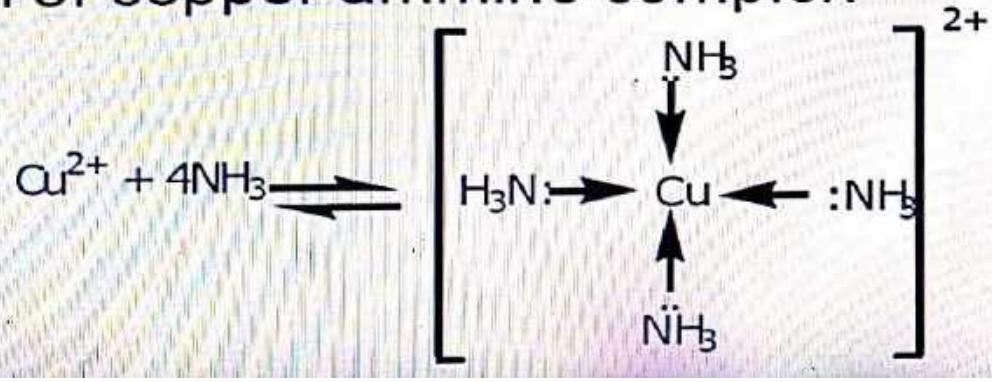
What is complex?????

Complex consists of an metal ion surrounded by molecules or anions.

How Complex forms????

Complex is formed by the combination of metal ion with electron donating group or nucleophile.

eg.: formation of copper ammine complex

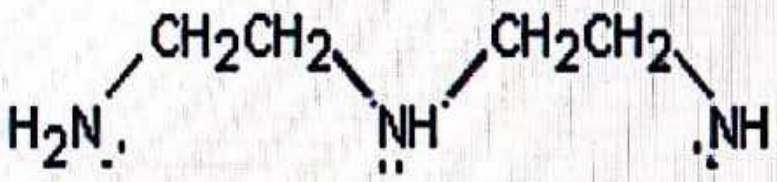


Complexes are compounds formed from combination of metal ions with ligands (complexing agents). A metal ionis an electron deficient species while a ligand is an electron rich, and thus, electron donating species. A metal ion will thus accept electrons from a ligand where coordination bonds are formed. Electrons forming coordination bonds come solely from ligands.

A ligand is called a monodentate if it donates a single pair of electrons (like :NH_3) while a bidentate ligand (like ethylenediamine, :$NH_2CH_2CH_2H_2N$:) donates two pairs of electrons. Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand. The ligand can be as simple as ammonia which forms a complex with Cu^{2+}, for example, giving the complex $Cu(NH_3)_4^{2+}$.

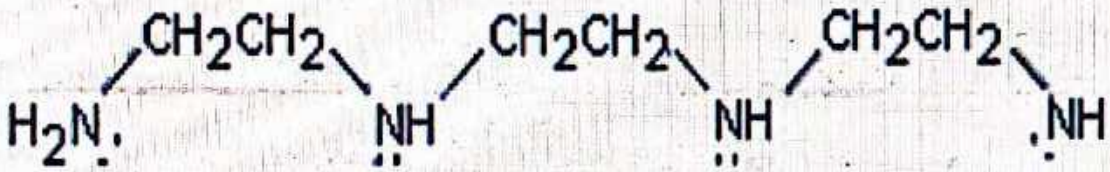
When the ligand is a large organic molecule having two or more of the complexing groups, like EDTA, the ligand is called a chelating agent and the formed complex, in this case, is called a chelate.

Tridentate Ligand:



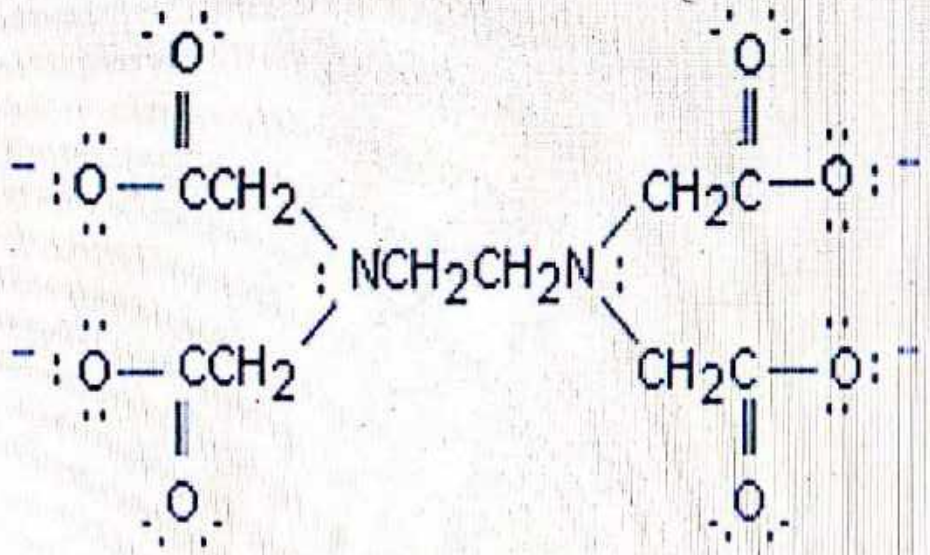
diethylenetriamine (dien)

Tetradentate Ligand:



triethylenetetraamine (trien)

Hexadentate Ligand:



ethylenediaminetetraacetate (EDTA)

e.g. $Ag^+ + 2CN^- \longrightarrow [Ag(CN)_2]^-$

$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$

$Fe^{3+} + 6SCN^- \longrightarrow [Fe(SCN)_6]^{3-}$

$M^{2+} + nL \longrightarrow [ML_n]^{2+}$

The **metal ion** acts as **Lewis acid** (electron acceptor) and the **ligand** is used as a titrant or **a complex forming agent** which acts as a **Lewis base** (electron pair donor or a negatively charged group).

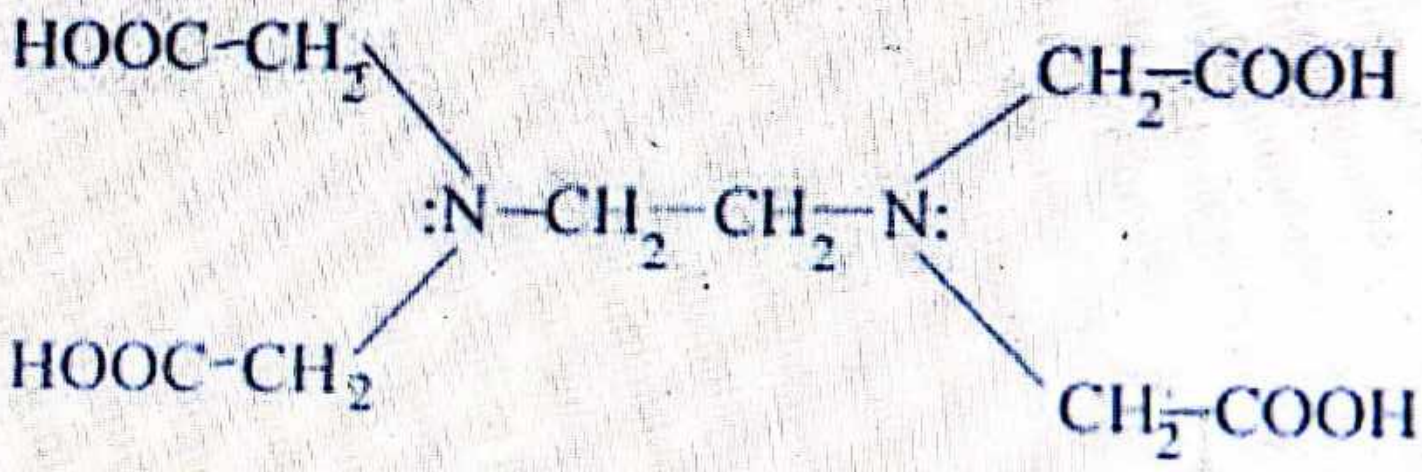
Complexometric Titrations:

- **A complexometric titration is technique of volumetric analysis in which a soluble, undissociated, stiochimetric complex is formed during the addition of titrant to the sample solution.**
- **In Complexometric titration the formation of a colored complex is used to indicate the end point of a titration.**
- Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution.
- An indicator capable of producing an definite color change is usually used to detect the end-point of the titration.

