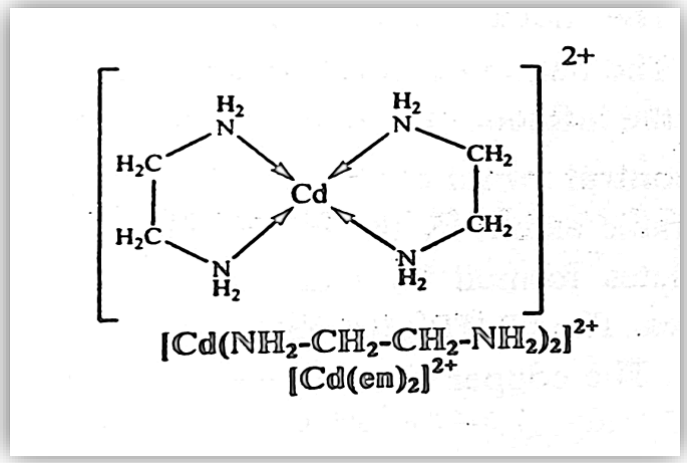
CHELATES

- **Definition: -**
  - ✓ The substance containing two or more donar atoms and forms ring structure with metal is called as chelate and this property is called as chelation.
  - ✓ The chelated complexes are more stable than non-chelated complexes.
  - ✓ More is the rings in the complex, more stable is the complex.

  E.g., $[Cd(en)_2]^{2+}$ or $[Cd\ (H_2N\text{-}CH_2\text{-}CH_2\text{-}NH2)_2]^{2+}$



- **Chelating Agents: -**

  The substance which can form chelated complexes is called as chelating agents.

  There are two types of chelating agents;

  a) Sequestering Agents

  b) Chelating Agents

- **Sequestering Agents: -**
  - ✓ This chelating agent forms water soluble chelates.
  - ✓ They are useful in removing objectional metal ions from aqueous solution.
  - ✓ They are useful for removal of boiler scale.
  - ✓ They are also useful for removal of harmful radioactive metals from the body fluids.

- **Chelating Agents: -**
  - ✓ These chelating agents forms metal chelate precipitate.
  - ✓ These chelating agents have many biological applications.
  - ✓ They play important role in life processes.

E.g., chlorophyll, haemoglobin, etc.

- **Basic Concept: -**

The metal chelate can be examined from at least three points of view.
a) Central metal atom
b) Chelating molecule
c) Nature of bond between central metal atom and chelating molecule.
The influence of each or all of these explains behaviour of metal chelates.

a) Central Metal Atom: -

The properties of metal complex depend upon size, electronic configuration and oxidation state of central metal atom / ion.
E.g., The chelates formed by Cu (II) and Ni (II) with DMG (dimethyl glyoxime) have different properties like;
i) The Cu (II) chelate is water soluble while Ni (II) chelate is insoluble in water.
ii) The copper chelate is tetragonal pyramidal geometry while nickel chelate is square planar geometry.

b) Chelating Molecule : -

The chelating molecule (chelating agent) must possess;
i) At least two functional groups
ii) They can form ring structure with metal atom.
But steric effect of the ligand affects the chelation.
E.g., 8-hydroxy quinoline forms tris complex with Al (III) but 2-methyl-8-hydroxy quinoline prevent the formation of complex.

c) Metal-Ligand Bond: -

The stability of the chelate depends upon the metal-ligand bonds.
The nature of metal ligand-bond depends upon the size and electronegativity of metal ion.

