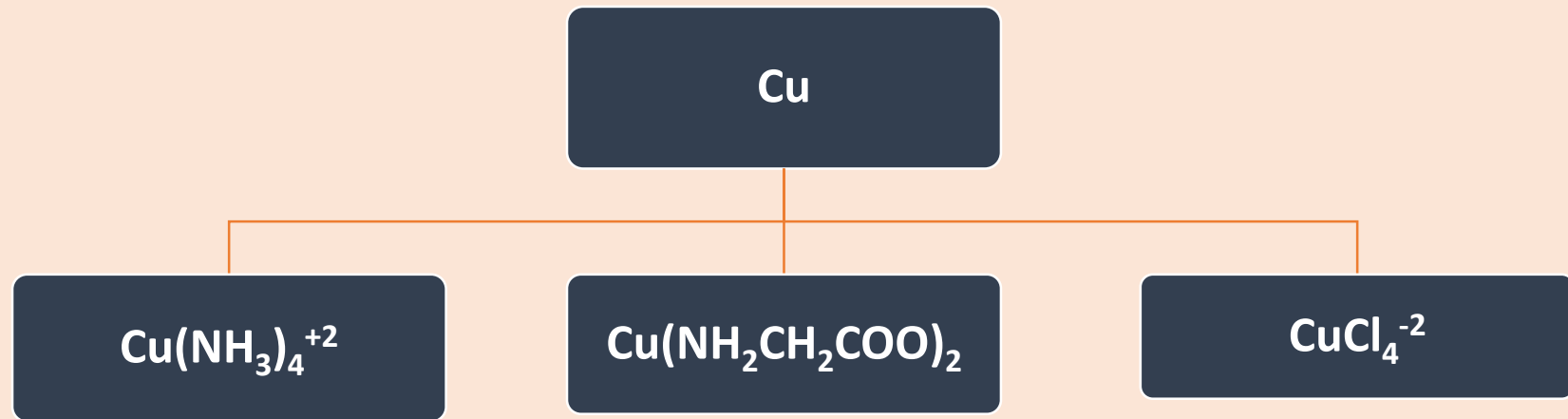




Complexometric Titration

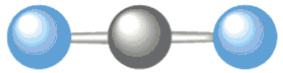
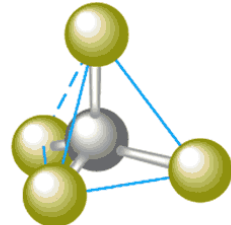
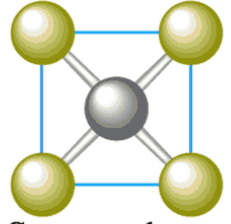
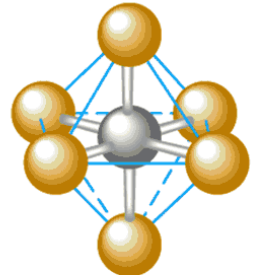
The formation of Complexes

- Metals ions, especially *transition metals*, act as *Lewis acids*, because they accept electrons from Lewis bases
- When metal cations combine with Lewis bases, the resulting species is called a *complex ion* or *coordination complex*



Coordination Number

- The number of covalent bonds that a cation tends to form with electron donors is called *coordination number*.
- Common coordination numbers are 2, 4 and 6
- The geometries of the ligands about the central atom are as shown

Coordination number	Geometry
2	 Linear
4	 Tetrahedral  Square planar
6	 Octahedral

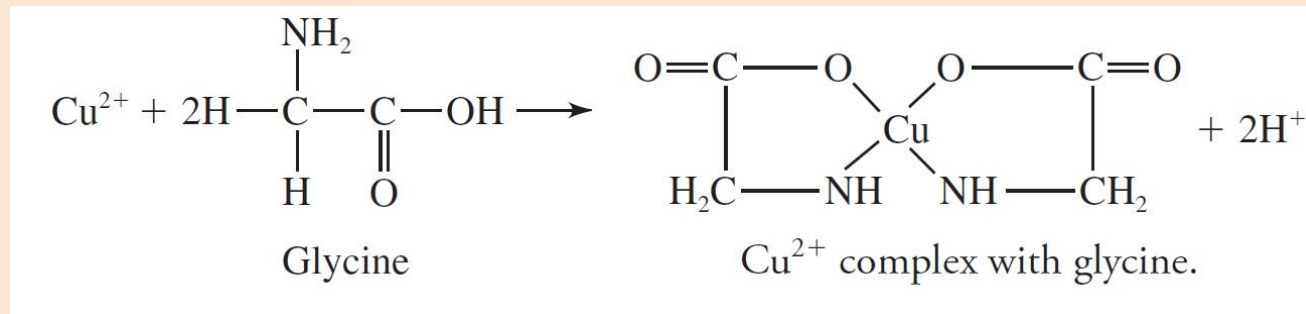
A titration based on the formation of a coordination complex is known as a *complexometric titration*.

Complex formation titrations are used to titrate cations via complex formation reagents.

- *Complexometric titrations* are particularly useful for the determination of a mixture of different **metal ions** in solution.
- A *ligand* is a neutral molecule or ion having lone pair that can be used to form a bond to a metal ion.
- The bonds are **either ordinary covalent bonds** in which the metal and the ligand contribute one electron each, **or co-ordinate bonds** in which both electrons are contributed by the ligand.

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.

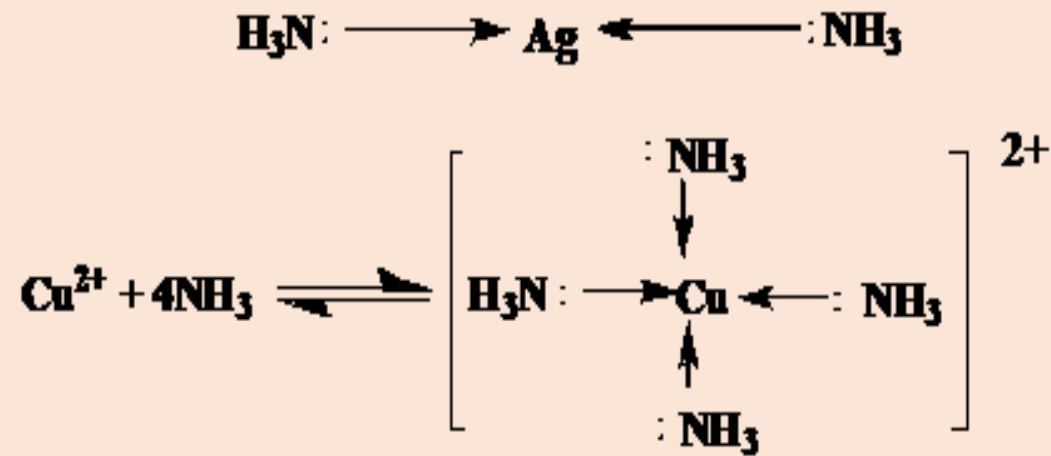


- **Chelates** are usually insoluble in water but soluble in organic solvent.

