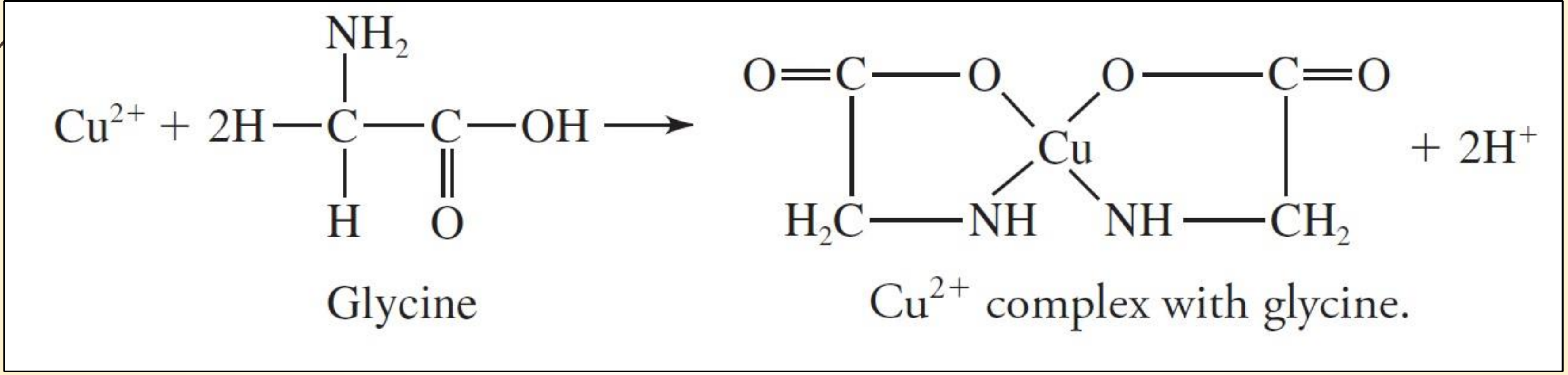
Complexometric Titration I

Lecture three 2024-2025

- 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 alone 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.



Glycine

Cu^{2+} complex with glycine.

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

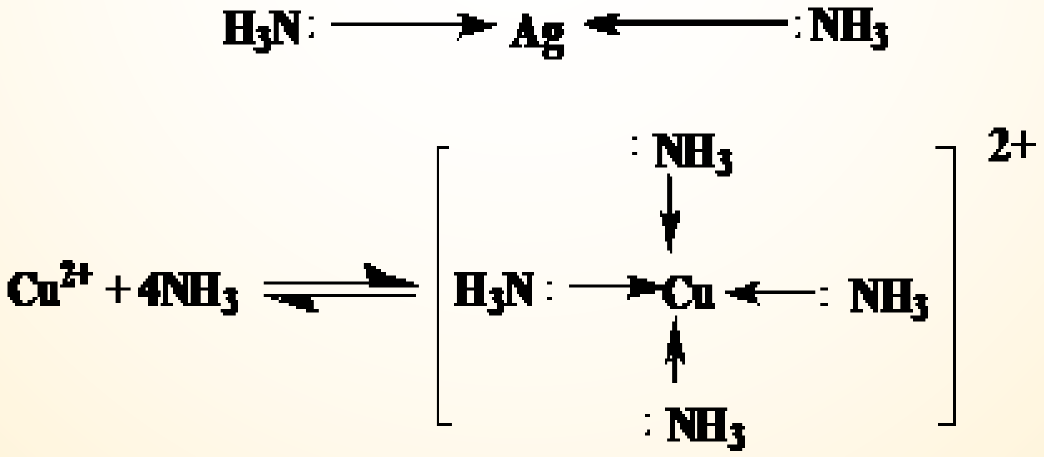
- The solubility of metal chelates in water depends upon:
- The <u>**presence**</u> of hydrophilic groups such as COOH, SO_3H, NH_2 and OH, when both acidic and basic groups are present, the complex will be soluble over a wide range of pH.