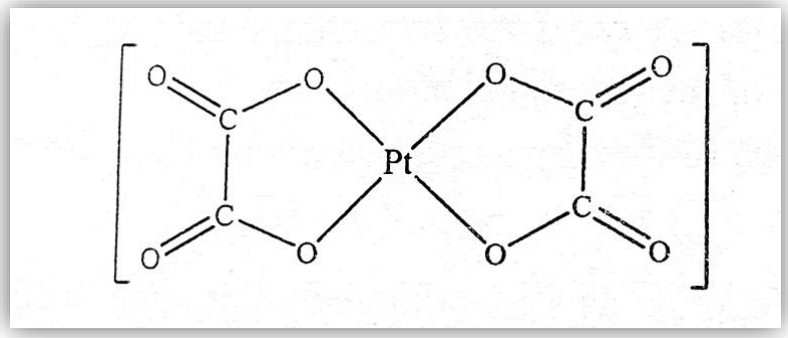
- **Classification of Chelates: -**

The chelates are classified on the basis of number of ligands and kind of attachment of ligands.

i) Bidentate Chelating Groups: -

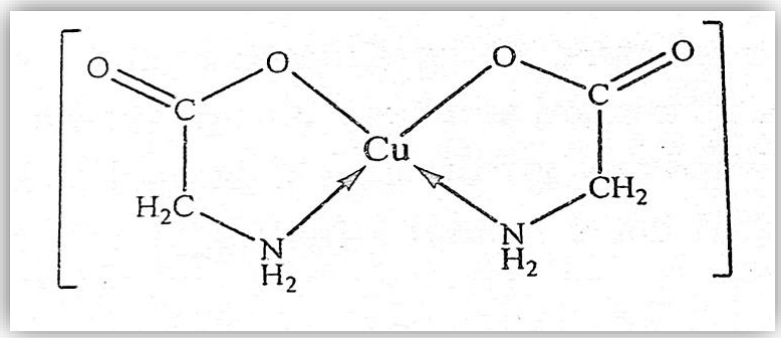
a) Two acidic groups: -

In this complexes, cation is combined through covalent bond only and ring is formed by the replacement of two hydrogen atoms of ligand with metal cation.



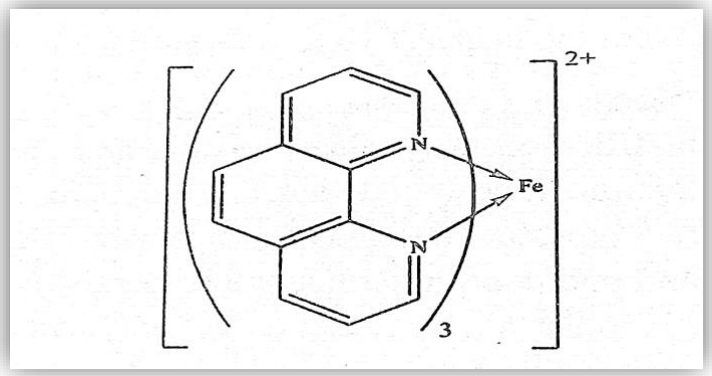
b) One acidic group and one coordinating group: -

In this glycine, molecule is attached to the copper atom by one covalent bond and one coordinate bond.



c) Two coordination groups: -

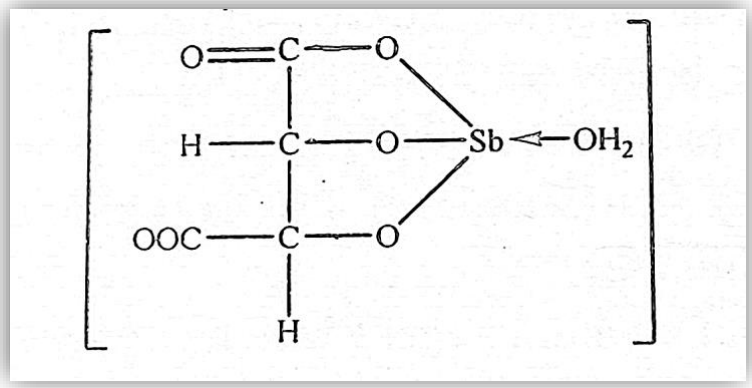
In this, three molecules of O-Phenanthroline containing two nitrogen atoms coordinated with ferrous ion.