- The solubility of metal chelates in water depends upon:
- *the presence of hydrophilic groups such as COOH , SO_3H , NH_2 and OH* , when both acidic and basic groups are present, the complex will be soluble over a wide range of pH.
- *When hydrophilic groups are absent*, the solubilities of both the chelating agent and the metal chelate will be low, but they will be soluble in organic solvents
- **Sequestering agent** : Ligands which form water soluble chelates (e.g. EDTA), **they** are used to liberate or solubilize metal ions.
- The agents which form water insoluble chelates are used to remove the metal ions from solution by precipitation.

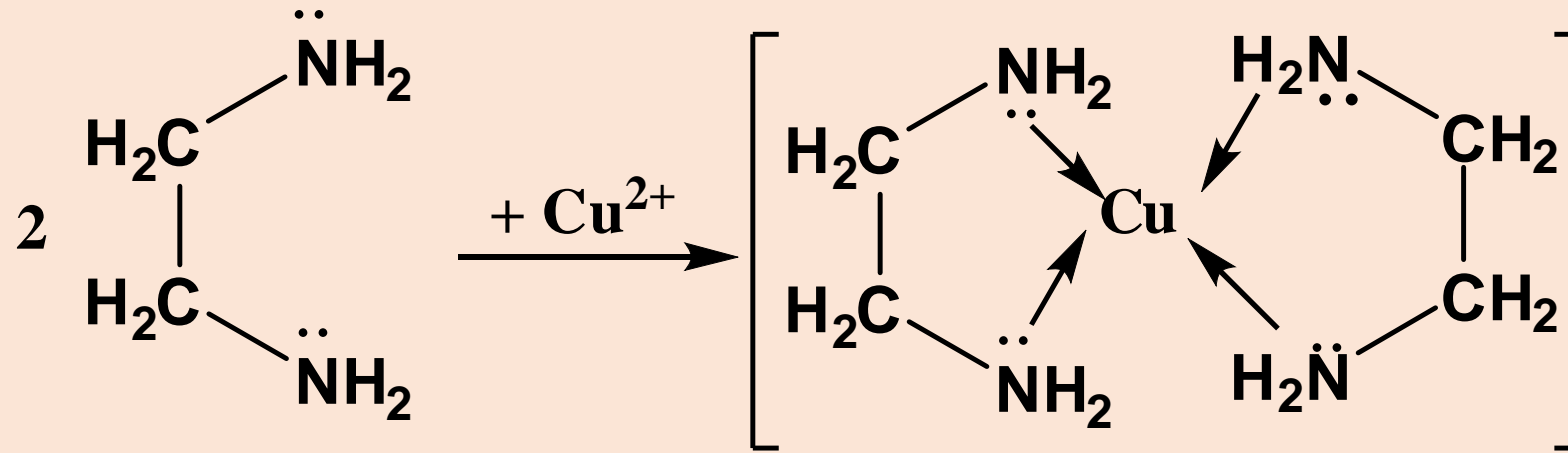
Types of complexing agents ((Classification of ligands according to the no. of sites of attachment to the metal ion))

- **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**

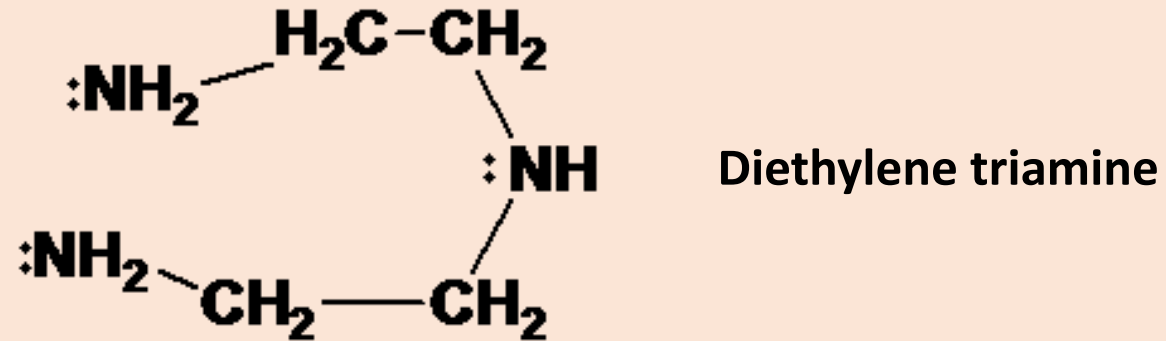
The ligand attached to metal at two sites.