☐ When hydrophilic groups are <u>**absent**</u>, the solubility of both the chelating agent and the metal chelate <u>**will be low**</u>, but they will be soluble in organic solvents

- **Sequestering agent** : Ligands which form water soluble chelates (e.g. EDTA), <u>**they** are used to liberate or solubilize metal ions</u>.
- The agents which form water insoluble chelates are used to remove the metal ions from solution by precipitation.

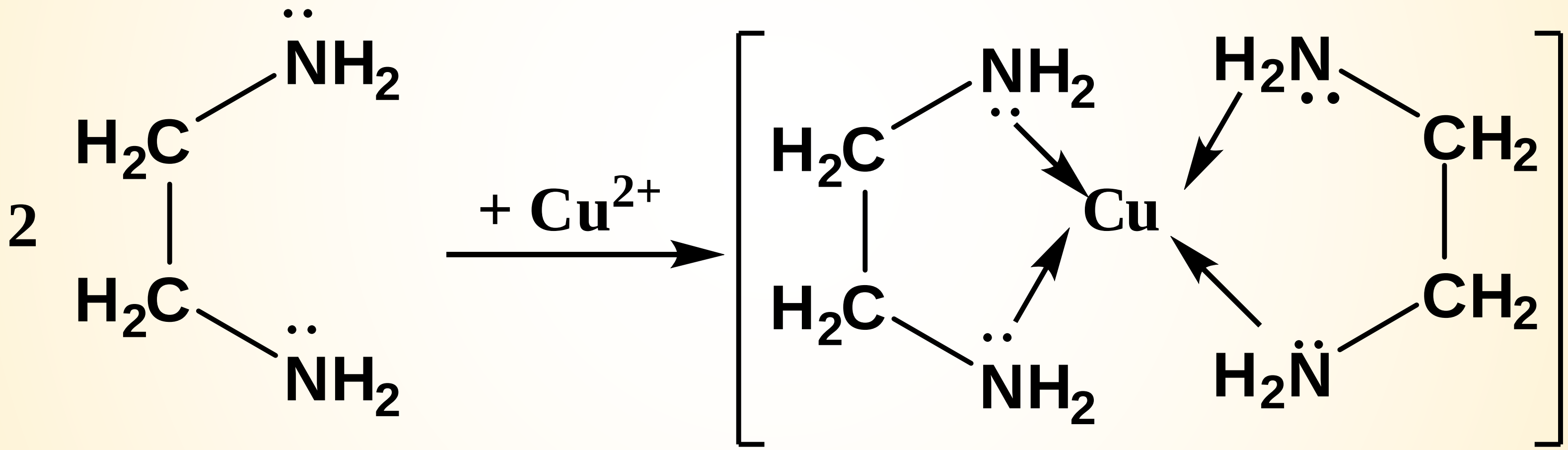
Types of complexing agents

- **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

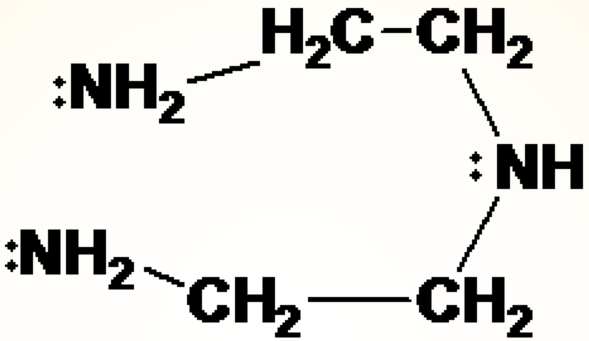
The ligand attached to metal at two sites.