EDTA Titrations:

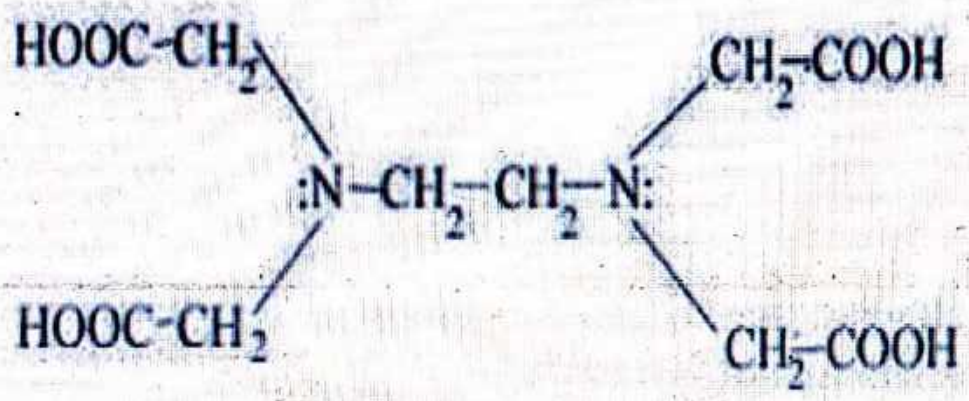
What is EDTA???

- ✓ **EDTA is Ethylene Diamine Tetra Acetic acid.**
- ✓ **It has four carboxyl groups and two amine groups.**



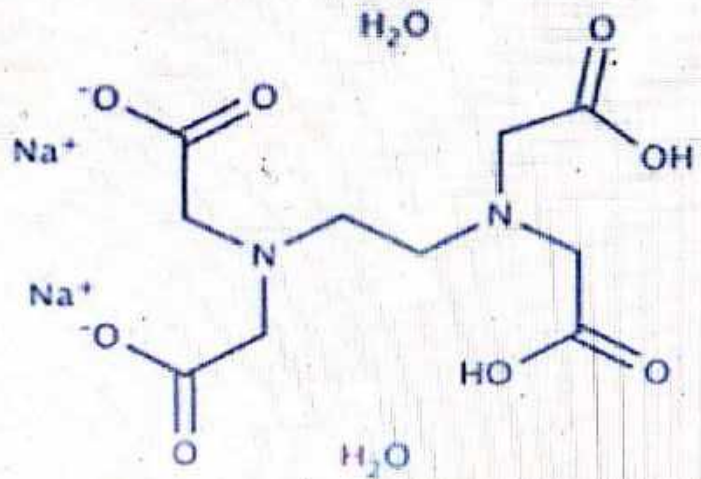
structure of EDTA

Commonly EDTA is represented in the acid form as H_4Y.



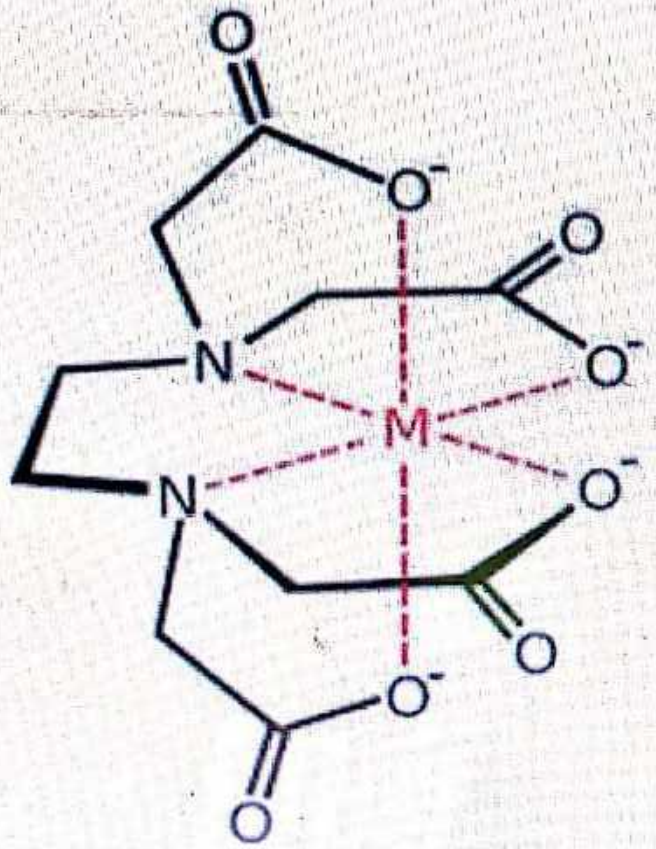
EDTA = H_4Y

Due to low solubility of acid form of EDTA in water, its disodium dihydrate EDTA salt i.e. $Na_2H_2Y.2H_2O$ is used



disodium dihydrate EDTA = $Na_2H_2Y.2H_2O$

EDTA is polydenated ligand as it donate its six lone pairs of electrons for the formation of coordinate covalent bonds with metal cations to form Metal-EDTA complex.