Ethylene diamine

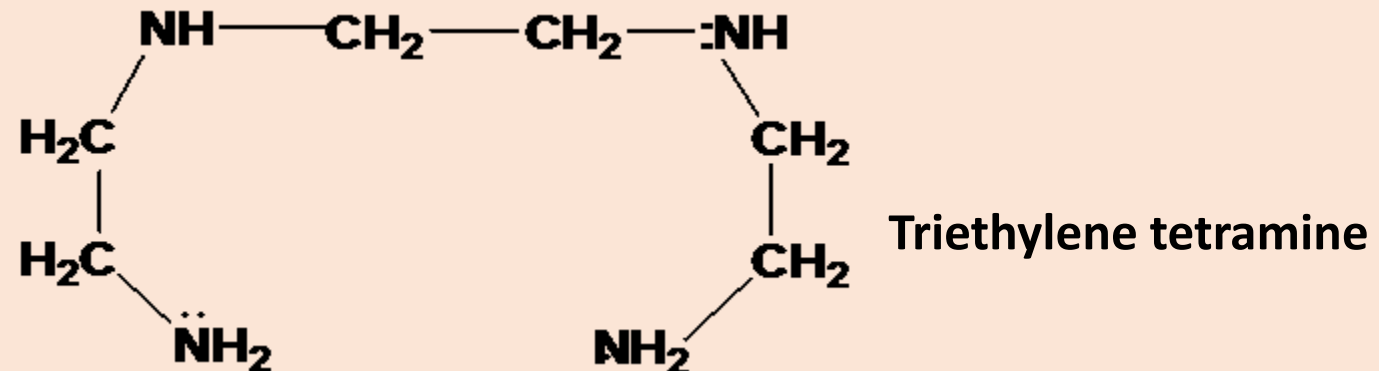
- **Tridentate Ligand:**

The Ligand attached to metal at 3 sites

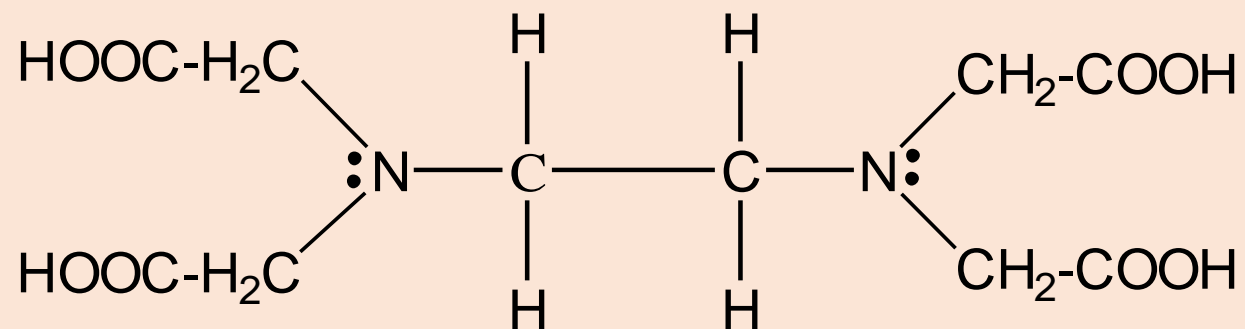


- **Tetradentate Ligand:**

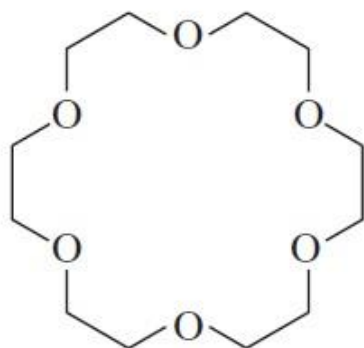
The Ligand attached to metal at 4 sites



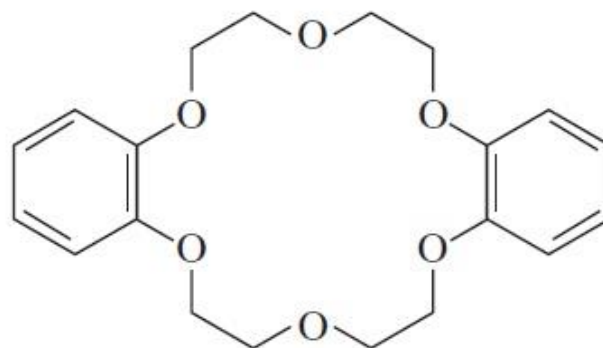
Ethylenediaminetetraacetic Acid (EDTA)



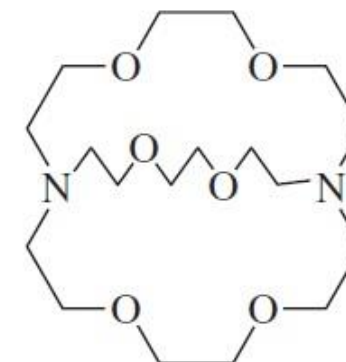
The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and two amino groups.