Ethylene diamine

- **Tridentate Ligand:**

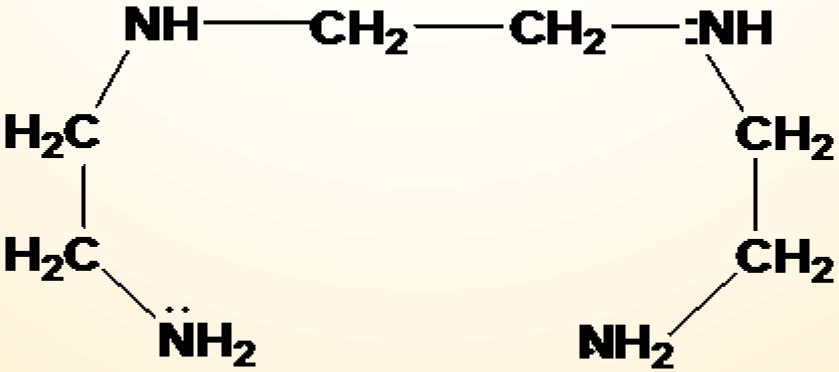
The Ligand attached to metal at 3 sites



Diethylene triamine

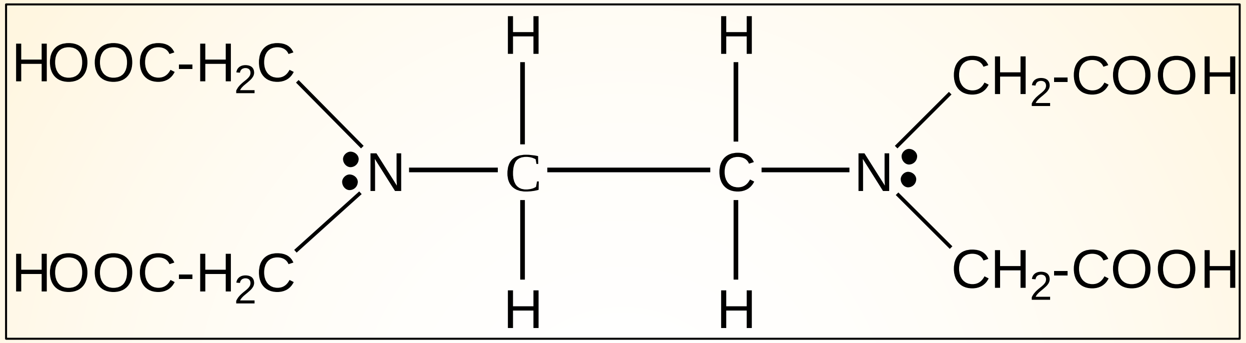
- **Tetradentate Ligand:**

The Ligand attached to metal at 4 sites

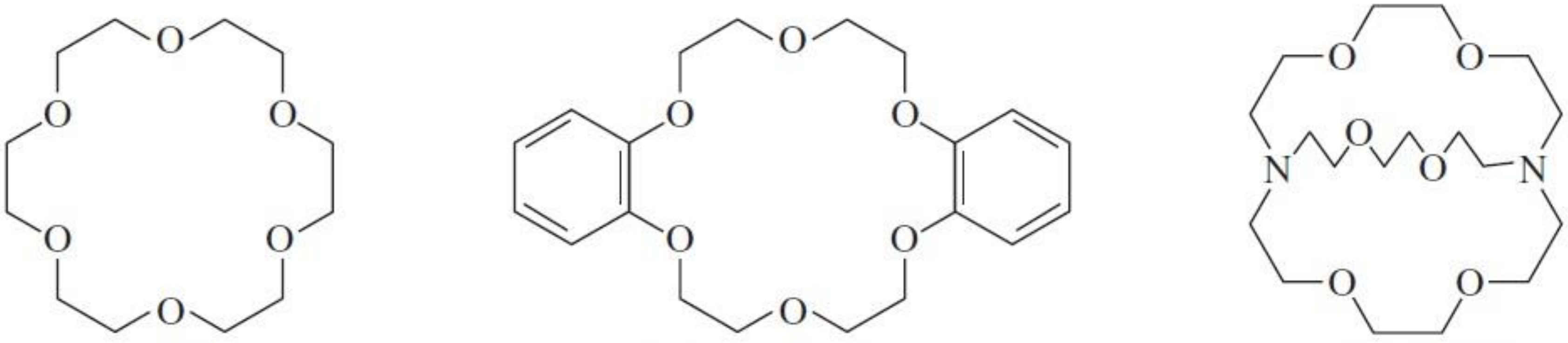


Triethylene tetramine

Ethylenediaminetetraacetic Acid (EDTA)