ii) Tridentate Chelating Groups: -

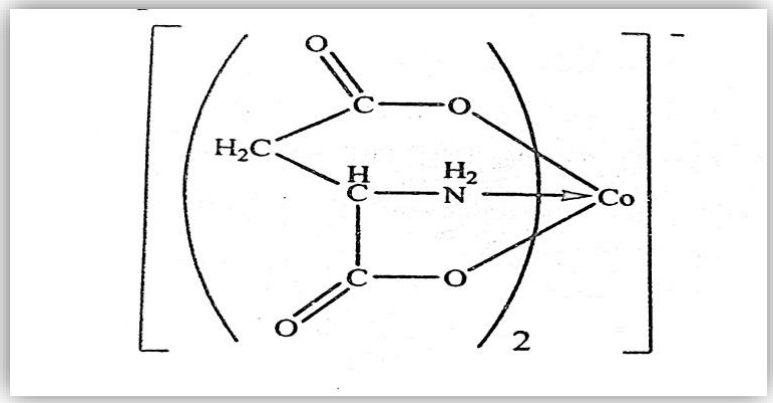
a) Three acidic groups: -

In this, tartarate ion is attached to antimony atom by three covalent bonds.



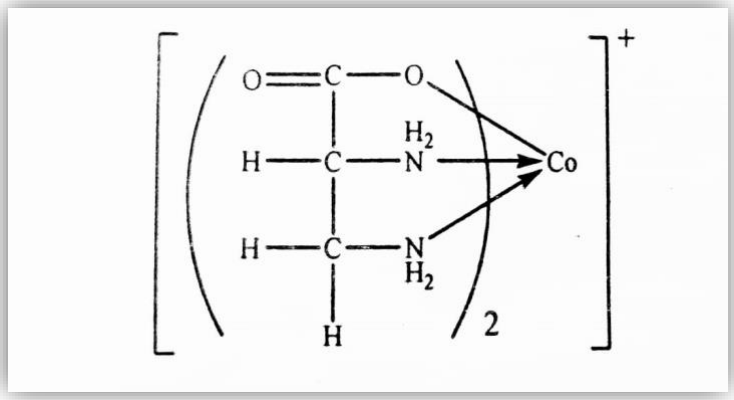
b) Two acidic groups and one coordinating group: -

Aspartic acid combines with Co^{3+} to form water soluble tridentate compound.



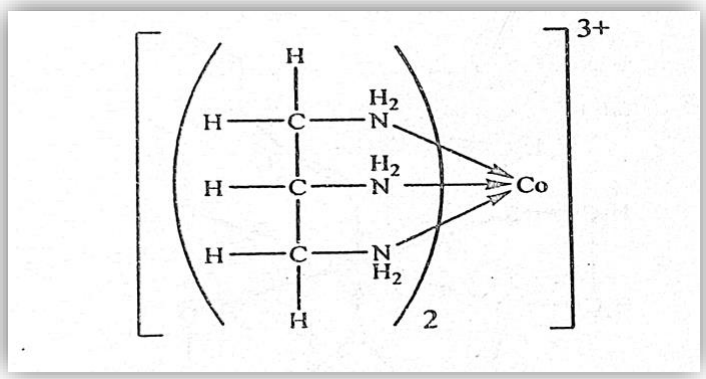
c) One acidic group and Two coordinating groups: -

Alpha, Beta diamine propionic acid combines with Co^{3+} to form chelate.