18-crown-6



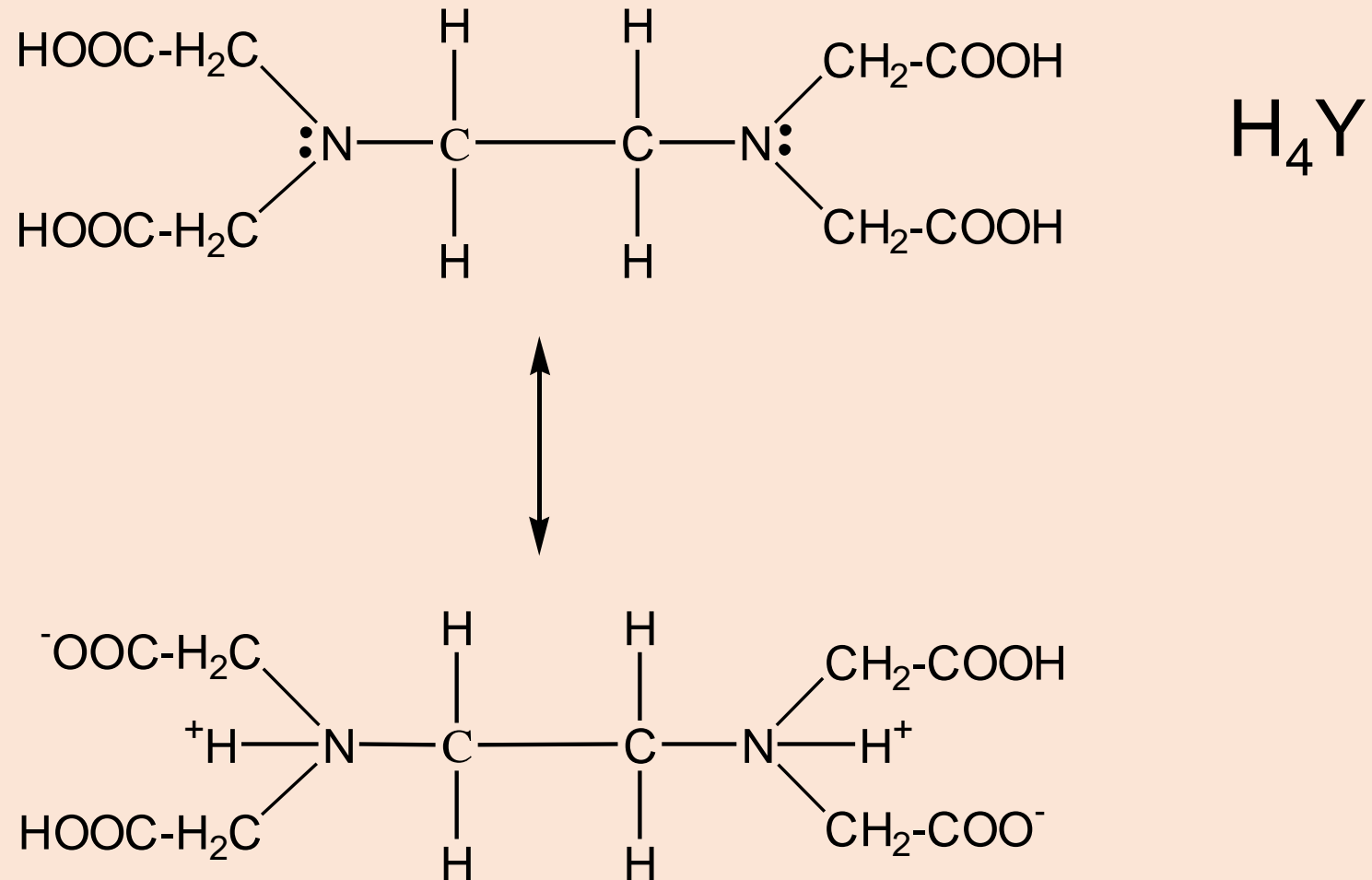
dibenzo-18-crown-6

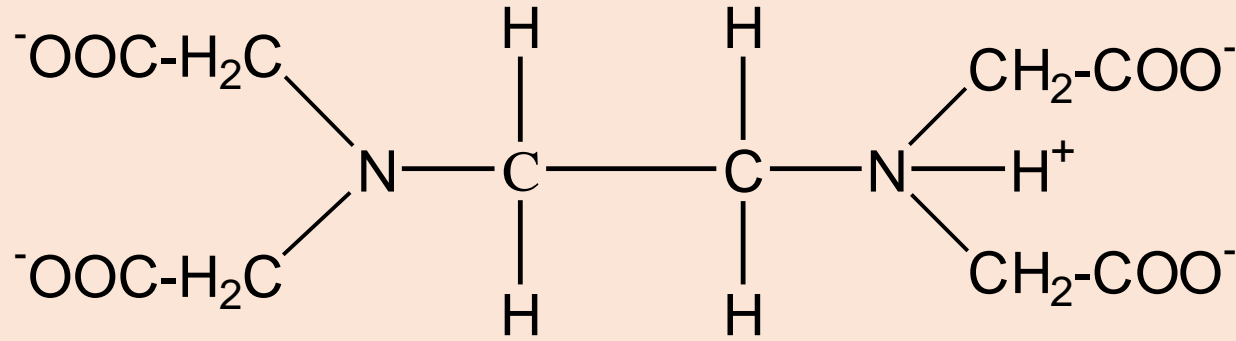


cryptand 2,2,2

Crown ethers and cryptands.

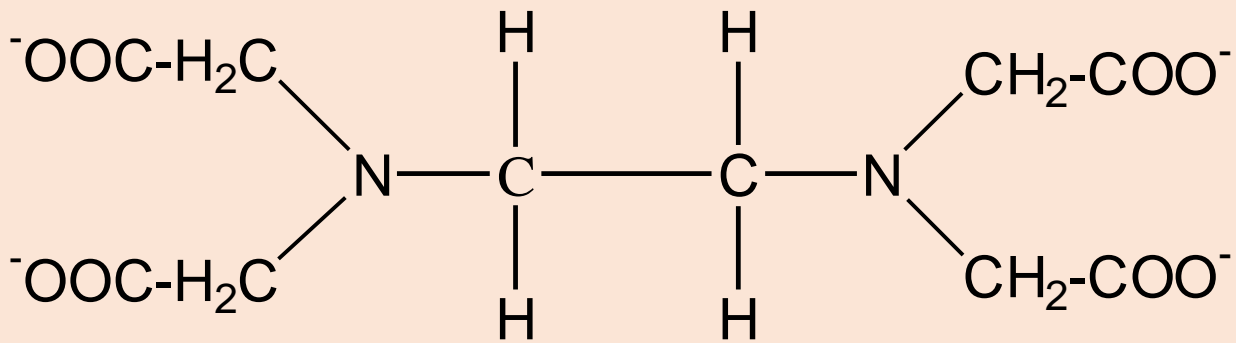
Acidic Properties of EDTA





HY⁻³

$$K_3 = 6.92 \times 10^{-7}$$

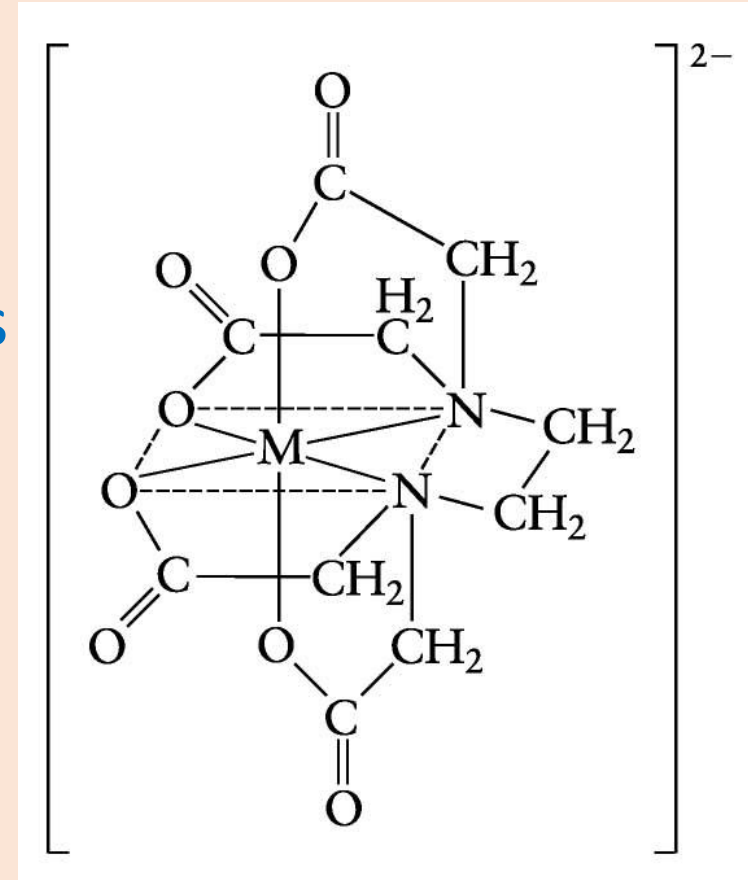


Y⁻⁴

$$K_4 = 5.5 \times 10^{-11}$$

Reagent EDTA

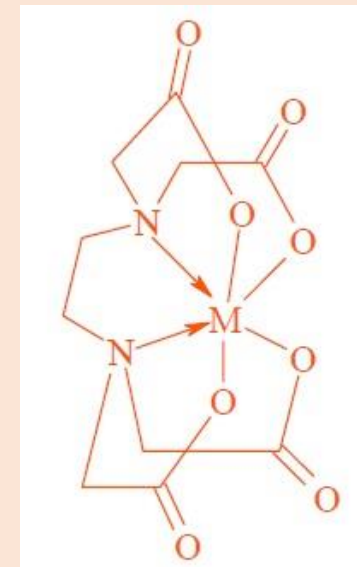
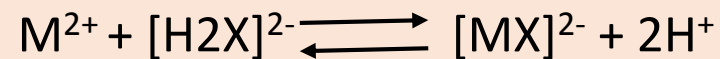
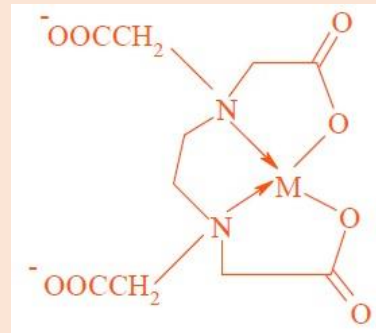
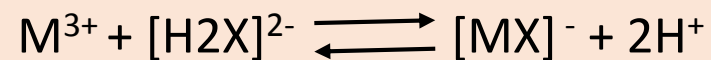
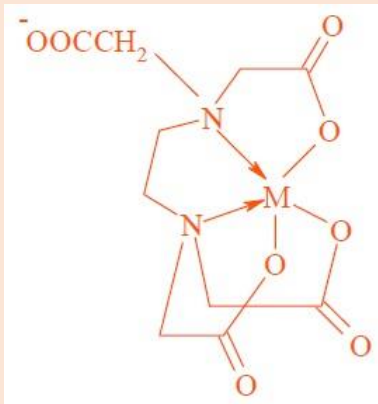
- **Disodium salt** of EDTA is a water soluble chelating agent and is always preferred. It is non-hygroscopic and a very stable sequestering agent.
- **8-hydroxy quinoline** a chelating agent that form an insoluble chelates with metal ion.
- EDTA has the widest general application because:
 1. It has low price
 2. The special structure, which has six ligands atoms
 3. It forms strainless five-membered rings



