

ORGANIC REAGENTS IN METAL ANALYSIS:

Stability Constant:

A stability constant which is also called formation constant or binding constant is equilibrium constant for the formation of a complex in solution. A high value of a stability constant shows that the ion is easily formed.

Stability Constant of Metal Complexes:

In the formation of metal complexes in an aqueous medium, equilibrium constant or stability constant is used to determine the strength of interaction between reagents that make the final product after the formation of bonds. Acutely, stability constant is applicable to measure the strength of interactions between the ligands and metal ions that are involved in complex formation in the solution

During the complex formation in aqueous medium, two types of stabilities are considered: one is the thermodynamic stability, and the other is kinetic stability. Stability of metal complexes may be affected by various factors like nature of central metal ion and ligand, chelating effect, etc., and some parameters like distribution coefficients, conductance, refractive index, etc. are useful for the determination of stability constants.

Factors effecting on stability constant:

The nature of central atom of metal complexes, dimension, its degree of oxidation, electronic structure of these complexes, and so many other properties of complexes are affected by the stability constant. Some of the following factors described are as follows.

Nature of central metal ion:

In the coordination chemistry, metal complexes are formed by the interaction between metal ions and ligands. For these type of compounds, metal ions are the coordination center, and the ligand or complexing agents are oriented surrounding it. These metal ions mostly are the transition elements. For the determination of stability constant, some important characteristics of these metal complexes may be as given below.

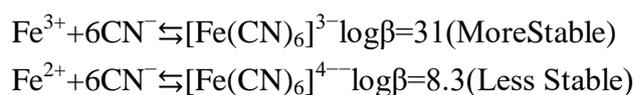
Ionic size:

Ligands are oriented around the central metal ions in the metal complexes. The sizes of these metal ions determine the number of ligand species that will be attached or coordinated (dative covalent) in the bond formation. If the sizes of these metal ions are increased, the stability of coordination compound defiantly decreased. Zn(II) metal ions are the central atoms in their complexes, and due to their lower size (0.74\AA) as compared to Cd(II) size (0.97\AA), metal ions are formed more stable.

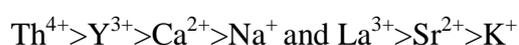
Hence, Al^{3+} ion has the greatest nuclear charge, but its size is the smallest, and the ion N^{3-} has the smallest nuclear charge, and its size is the largest. Inert atoms like neon do not participate in the formation of the covalent or ionic compound, and these atoms are not included in isoelectronic series; hence, it is not easy to measure the radius of this type of atoms.

Ionic charge

The properties of stability depend on the size of the metal ion used in the complexes and the total charge thereon. If the size of these metal ions is small and the total charge is high, then their complexes will be more stable. That is, their ratio will depend on the charge/radius. This can be demonstrated through the following reaction:



An ionic charge is the electric charge of an ion which is formed by the gain (negative charge) or loss (positive charge) of one or more electrons from an atom or group of atoms. If we talk about the stability of the coordination compounds, we find that the total charge of their central metal ions affects their stability, so when we change their charge, their stability in a range of constant can be determined by propagating of error. If the charge of the central metal ion is high and the size is small, the stability of the compound is high:



In general, the most stable coordination bonds can cause smaller and highly charged cations to form more stable coordination compounds.

Electronegativity

When an electron pair attracts a central ion toward itself, a strong stability complex is formed, and this is due to electron donation from ligand \rightarrow metal ion. This donation process is increasing the bond stability of metal complexes exerted the polarizing effect on certain metal ions. Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , etc. are such type of metal cation which is not able to attract so strongly from a highly electronegative containing stable complexes, and these atoms are O, N, F, Au, Hg, Ag, Pd, Pt, and Pb. Such type of ligands that contains P, S, As, Br and I atom are formed stable complex because these accept electron from M \rightarrow π -bonding. Hg^{2+} , Pb^{2+} , Cd^{2+} , and Bi^{3+} metal ions are also electronegative ions which form insoluble salts of metal sulfide which are insoluble in aqueous medium.