d) Three coordinating groups: -

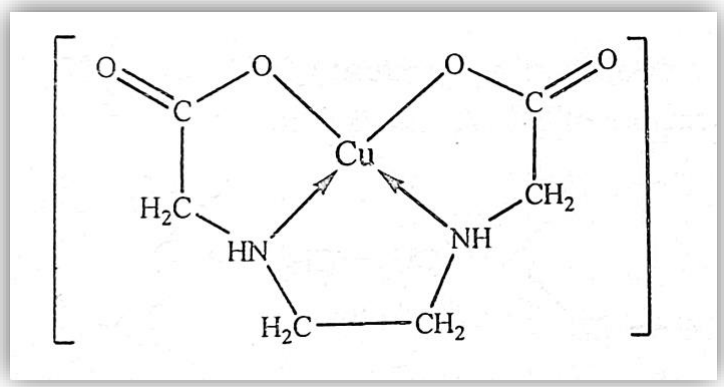
Triamino-propane combines with Co^{3+} to form chelates.



iii) Quadridentate Chelating Groups: -

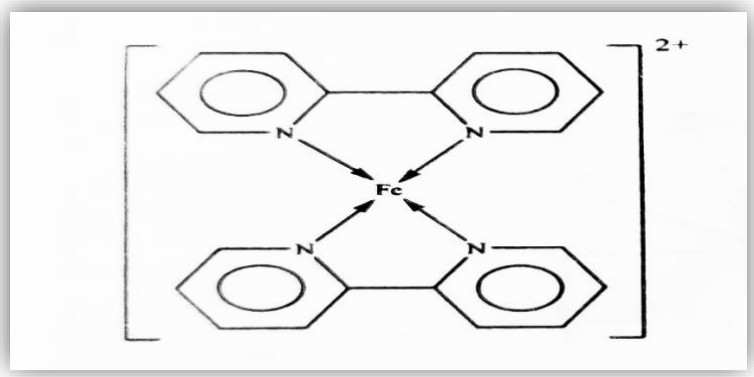
a) Two acidic and Two coordinating groups: -

Ethylene diamine acetic acid combine with Cu^{2+} to form a such type of chelate.



b) Four coordinate groups: -

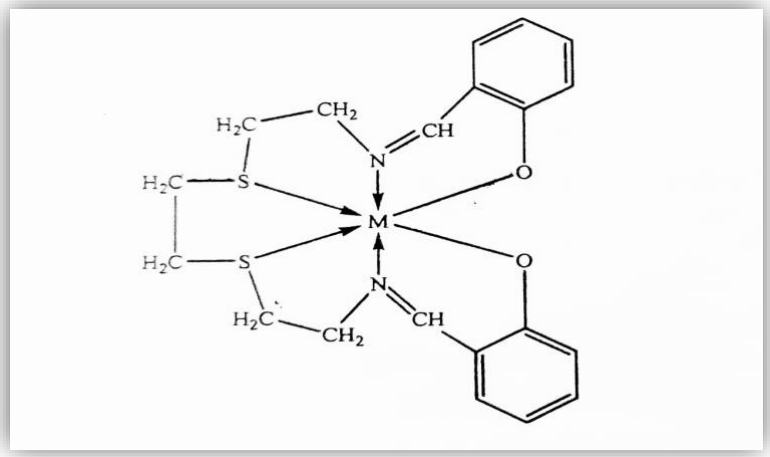
In this, 2,2-bipyridyl reacts with $Fe^{2+,}$ Co^{2+}, Ni^{2+} and Zn^{2+} to form chelate.



iv) Hexadentate Chelate Groups: -

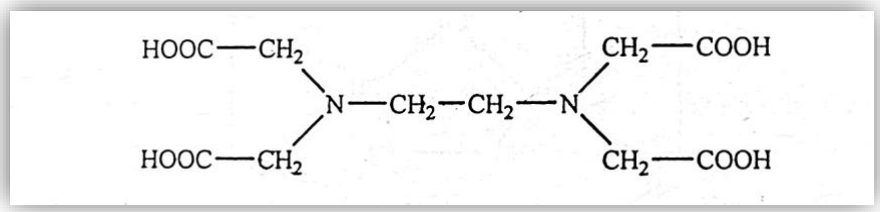
a) Two acidic and four coordinating groups: -

1,8-bis-salicylidineamino-3,6-dithioctane reacts with Zn^{2+}, Ni^{2+}, Co^{2+}, ion to form chelate.