Metal-EDTA complex

Role of pH in EDTA titrations

- EDTA titrations are carried out in buffered solution of the metal ions to be estimated.
-The use of proper pH is important and is related to the stability constant of a metal-EDTA complex.
- E.g. Alkaline pH is required for the metals having low stability constant.
Low Alkaline to mild acidic pH is required for the metals having high stability constant.
- The dissociation reactions of acid form EDTA, H_4Y are also pH dependant. pH is also an important criteria for the proper functioning of the indicator substance.

Thus it is very important to maintain the pH during the EDTA titrations

Advantages of EDTA as titrant:

1. ETDA **form stable complex** with various metal ions.
2. The complexation occurs in a **single step** and hence the titration of the metal **produce a sharp change** in the metal ion concentration at the equivalence point.
3. The **Metal-EDTA complexes are all water soluble** and hence all studies can be performed in aqueous media.
4. EDTA **forms 1:1 complex with all metal ions** irrespective of all charge on the metal ions. The stoichiometry is hence same for all metal ions. The reaction can be represented as:

$$M^{n+} + H_2Y^{-2} + H_2O \longrightarrow MY^{(n-4)} + 2H^3O^+$$

Metallochromic indicator

✓ **The metallochromic indicators are organic compounds which are capable of forming intensely coloured complex with EDTA.**

✓ This metal –indicator complex is weaker than the Metal-EDTA complex and it has different colour than uncomplexed indicator.

✓ During the course of titration, the metal ion from metal –indicator complex is replaced to form Metal-EDTA complex.

5. The colour reaction of the indicator should be selective.
6. The indicator must be very sensitive to metal ions so that the colour change occurs at near the equivalence point.
7. The indicator must be stable in the titration medium.
8. The indicator must be stable on storage also.
9. All the above requirements must be fulfilled in the pH range in which the proposed titration is to carried out.
10. It should be commercially available in adequate purity.