Temperature and pressure

Volatile ligands may be lost at higher temperature. This is exemplified by the loss of water by hydrates and ammonia:



The transformation of certain coordination compounds from one to another is shown as follows:



Ligand nature

A ligand is an ion or small molecule that binds to a metal atom (in chemistry) or to a biomolecule (in biochemistry) to form a complex, such as the iron-cyanide coordination complex Prussian blue or the iron-containing blood-protein hemoglobin. The ligands are arranged in spectrochemical series which are based on the order of their field strength. It is not possible to form the entire series by studying complexes with a single metal ion; the series has been developed by overlapping different sequences obtained from spectroscopic studies. The order of common ligands according to their increasing ligand field strength is

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^-$ (S-bonded) $< Cl^- < N^{3-} < F^- < NCO^- < OH^- < C_2O_4^{2-} < H_2O$
 $< NCS^-$ (N-bonded) $< CH_3CN < gly$ (glycine) $< py$ (pyridine) $< NH_3 <$

en (ethylenediamine) $< bipy$ (2,2'-bipyridine) $< phen$ (1,10-phenanthroline)
 $< NO^{2-} < PPh_3 < CN^- < CO < CH_2$

The above spectrochemical series help us to for determination of strength of ligands. The left last ligand is as weaker ligand. These weaker ligand cannot forcible binding the 3d electron and resultant outer octahedral complexes formed. It is as- $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$. For the given ligand, it is not possible to say about the exerted strong or weaker field on the central metal ion. The values of Δ are observed as:

Increasing the oxidation number the value of Δ increased.

Δ increases from top to bottom.

However, when we consider the metal ion, the following two useful trends are observed:

Δ increases with increasing oxidation number.

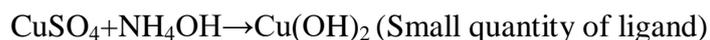
Δ increases down a group. For the determination of stability constant, the nature of the ligand plays an important role.

The following factors described the nature of ligands.

Size and charge

The size and charge are two factors that affect the production of metal complexes. The less charges and small sizes of ligands are more favorable for less stable bond formation with metal and ligand. But if this condition just opposite the product of metal and ligand will be a more stable compound. So, less nuclear charge and more size= less stable complex whereas if more nuclear charge and small in size= less stable complex. We take fluoride as an example because due to their smaller size than other halide and their highest electro negativity than the other halides formed more stable complexes. So, fluoride ion complexes are more stable than the other halides:





Chelating effect

For a metal ion, chelating ligand is enhanced and affinity it and this is known as chelate effect and compared it with non-chelating and monodentate ligand or the multidentate ligand is acts as chelating agent. Ethylenediamine is a simple chelating agent (Figure 1).

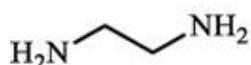


Figure 1. Structure of ethylenediamine.

Due to the bidentate nature of ethylenediamine, it forms two bonds with metal ion or central atom. Water forms a complex with Ni(II) metal ion, but due to its monodentate nature, it is not a chelating ligand (Figures 2 and 3).

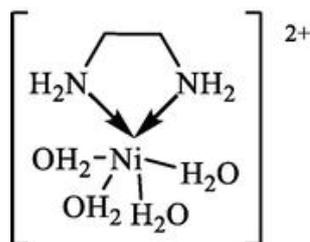


Figure 2. Structure of chelating configuration of ethylenediamine ligand.

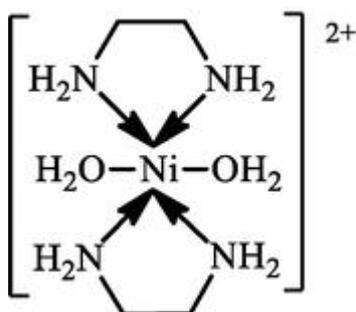
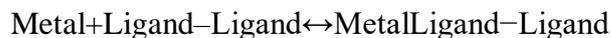


Figure 3. Structure of chelate with three ethylenediamine ligands.

The dentate cheater of ligand provides bonding strength to the metal ion or central atom, and as the number of dentate increased, the tightness also increased. This

phenomenon is known as chelating effect, whereas the formation of metal complexes with these chelating ligands is called chelation:



Some factors are of much importance for chelation as follows.

Ring size

The sizes of the chelating ring are increased as well as the stability of metal complex decreased. According to Schwarzenbach, connecting bridges form the chelating rings. The elongated ring predominates when long bridges connect to the ligand to form a long ring. It is usually observed that an increased a chelate ring size leads to a decrease in complex stability.

He interpreted this statement. The entropy of complex will be change if the size of chelating ring is increased, i.e., second donor atom is allowed by the chelating ring. As the size of chelating ring increased, the stability should be increased with entropy effect. Four-membered ring compounds are unstable, whereas five-membered are more stable. So the chelating ring increased its size and the stability of the formed metal complexes.