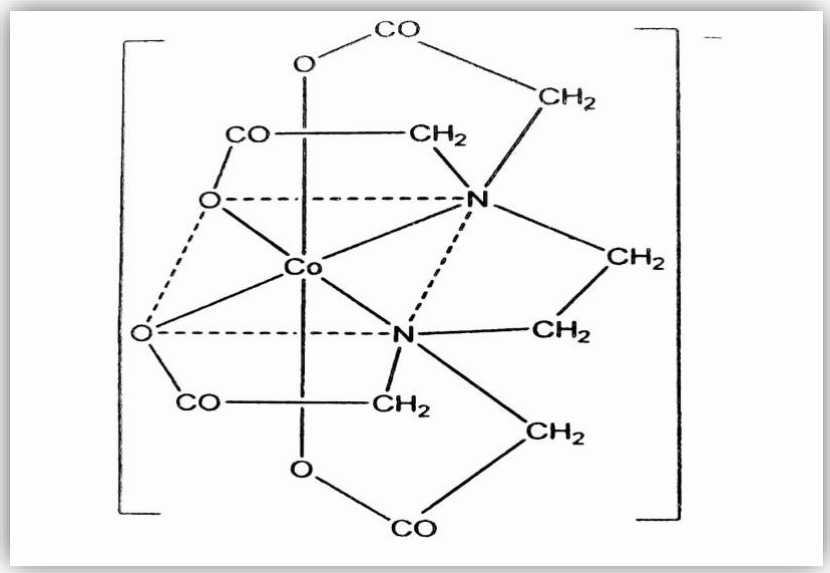


b) Four acidic and two coordinating groups: -

EDTA reacts with number of metal and forms a chelates.



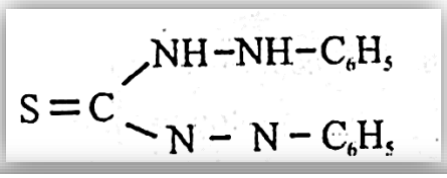
Ethylene Diamine Tetra Acetic Acid (EDTA)