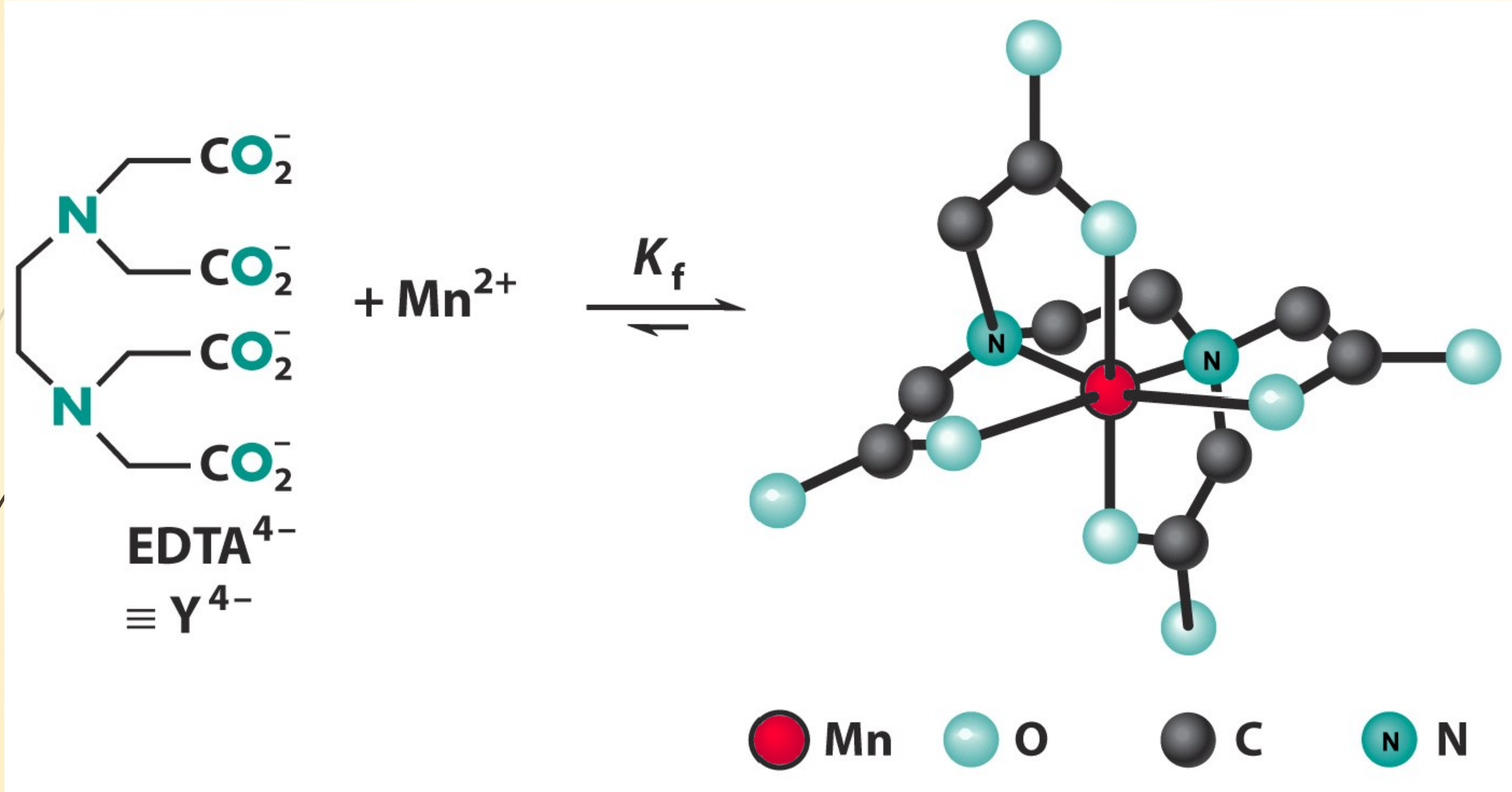


The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and two amino groups. (EDTA is a hexadentate ligand…..why?)