Factors influencing EDTA reactions

A. The nature and the activity of metal ion:

EDTA forms complexes with complexes with most cations in a 1:1 ratio, irrespective of the valency of the ion:



Factors influencing EDTA reactions

B. Effect of pH:

If the solubility product of the metal hydroxide is low, it may be precipitated if the hydroxyl ion concentration is increased too much.

On the other hand, at lower pH values when the concentration of Y^{4-} is lower, the stability constant of the complexes will not be so high.

Complexes of most **divalent metals** are stable in ammonical solution. Those of the alkaline earth metals, such as Cu, Pb and Ni, are stable down to **pH 3** and hence can be titrated selectively in the presence of alkaline earth metals.

Trivalent metal complexes are usually still more firmly bound and stable in strongly acid solutions; for example, Co(III)-EDTA complex is stable in conc. HCl. Although most complexes are stable over a fair range of pH, solutions are usually buffered at a pH at which the complex is stable and at which the colour change of the indicator is most distinct.

Factors influencing EDTA reactions

C. Effect of presence of interfering ions:

There is always a change in the absorption spectrum when complexes are formed and this forms the basis of many colorimetric assays.

D. Effect of organic solvents on complex stability:



- High temperature causes a slight increasing in ionisation of the complex and lowering in stability constant (K).
- Presence of ethanol increases (K), due to suppression of ionisation.
- Presence of electrolytes having no ion in common with complex decreases (K).

Factors affecting stability of complex

- [A]- Effect of central metal ion :

- (1)- Ionic size (metal radius):

Smaller an ion (small radius of metal), greater its electrical field, more stable complex

- (2)- Ionic charge (metal charge):

Metal of higher charge give more stable complexes. e.g. Ferricyanide [hexacyanoferrate III] is more stable than Ferrocyanide [hexocyanoferrate II].

- (3)- Electronegativity :

The higher acidity (electronegativity) of metal (M^{n+}), the higher stability of complex.

- (4)- Metal which has incomplete outer shell (has high acidity) have more tendency to accept electrons, more stable complex. e.g. Ca^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+}

- **[B]- Effect of Ligand:**
- **[1]- Basic character:**

The higher the basicity (strong base is good electron donor), the higher the ability of ligand to form complex. **e.g.** ligand contain electron donating atom.

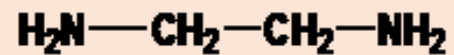
- **e.g.** $\text{N} > \text{O} > \text{S} > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

- **[2]- The extent of chelation:**

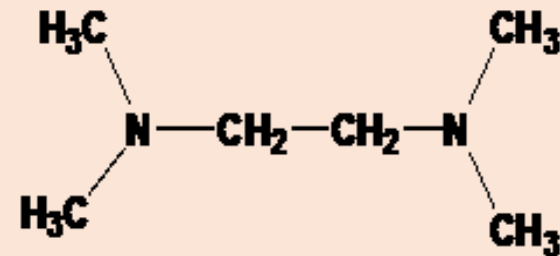
Multidentate ligands form more stable complexes than monodentate.

- **[3]- Steric effect:**

Large, bulky ligand form less stable complexes than smaller ones due to steric effect. **e.g.** ethylene diamine complexes are more stable than those of the corresponding tetramethyl ethylene diamine.