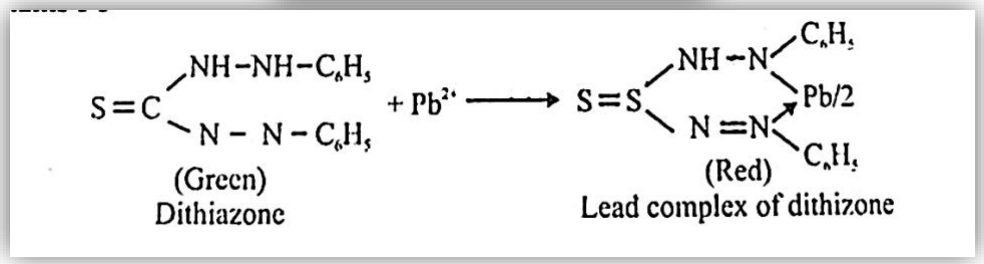


➢ **Applications of Chelates in Analytical Chemistry: -**

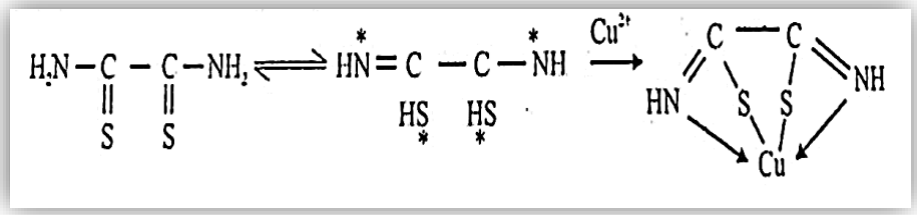
- **It is used as metal precipitants: -**
  i) DMG is used to precipted nickel under appropriate PH condition.
  ii) Oxalate is used to precipted calcium in radio chemical determination of strontium-85 and calcium-45.
  iii) 8-quinolinol is used for gravimetric estimation of tungsten.
  iv) 1,10-phenanthroline is used to precipted metals like Ni, Co, Cu, Pb in presence of thiocyanate.
- **It is used in quantitative determination of metal ion: -**
  The metal ion in the solution can be detected by specific chelating agents.
  E.g., i) Ni (II) is detected by DMG in alkaline medium which forms red rose colour chelate compound.
  ii) Co (II) is detected by thiocyanate chelating agent which forms blue colour.
  iii) Cu (II) is detected by ammonia which forms blue colour.
  iv) Fe (II) is detected by isothiocyanate which forms blood red colour.

- **Application in Qualitative Analysis: - (Spot Test for Basic Radicals)**
  a) Spot test for group – I [Pb^{2+}, Hg^{2+} and Hg^{+}]: -
  Chelating agent is Dithiazone.

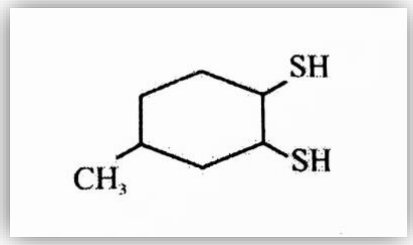


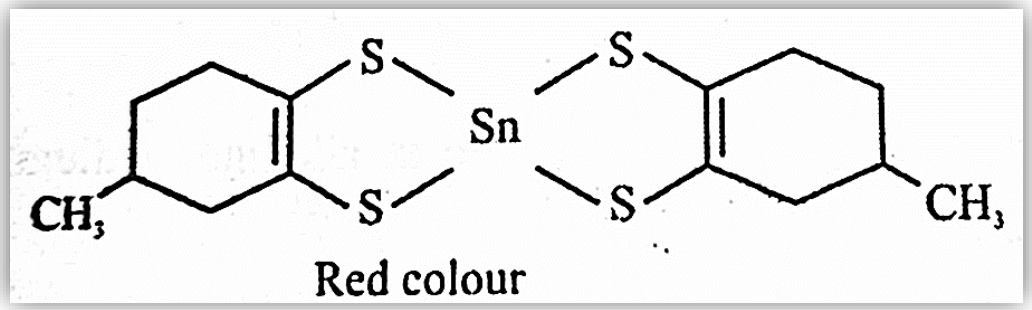


b) Spot test of group – IIA [Hg^{2+}, Bi^{3+}, Cu^{2+}, and Cd^{2+}]
E.g., Test for Cu^{2+}: -