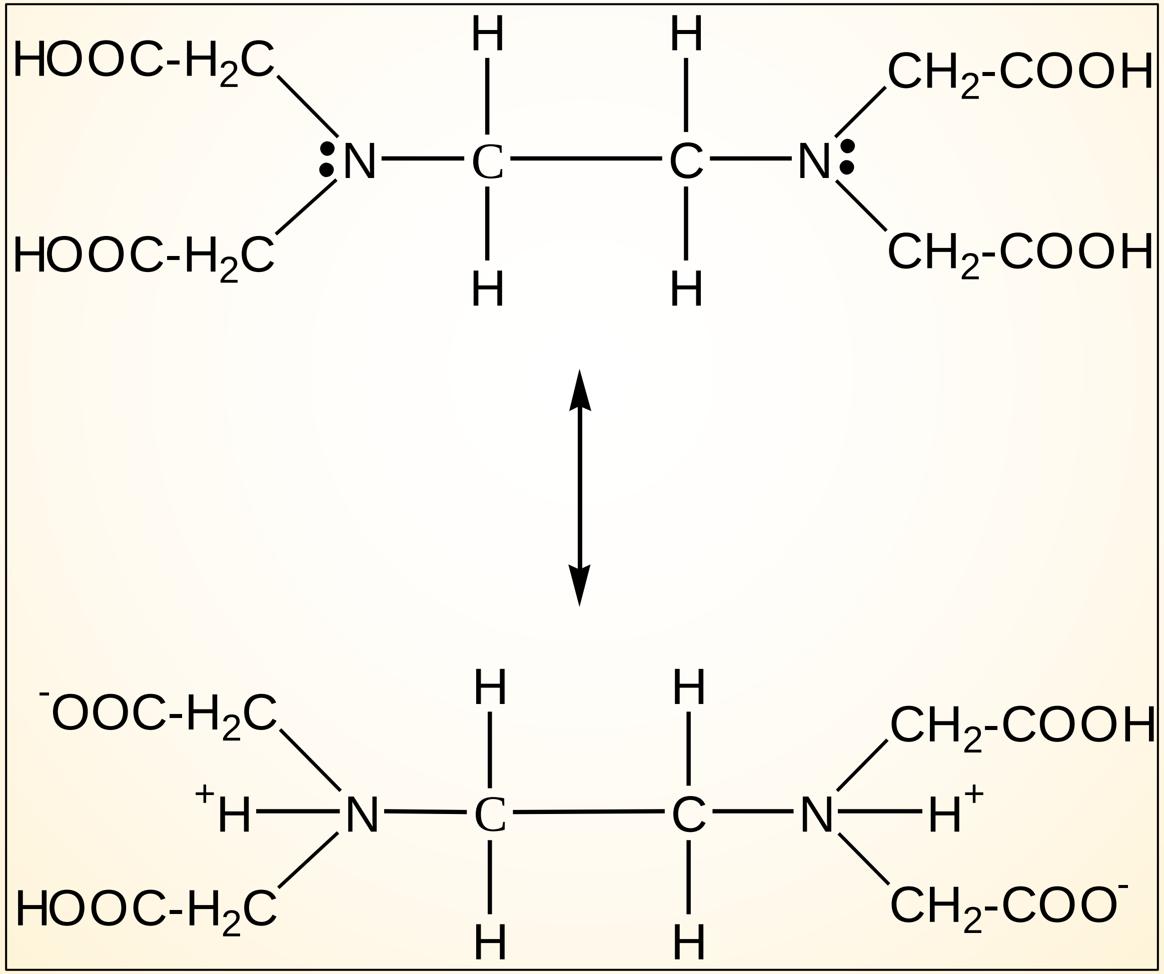


18-crown-6 dibenzo-18-crown-6 cryptand 2,2,2

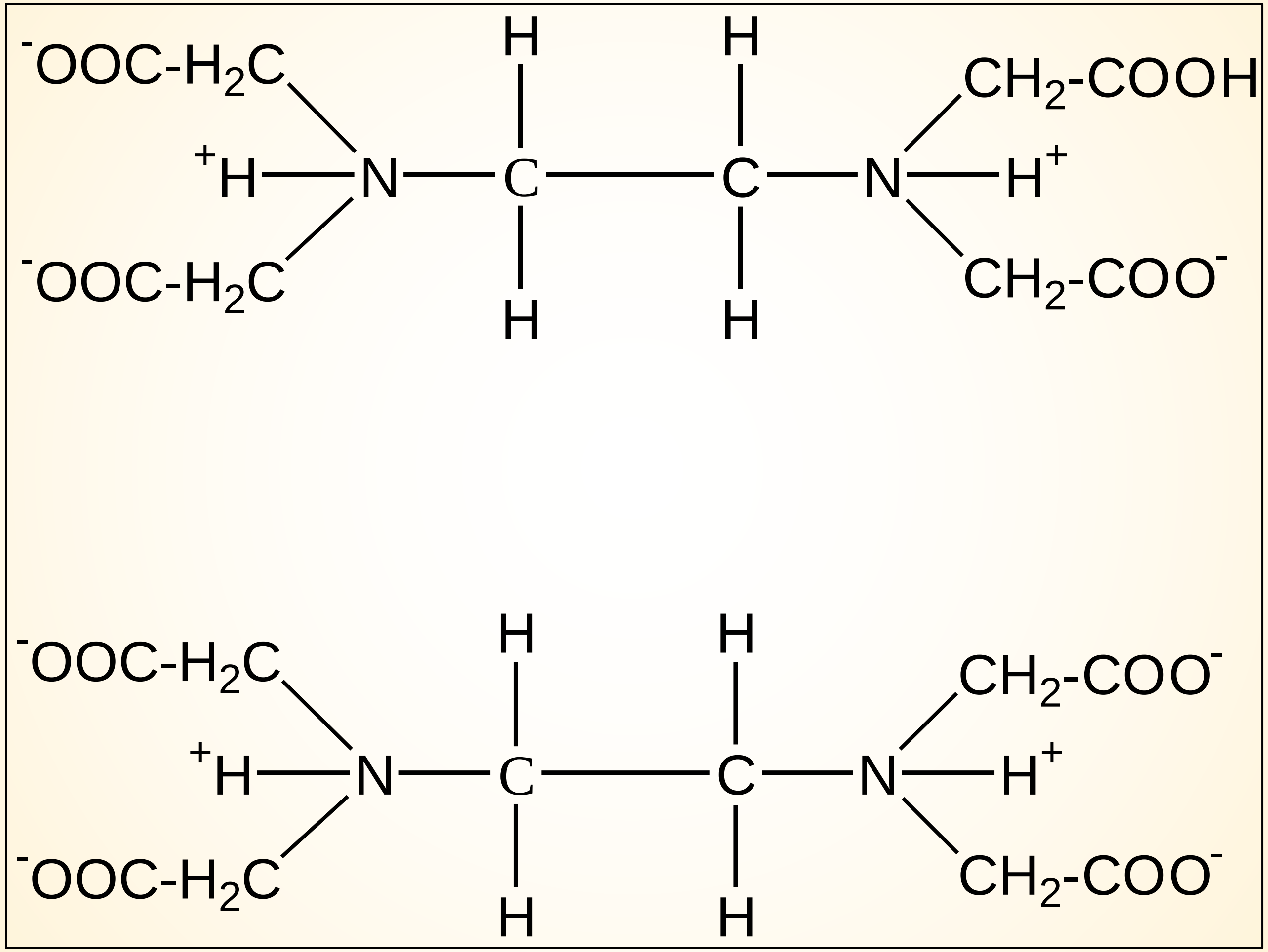
Crown ethers and cryptands.


CO_2^-
N
CO_2^-
CO_2^-
N
CO_2^-
$EDTA^{4-}$
$\equiv Y^{4-}$
$+ Mn^{2+}$
K_f
N
N
Mn
O
C
N