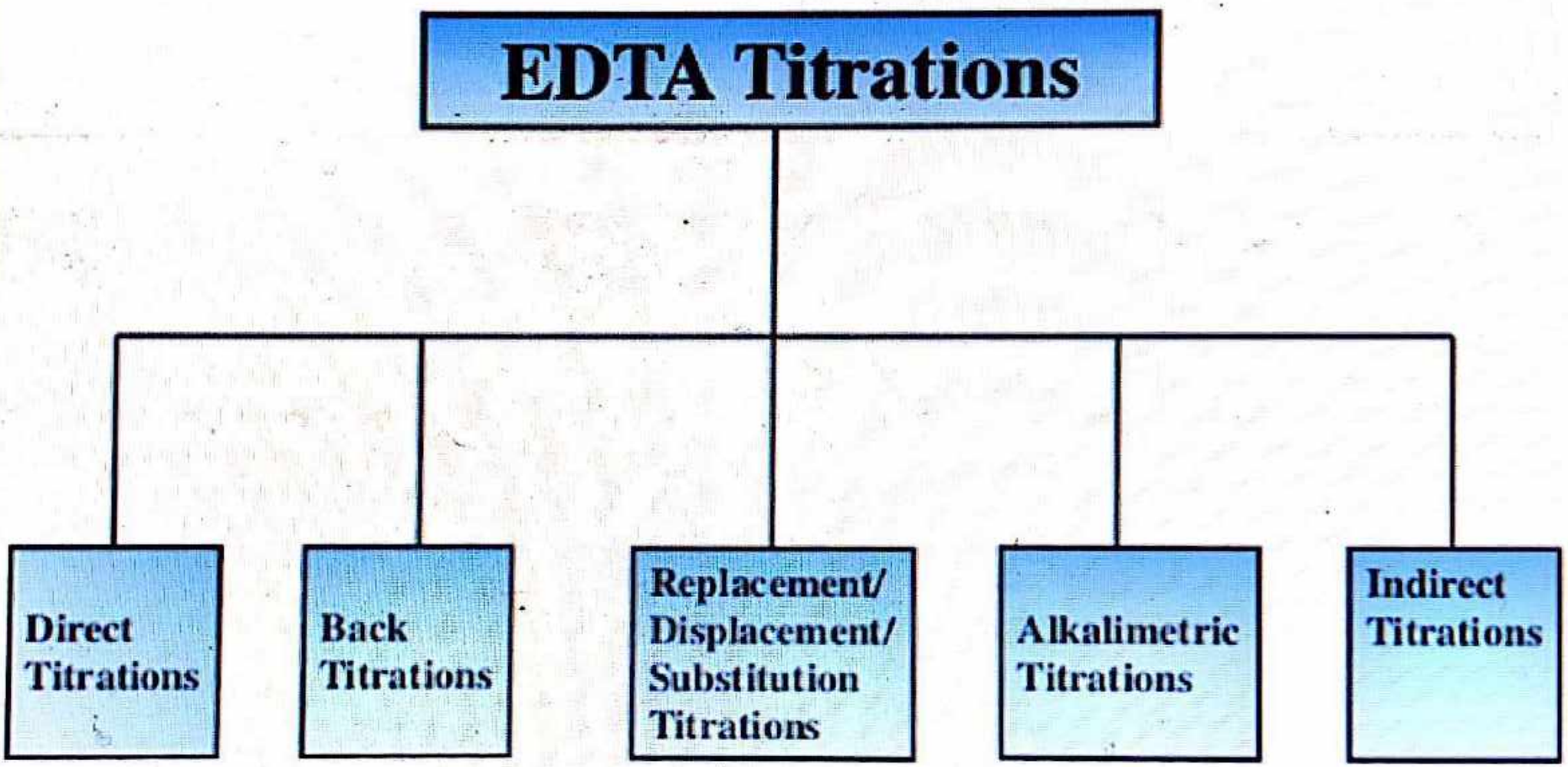
Eriochrome Black T Mordant black II EDT

Chemically it is sodium salt of 1-(1-hydroxy-2 naphthylazo)-6 nitro-2-naphthol-4-sulphonic acid.

It is dark powder with a slight metallic luster

EBT	Acidic pH	H_3D	Black
EBT	pH- 6	H_2D^-	Red
EBT	pH- 7-11	HD^{-2}	Blue
EBT	pH > 12	D^{-3}	Orange

Types of EDTA Titrations:



From the desk of

Aim 1 To determine the (strength) amount of Mg(II) in the given $MgSO_4$ solution using EDTA ($\frac{M}{40}$) as an intermediate & Erichrome black-T as an indicator.

DATE

Preparat^{n} of std $MgSO_4 \cdot 7H_2O$ Sol^{n} $\left(\frac{M}{40}\right)$

$$W = \frac{x}{\text{Mol wt}} \times \frac{1000}{100}$$

$$0.025 = \frac{x}{246.47} \times \frac{100}{100} = 0.616\,g$$

$$EDTA = 0.025 = \frac{x}{\text{mol wt}} \times \frac{1000}{500}$$

$$.025 = \frac{x}{372.14} \times \frac{100}{500}$$

$$x = 46.525\,g/5\,lit$$

Procedure (1) Preparat^{n} of std $MgSO_4 \cdot 7H_2O$ Sol^{n}

0.616 g $MgSO_4 \cdot 7H_2O$
make up it upto 100 ml

(2) Standardisation of EDTA with std $MgSO_4 \cdot 7H_2O$
(Titration of std $MgSO_4 \cdot 7H_2O$ sol^n with EDTA sol^n

$MgSO_4 \cdot 7H_2O$ + 10 ml + buffer + EBT
Water (2 ml) (1-Pinch)

↓ Δ 30-35°C

Red- to blue

(3) Titration of given $MgSO_4 \cdot 7H_2O$ sol^n with EDTA sol^n.

Above procedure is repeated with unknown sol^n.

Procedure :

→ Firstly, the standard Magnesium sulphate solu. was prepared. by weighing 0.246 g in the weighing bottle.

→ Then 10 ml. from the standard solu. was pipetted out in a conical flask which had 10 ml. of dionized water, 2-3 ml. buffer (NH_4Cl. NH_4OH) and a pinch of Eriochrome Black T.

→ The pink solu. was then titrated with EDTA till the colour changed to blue.

→ The whole process was repeated to obtain 3 concordant readings.

→ Now the same titration was performed using the given sample of $MgSO_4 . 7H_2O$.

→ And again the 3 concordant readings were obtained.