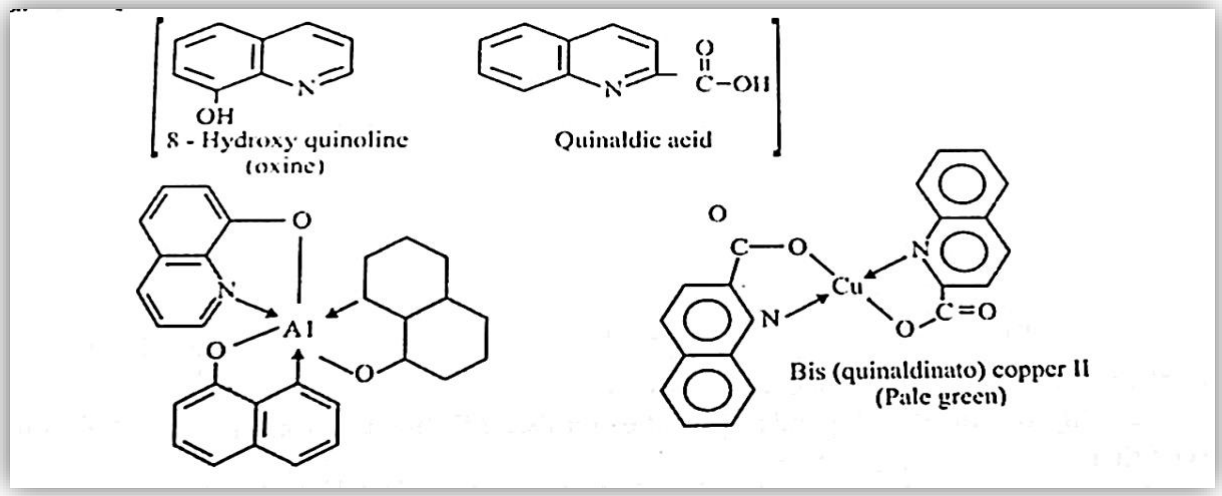


c) Spot test for group (II) B (As^{3+}, Sb^{3+}, Sn^{2+})
E.g., Test for Sn^{2+}: - Chelating agent is Ditial



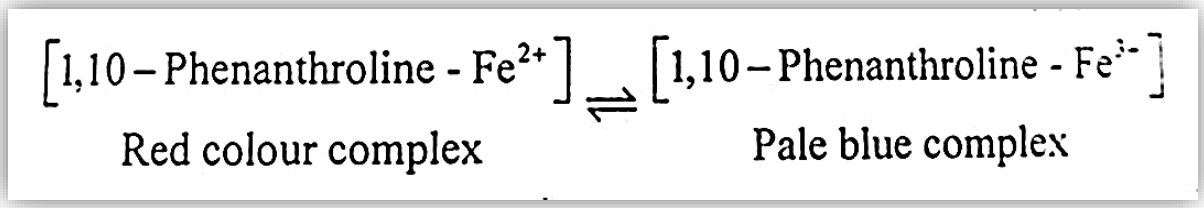


- **It is used in the gravimetric analysis: -**
  The metals like K^{+}, Ni^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+} are determined by using different complexing agents in gravimetric analysis.
  E.g., i) Ni-DMG
  ii) 8-hydroxy quinoline is used as the complexing agent for the determination of Al^{3+}, Mg^{2+}, Zn^{2+}.
  iii) quinaldic acid is used for Cu^{2+}.



- **It is used in volumetric analysis: -**

1,10-phenanthroline complex of iron is used as indicator in redox titration of Fe^{2+} to Fe^{3+}.



- It is used in Spectro photo-metric estimation of trace quantities of metal ions.
- It is also used in water softening, paint industry, drug industry, etc.

➢ **Stability of chelates: -**

The stability of chelates can be explained on the basis of

i) Basic strength of ligand: -

Higher is the basic strength of ligand, greater is the tendency of ligand to form stable metal complexes.

ii) The nature of donar atom in the obelating ligand: -

The donar atom of low polarizability and high electronegativity like N, O, F can form more stable chelate complexes.

iii) Number of metals chelate rings: -

Larger is the number of chelate ring, greater is the stability of the complex.

iv) Number of atoms in each ring: -

The stability of complex depends upon the number of atoms in the ring.
It is observed that 5 or 6 membered chelate rings have greater stability than 4 or more than 6 membered chelate ring. Because 5 or 6 membered rings has less strain to the molecule.

v) Steric Effect: -

When bulky group is present at or near a donar atom then it causes repulsion among the ligands, therefore M-L bond become weak and stability of chelate decreases. Therefore, steric effect or steric hindrance decreases the stability of chelates.

vi) Entropy changes or Entropy effect: -

Higher is the entropy during chelation, more stable is the chelate. Because increase in the entropy in the reaction increases number of independent species and gives stable product.

$[Ni\ (H_2O)_6]^{2+} + 3\ en \rightarrow [Ni\ (en)_3]^{2+} + 6\ H_2O$

vii) Chelate Effect: -

The complex with chelating ligands is more stable than unidentate ligands.

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