Number of rings

The number of chelating rings also decides the stability of complexes. Non-chelating metal compounds are less stable than chelating compounds. These numbers increase the thermodynamic volume, and this is also known as an entropy term. In recent years ligands capable of occupying as many as six coordination positions on a single metal ion have been described. The studies on the formation constants of coordination compounds with these ligands have been reported. The numbers of ligand or chelating agents are affecting the stability of metal complexes so as these numbers go up and down, the stability will also vary with it.

For the Ni(II) complexes with ethylenediamine as chelating agent, its log K_1 value is 7.9 and if chelating agents are trine and penten, then the log K_1 values are 7.9 and 19.3, respectively. If the metal ion change Zn is used in place of Ni (II), then the

values of $\log K_1$ for ethylenediamine, trine, and penten are 6.0, 12.1, and 16.2, respectively.

$\text{Ni}(\text{NH}_3)_6^{2+}$ is an octahedral metal complex, and at 25 °C its $\log \beta_6$ value is 8.3, but $\text{Ni}(\text{ethylenediamine})_3^{2+}$ complex is also octahedral in geometry, with 18.4 as the value of $\log \beta_6$. The calculated stability value of $\text{Ni}(\text{ethylenediamine})_3^{2+}$ 1010 times is more stable because three rings are formed as chelating rings by ethylenediamine as compared to no such ring is formed.

Ethylenediaminetetraacetate (EDTA) is a hexadentate ligand that usually formed stable metal complexes due to its chelating power.

Steric effect

A special effect in molecules is when the atoms occupy space. This is called steric effect. Energy is needed to bring these atoms closer to each other. These electrons run away from near atoms. There can be many ways of generating it. We know the repulsion between valence electrons as the steric effect which increases the energy of the current system. Favorable or unfavorable any response is created.

For example, if the static effect is greater than that of a product in a metal complex formation process, then the static increase would favor this reaction. But if the case is opposite, the skepticism will be toward retardation.

This effect will mainly depend on the conformational states, and the minimum steric interaction theory can also be considered. The effect of secondary steric is seen on receptor binding produced by an alternative such as:

Reduced access to a critical group.

Stick barrier.

Electronic resonance substitution bond by repulsion.

Population of a conformer changes due to active shielding effect.

Organic reagents in various techniques:

Complexing agents are becoming of increasing importance in analytical chemistry such as in gravimetric, titrimetric and colorimetric measurements. New types of

complexing agents are constantly under investigation, for possible analytical and industrial applications.

Prior to the 1980's, research in the field of complexing agents was one of the most active research areas in inorganic, analytical chemistry. The development of complexing agents was stimulated by research and progress in coordination chemistry and by studies of complex equilibria in solution. At present the significance of complexing agents is considered by many as having decreased in favor of instrumental methods, especially for routine, trace and automated analysis. However, complexing agents remain essential for many current, frequently used, methods such as molecular spectrophotometry in the UV visible region, luminescence analysis and the liquid-liquid extraction of neutral, anionic and cationic species. In addition, complexing agents are essential in the application of highly efficient separation procedures such as high performance liquid chromatography, pre concentration of trace elements, a variety of continuous and automated analytical procedures, methods such as AAS, ESR, NMR, NAA and some electroanalytical methods.

Applications of organic reagents:

- **Qualitative Analysis**

Organic reagents have found wide application in the qualitative analysis of inorganic substances because of the high degree of sensitivity and selectivity that can be achieved by proper choice of experimental conditions. Sometimes a test can be made specific.

- **Gravimetric Analysis**

The use of organic reagents for gravimetric determination of inorganic substances offers a number of advantages, the outstanding feature being the high selectivity or even specificity. The precipitates are easy to filter off and wash, and after drying can often be weighed directly, provided they have a defined stoichiometry. Another important advantage is that the precipitates are not hygroscopic. Also the high molecular weights of the complexes mean that the conversion factors are very favorable.