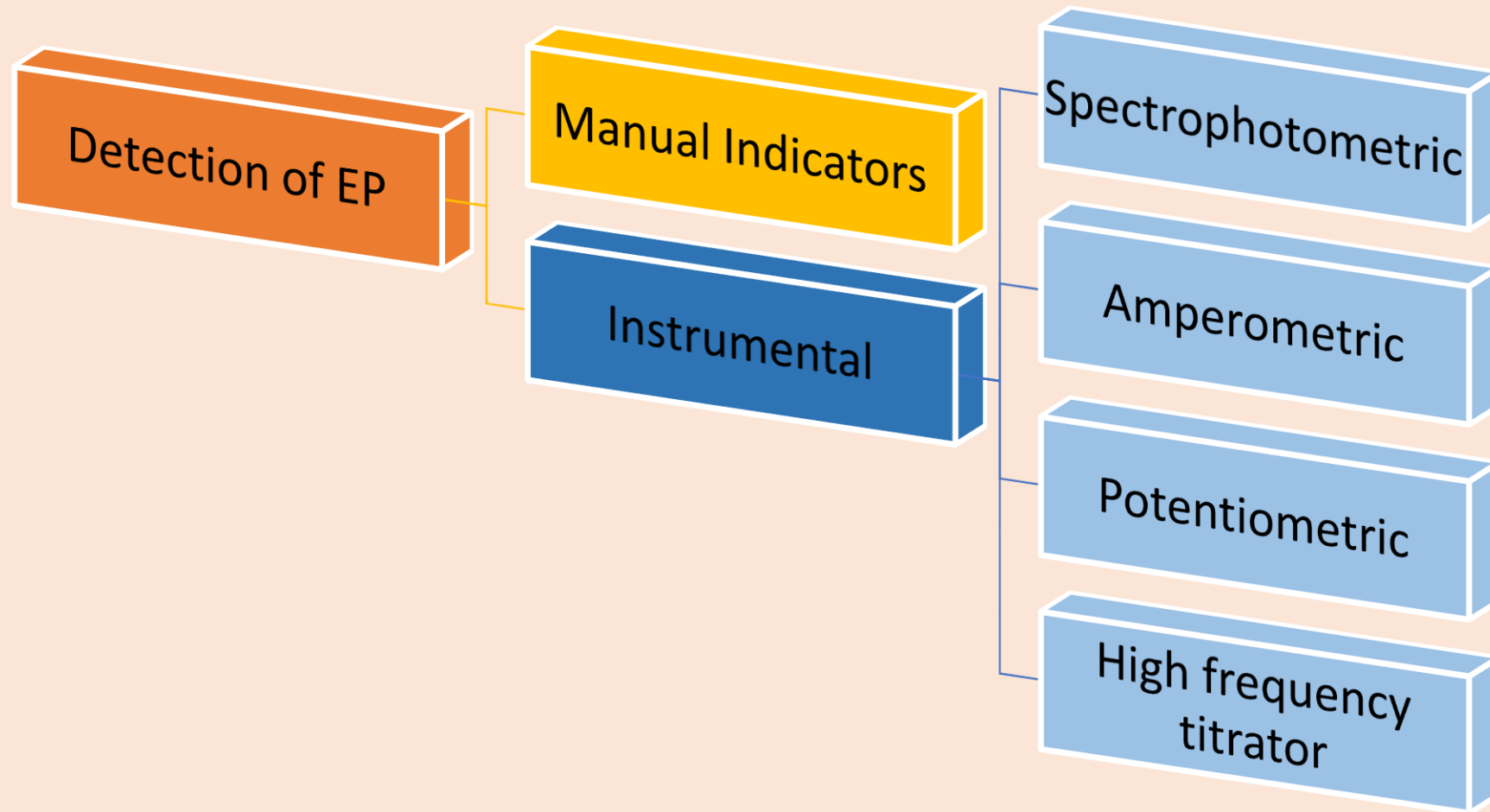


ethylene diamine



tetramethylethylene diamine

Methods of end point detection



Indicators

- **Indicator** is a dye which is capable of acting as a chelating agent to give a dye-metal complex.
- The latter is different in colour from the dye itself and also **has a low stability constant than the chelate-metal complex**.
- The colour of the solution, therefore, remains that of the dye complex until the end point, when an equivalent amount of sodium EDTA has been added.
- As soon as there is the slightest excess of EDTA, the metal-dye complex decomposes to produce free dye; this is accomplished by a change in colour.

The concept of pM indicators

- If K is the stability constant,

then,
$$K = [MX] / [M][X]$$

$$[M] = [MX] / [X]K$$

Or
$$\log [M] = \frac{\log [MX]}{[X]} - \log K$$

$$pM = \frac{\log [X]}{[MX]} - pK \quad \text{if } ([X] = [MX])$$

then
$$pM = -pK$$

Or
$$pM = pK' \quad (pK' \text{ is dissociation constant})$$

This means that, in a solution containing equal activities of metal complex and free chelating agent, the concentration of metal ions will remain roughly constant and will be buffered in the same way as hydrogen ions in a pH buffer.

In general,

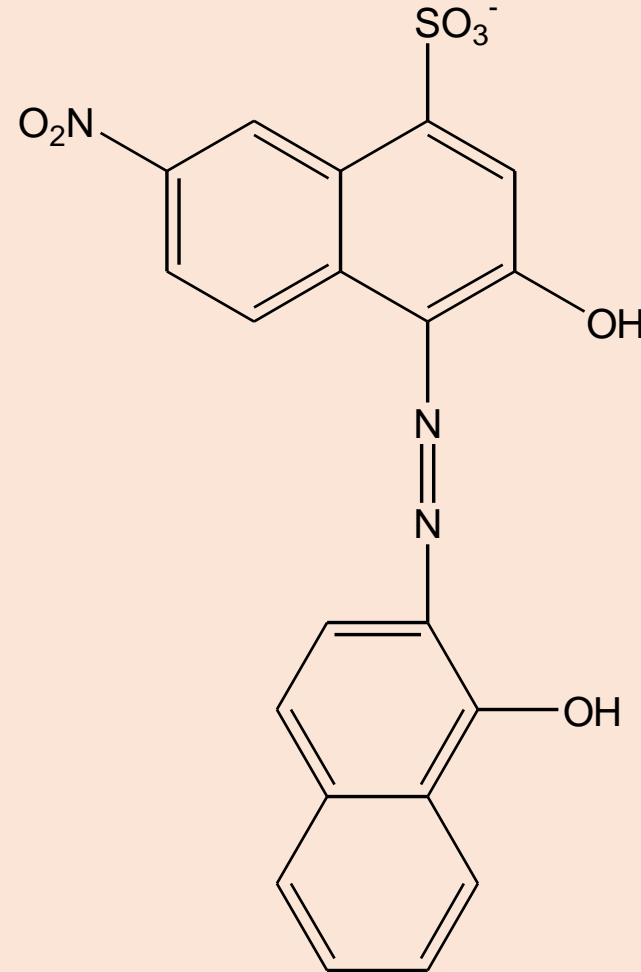
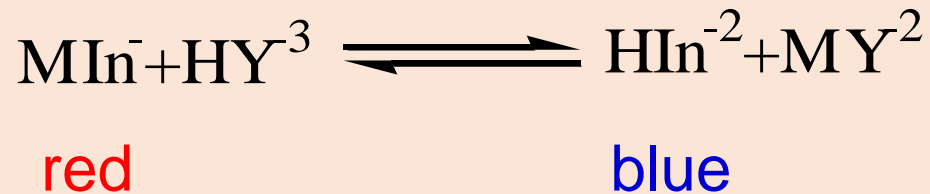
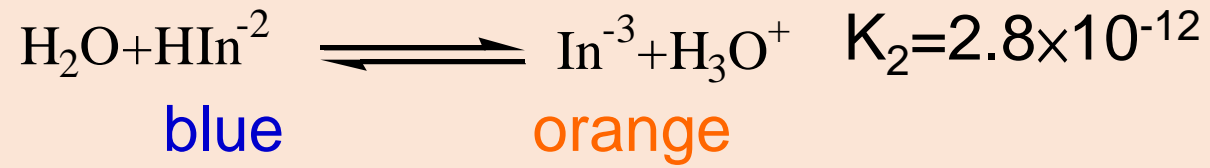
For chelating agents of the amino acid type (e.g., EDTA and ammonia triacetic acid), it may be said that when $[X] = [MX]$, pM increases with pH until about pH 10, when it attains a constant value. This pH is, therefore, usually chosen for carrying out titrations of metals with chelating agents in buffered solutions.

Metal indicators must comply with the following requirements:

- Metal-indicator complex *must be less stable than the metal-EDTA complex*.
- Binding between metal and indicator *must not be too weak*. It has to avoid EDTA replacing at the beginning of the titration.
- In general, the metal-indicator complex *should be 10 to 100 times* less stable than the metal-titrant complex.
- Colour of the indicator and the metal complexed indicator must be sufficiently different.

