⁻** can be removed by:
 - mixture of formaldehyde – acetic acid
 - on addition of demasking agent to **[Zn(CN)₄]²⁻**, **Zn** is liberated and titrated.



(less stable)



Cyanohydrin (more stable)

Reference

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- 3. Beckett, A.H., and Stenlake, J.B., Practical Pharmaceutical Chemistry, Vol. I&II. The Atherden Press of the University of London.
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