- **Titrimetric Analysis**

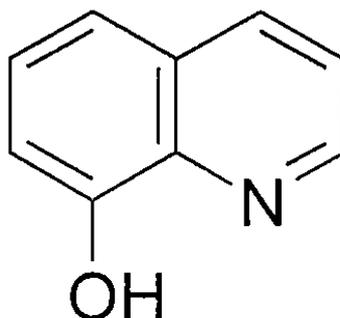
Organic reagents find extensive applications in titrimetry. In acid-base titrations organic substances of the suitable properties are mainly applied as color or fluorescent pH change (sulphophthaleins, azo-compounds, nitrophenols etc.), or as standards (oxalic acid, potassium hydrogen phthalate) or as titrants suited for non-aqueous media (tetra-alkylammonium hydroxides). Some are the examples of titrations mentioned below;

- Chelometric titrations
- Chelometric-back titrations
- Displacement titrations
- Potentiometric titrations
- Visual titrations
- Photometric titrations
- Amperometric titrations
- Conductometric titrations
- Thermometric titrations

Various types of organic reagents:

Oxine (8-hydroxyquinoline) and its derivatives:

Oxine (8-hydroxyquinoline, HQ) and its derivatives occupy a unique place in analytical chemistry, perhaps second only to EDTA and its analogues.



8-Hydroxyquinoline is an almost colourless, crystalline solid of MP 75-76°C. It is almost insoluble in water but soluble in acetic acid. It is also soluble in methanol. Its ability to chelate with a variety of metals forming insoluble compounds has been known for at least 50 years, or ethanol.

The hydrogen of the OH group is replaced by metals. Most often, precipitates are obtained under suitable conditions, when the reagent is added to solutions containing ions of magnesium, aluminium, copper, bismuth, cadmium, zinc, mercuric mercury, lead, antimony, tin, vanadium, uranium, iron, titanium, zirconium, tantalum, niobium, manganese, nickel or cobalt. The reagent is not specific for any particular ion, but the solubility of the precipitate varies, so that it can be used for numerous separations. The precipitates are normally obtained from solutions containing acetic acid and alkali acetate, some from solutions which are ammoniacal and still others from solutions which are made alkaline with sodium hydroxide. The conditions of precipitation for many of the metal ions by oxine are given in Table 1. It is stated that the alcoholic solutions of the reagent may be employed in cases where precipitation occurs at high pH and the acetic acid solution for precipitations at low pH.

Table 1. Conditions for precipitation of Metal Complexes of Oxine

Metal	pH	
	Initial precipitation	Complete precipitation
Aluminium	2.9	4.7-9.8
Bismuth	3.7	5.2-9.4
Cadmium	4.5	5.5-13.2
Calcium	6.8	9.2-12.7
Chromium	3.7	4.9-9.3
Cobalt	3.6	4.9-11.6
Copper	3.0	3.3
Iron(III)	2.5	4.1-11.2
Lead	4.8	8.4 -12.3
Magnesium	7.0	7.0-8.7
Manganese	4.3	5.9-9.5
Molybdenum	2.0	3.6-7.3
Nickel	3.5	4.6-10.0
Thorium	3.9	4.4-8.8
Titanium	3.6	4.8-8.6
Tungsten	3.5	5.5-5.7
Vanadium	1.4	2.7-6.1
Zinc	3.3	4.4

The general conditions for precipitation of metal oxinates are summarized below.

- (1) The reagent is added to the cooled solution of the concerned metal ion until the yellow or orange-yellow colour of the supernatant liquid indicates that a small but definite excess of the reagent is present.
- (2) The precipitate is coagulated by a short period of heating at a temperature, not exceeding 70°C.
- (3) The precipitate may be filtered through filter paper or filtering crucible.
- (4) The filtrate should possess an yellow or orange colour, indicating the presence of excess of precipitant. If turbidity appears, a portion should be heated. If the turbidity disappears, it may be assumed to be due to excess of reagent crystallising out. Otherwise, more reagent should be added and the solution filtered again.
- (5) Washing of the precipitate may often be effected with hot or cold water (according to the solubility of the metal "Oxinate") and is continued until the filtrate become colourless. The use of alcohol is permissible if it is known to have no effect on the precipitate.

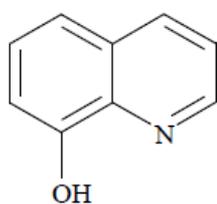
(6) The washed precipitate may be dried at 105-110°C (anhydrous oxinate). In cases where prolonged heating at 130-140°C is required, slight decomposition may occur. The determination may also be completed volumetrically by dissolving the precipitate in dilute hydrochloric acid and titrating with a standard solution of potassium bromate. The oxinates, thus precipitated, have the composition $M(C_9H_6ON)_2$, if the coordination number of the metal is four (e.g. magnesium, zinc, copper, cadmium, lead and indium); $M(C_9H_6ON)_3$ if the coordination number is six (e.g. aluminium, iron, bismuth and gallium) and $M(C_9H_6ON)_4$ if the coordination number is eight (e.g. thorium and zirconium).