Indicator for EDTA Titrations

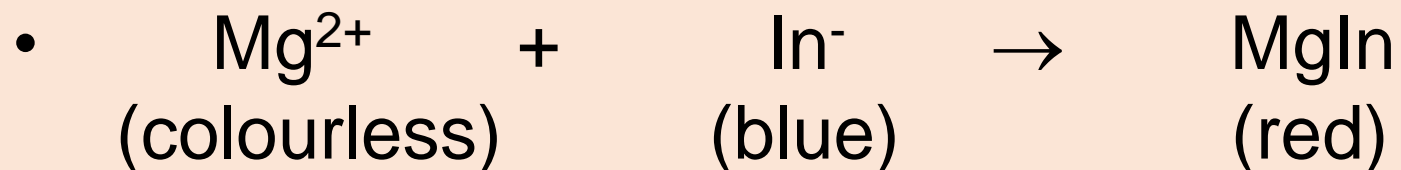
Ertichrome Black T



Compounds changing colour when binding to metal ion.

K_f for Metal-In⁻ < K_f for Metal-EDTA.

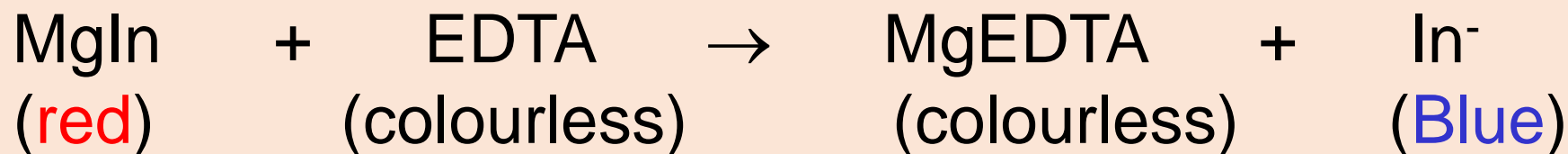
Before Titration:



During Titration: Before the end point



At the end point:



Indicators used in complexometric titrations

S.No.	Name of the Indicator	Colour change	pH range	Metals detected
1.	Mordant black II	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
	Eriochrome blackT			
	Solochrome blackT			
2.	Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
3.	Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
4.	Methyl Blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
	Thymol Blue	Blue to Grey	10-12	
5.	Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
6.	Sodium Alizarin sulphonate	Blue to Red	4	Al, Thorium
7.	Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
			4-5	Pb, Zn
			5-6	Cd, Hg

EDTA Titration Techniques

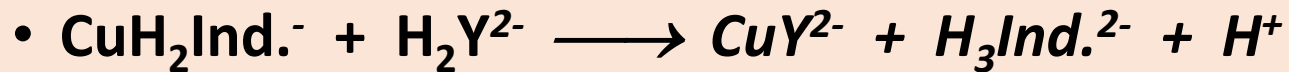
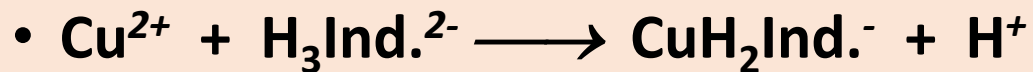
• *Direct Titration*

Many metals can be determined by direct titrations with EDTA.

Weak metal complexes such as Ca^{2+} and Mg^{2+} should be titrated in basic solution using EBT, Calmagite, or Arsenazo I as the indicator.

• **Direct determination of Cu^{2+} with EDTA**

• The complex of Cu^{2+} with **EDTA** is more stable than its complex with murexide ind.



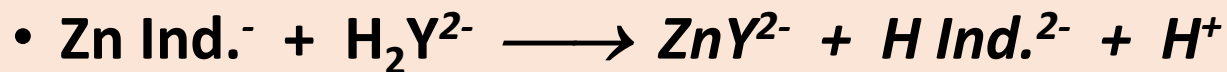
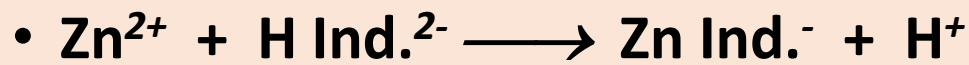
yellow

violet

•

• **Direct determination of Zn^{2+} with EDTA**

• - The complex of Zn^{2+} with **EDTA** is more stable than its complex with **EBT** ind.



wine red

Blue

EDTA Titration Techniques

• *Back Titration (indirect)*

- It can be performed for the determination of several metal ions can not be titrated directly but form stable EDTA complexes.

The procedure, a known amount of EDTA is added to the analyte sample solution and the excess is back titrated with a standard solution of “weak” metal ion, Mg^{2+} .

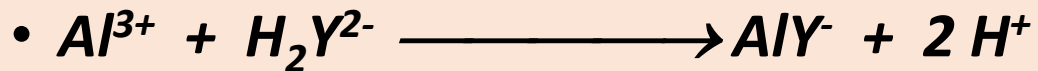
The weak metal ion will not displace the analyte from its EDTA complex.

• *It is used in the following cases:*

- Insoluble substances e.g. $BaSO_4$, $Ca(C_2O_4)_2$, $PbSO_4$, $Mg_3(PO_4)_2$... 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. $Al(OH)_3$.

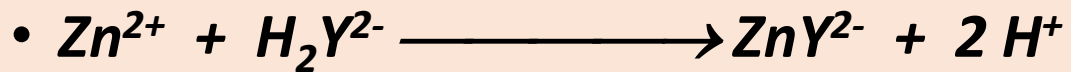
- **Determination of Aluminium salts:**
- Sample of Al^{3+} is heated with known excess. of st. **EDTA** at pH 7-8.
- The soln. is then adjusted to pH=10 using ammonia buffer.
- The residual **EDTA** is titrated against st. Zn^{2+} using EBT indicator.
- The colour change from blue to wine red.

pH 7-8



Boil

pH 10



Blue

wine red

EDTA Titration Techniques

- *Displacement Titration*

- The technique only works when the unknown metal has tighter binding to EDTA than the Zn^{2+} or Mg^{2+} .
- Metal ions with no satisfactory indicator.
- MgY^{2-} or ZnY^{2-} complex is added to the solution of unknown metal ion composition.
- The unknown metal displaces the Mg^{2+} or Zn^{2+} , which is then back titrated.



- K_f' for $MY^{n-2} > K_f'$ for MgY^{n-2}

Titration of Mixtures

- **EDTA** is not a selective reagent (it chelates with most metal ions)
- Selectivity of **EDTA** can be increased by one of the following procedures:
 - Control of pH of the medium
 - Adjustment of oxidation number of metal ion
 - Masking and demasking agent

- Control of pH of the medium

- **First group:** Trivalent & tetravalent cations e.g. (Bi^{3+} , Fe^{3+} , Th^{4+}) and Hg^{2+} titrated (form stable complex) at pH 1-3 using conc. HNO_3 .
- **Second group:** Divalent metals e.g. (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+}) titrated (form stable complex) at pH 4-6 using acetate buffer.
- **Third group:** Alkaline earth metal e.g. (Ba^{2+} , Sr^{2+} , Ca^{2+}) and Mg^{2+} titrated (form stable complex) at pH=10 using ammonia buffer or 8% $NaOH$.
- From the mentioned above, we can titrate M^{n+} of the first group at pH 1-3 without interference of the second and third groups or at pH 4-6 we can titrate M^{n+} of the second group without interference of the third group.
- e.g. Mixture of Bi^{3+} & Pb^{2+} : First titrating Bi^{3+} at pH = 2 using xylenol orange as ind., then increased pH to 5 by adding hexamine and titrating Pb^{2+} .