Acidic Properties of EDTA



H_4Y

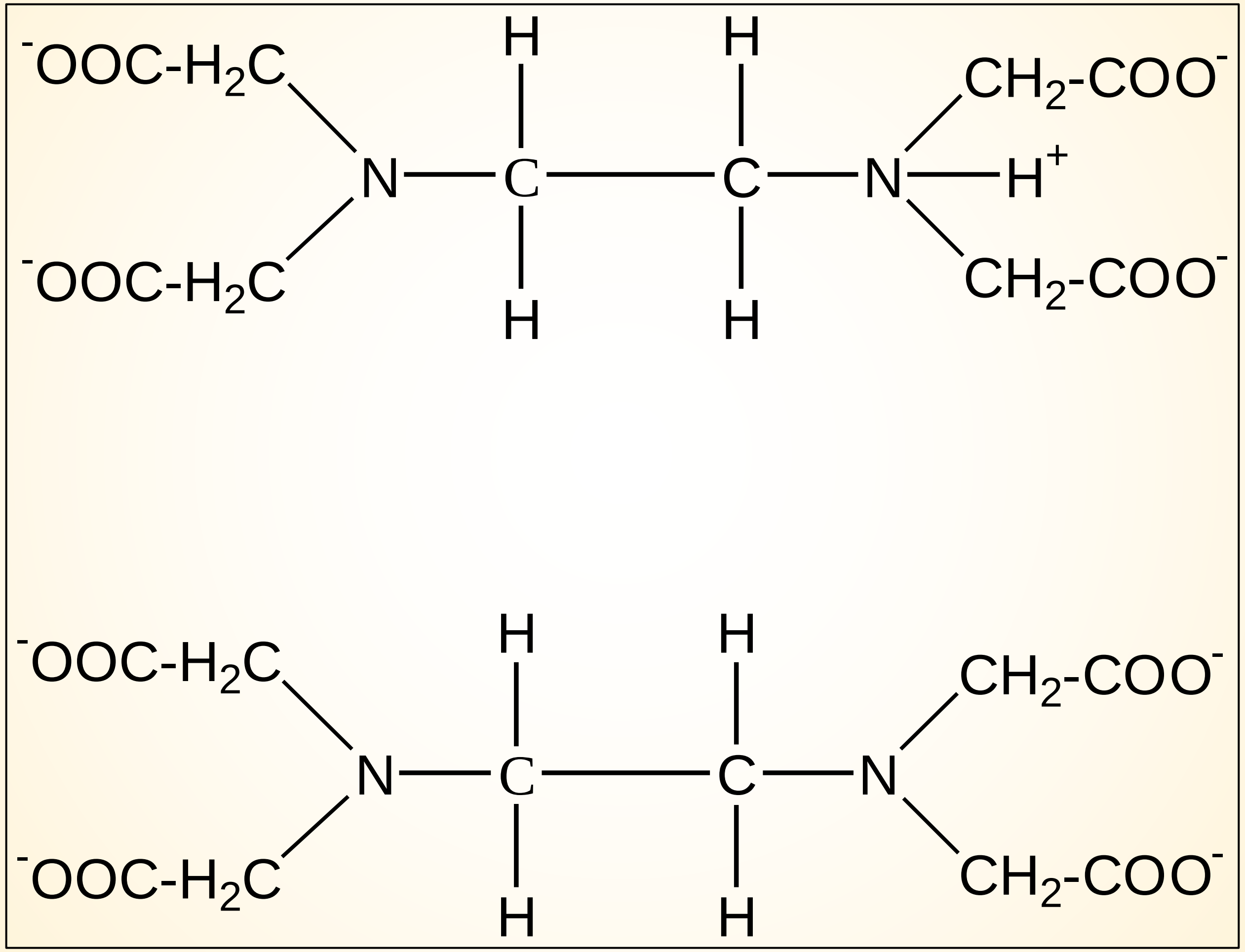


H_3Y^-

$K_1 = 1.02 \times 10^{-2}$

H_2Y^{-2}

$K_2 = 2.14 \times 10^{-3}$



HY^{-3}

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

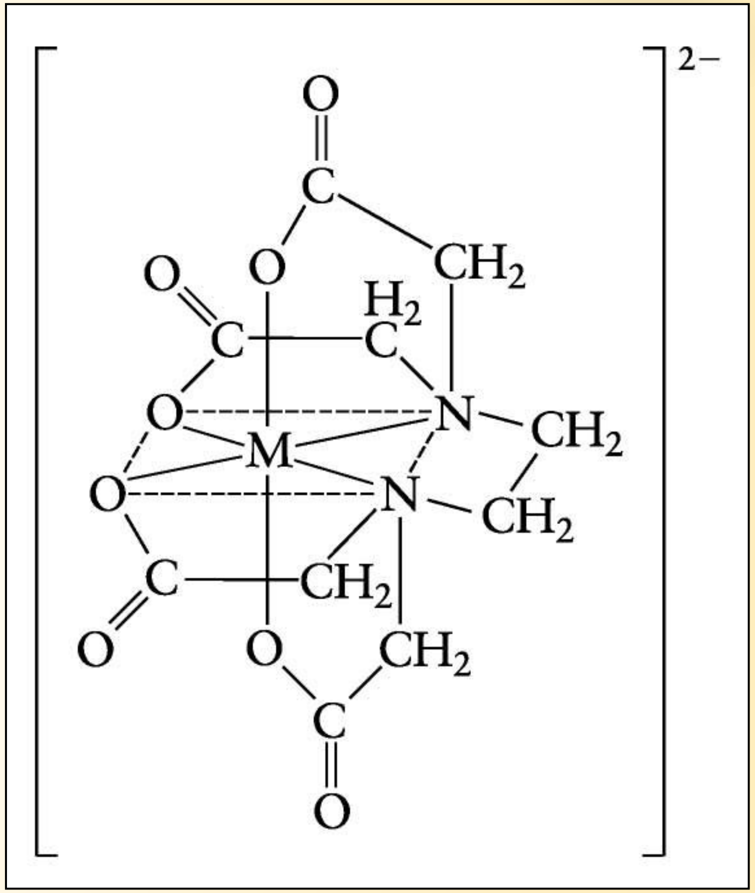
Y^{-4}

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

Reagent of 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:

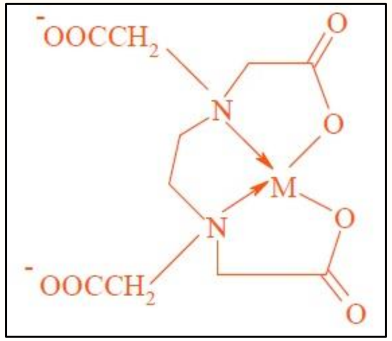
1. It has low price
2. The special structure, which has six ligands atoms
3. It forms strainless five-membered rings



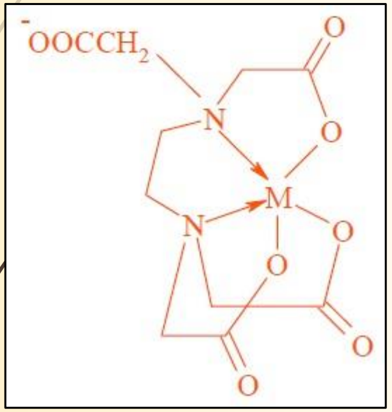
Factors influencing EDTA reactions

A. The nature and the activity of metal ion:

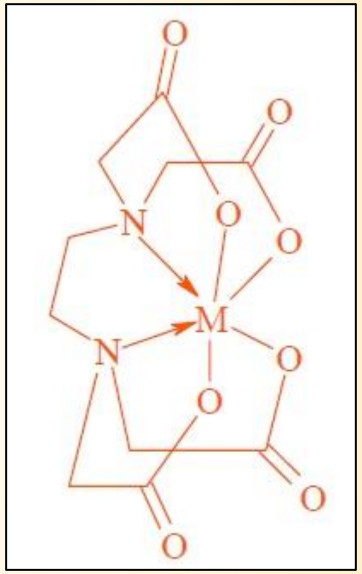
EDTA forms complexes with most cations in a 1:1 ratio, irrespective of the valency of the ion:



$$M^{2+} + [H2X]^{2-} \rightleftharpoons [MX]^{2-} + 2H^{+}$$



$$M^{3+} + [H2X]^{2-} \rightleftharpoons [MX]^{-} + 2H^{+}$$



$$M^{4+} + [H2X]^{2-} \rightleftharpoons [MX] + 2H^{+}$$

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.

- **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*.

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:

$$M + X \rightleftharpoons MX \longrightarrow K = \frac{[MX]}{[M][X]}$$

- **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+}**

Factors affecting stability of complex

[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. N > O > S > I^- > Br^- > Cl^- > 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.