- Adjustment of oxidation number of metal ion

- - This solves the interference between M^{n+} of the same group of pH.

- **Examples:**

- Ascorbic acid (vit. C) is reducing agent used in:

- Removal of interference of Fe^{3+} in first group (pH 1-3) \longrightarrow reduced to Fe^{2+}

- Removal of interference of Hg^{2+} in first group (pH 1-3) \longrightarrow reduced to Hg^0 (pptd.).

- Removal of interference of Cu^{2+} in second group (pH 4-6) \longrightarrow reduced to *cuprous* (Cu^{1+}).

- Oxidation of Cr^{3+} $\xrightarrow[\text{H}_2\text{O}_2]{\text{alkaline}}$ to CrO_4^{2-}

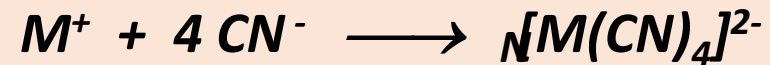
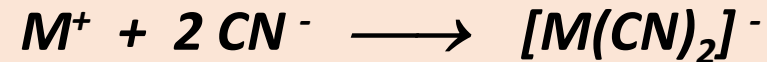
- Fe^{2+} , Hg^0 , *Cuprous* , CrO_4^{2-} do not react with **EDTA**

- Masking and demasking agent

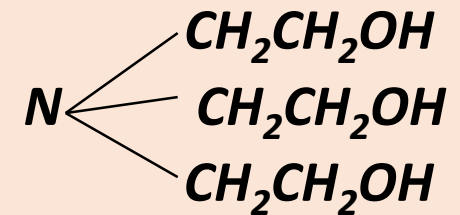
- **Masking agents:** Protects some component of analyte from reacting with EDTA. These reagents form complexes with interfering ions which are more stable than complexes formed with ind. & **EDTA**.

- **Examples of masking agent:**

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



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

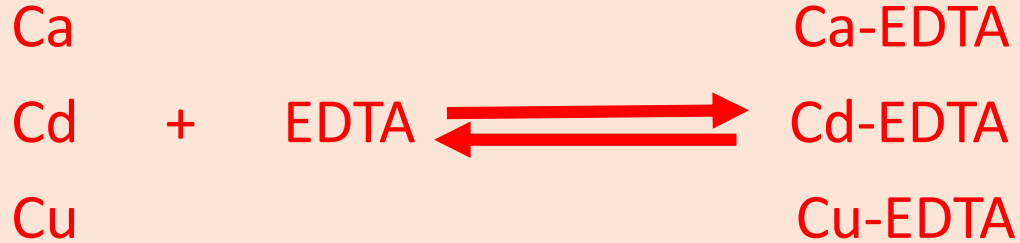


Fluoride (e.g. NH_4F): It is used as masking agent for **Fe^{3+}** and **Al^{3+}** to give **$[FeF_6]^{3-}$** and **$[AlF_6]^{3-}$**

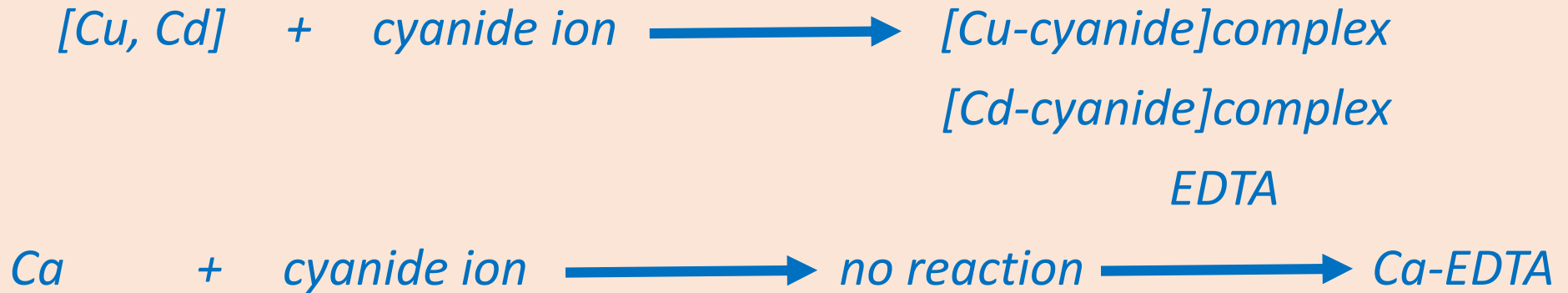
Iodide (KI): It is used as masking agent for **Hg^{2+}** to give tetraiodo complex (**HgI_4**)

- **Demasking agent** : Releasing masking agent from analyte.
- **Example:**
- Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd and Ca. the following method of analysis is followed

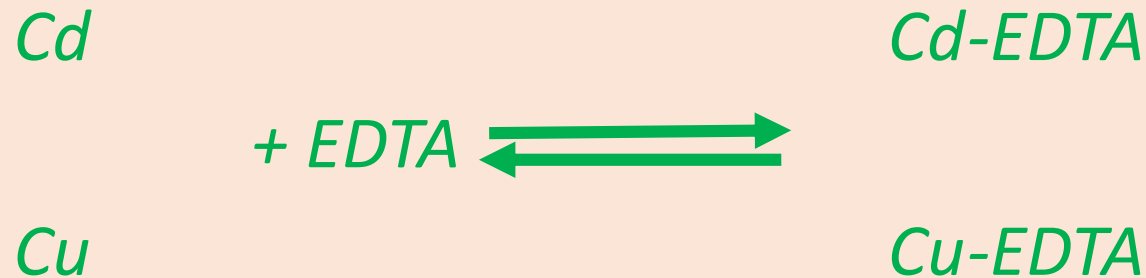
Step 1: All metals are titrated



Step 2: Only Ca titrated



- *Step 3: Cd and Ca are titrated*
- *[Cd-cyanide]complex + HCHO \rightleftharpoons Cd²⁺ (free)*
- *demasking agent*
- *[Cu-cyanide]complex + HCHO \longrightarrow no reaction*



Oxidation with H₂O₂ releases Cu²⁺ from [Cu⁺-Thiourea] complex.