The fact that different metallic complexes precipitate from solution at different pHs has been utilized for the separation of metals. The discovery that certain metal complexes are soluble in organic solvents forming highly coloured solutions. The intensity of which, with certain reservations, is proportional to the amount of metal present, has led to the introduction of colorimetric techniques for the determination of trace metals in solution.

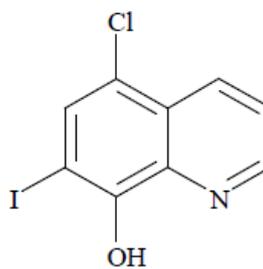
Oxine itself is inactive, and exerts activity by virtue of the metal chelates produced in its reaction with metal ions in the medium. Used by itself or as the sulfate (Chinosol) or benzoate in antiseptics, the effect is bacteriostatic and fungistatic rather than microbiocidal. Inhibitory action is more pronounced upon gram-positive than gram-negative bacteria; the growth preventing concentrations for staphylococci being 10 ppm; for streptococci 20 ppm; for *Salmonella typhosa* and for *E. coli* 100 ppm. However, a 1% solution requires at least 10 hours to kill staphylococci and 30 hours for *E. coli* bacilli. The oxine benzoate was the most active antifungal agent in a series of 24 derivatives of quinoline tested. A 2.5% solution of this compound was successful in treating dermatophytosis. Iron and cupric salts were found to prolong the antibacterial effect of oxine on teeth.

Oxine (8-hydroxyquinoline) and its derivatives are widely used as analytical reagents and anti-amoebic agents. Oxine, in its deprotonated form, is a bidentate chelator,

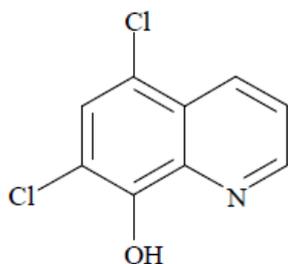
forming complexes with a number of metal ions. The deprotonated O atom and the ring N atom are involved in the metal chelation. Metal chelation has been implicated in the biological activity of derivatives of oxine. The literature survey reveals that 5-Chloromethyl-8-hydroxy quinoline (CMQ) is a versatile derivative of 8-hydroxyquinoline. It can be easily prepared by the room temperature reaction of 8-hydroxyquinoline, formaldehyde, conc.HCl and dry HCl gas. It is stable in form of hydrochloride otherwise it hydrolyzes to methyl group.



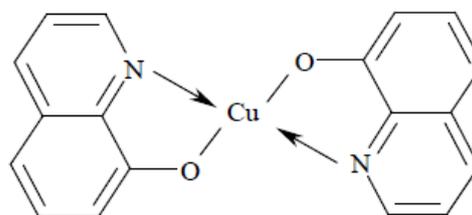
8-Hydroxyquinoline



5-Chloro-8-hydroxy-7-iodoquinoline



5,7-dichloro-8-hydroxyquinoline



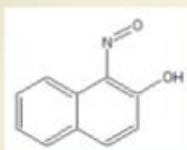
Copper Oxinate

Certain halogen derivatives of 8-hydroxyquinoline have a record of therapeutic efficacy in the treatment of cutaneous fungus infections and also of amebic dysentery. Among these are 5-chloro-7-iodo-8-quinolinol (iodochlorhydroxyquin, Vioform), 5,7-diiodo-8-hydroxyquinoline (diiodohydroxyquin), and sodium 7-iodo-8-hydroxyquinoline-5-sulfonate (chiniofon).

Copper 8-quinolinolate (copper oxinate), the copper compound of 8-hydroxyquinoline, is employed as an industrial preservative for a variety of purposes, including the protection of wood and textiles against fungus-caused rotting, and interior paints for food plants. It has 25 times greater antifungal activity than oxine.

1-Nitroso-2-naphthol:

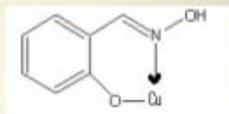
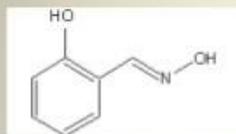
It is a brown powder with MP 109°C, and is insoluble in water, soluble in ethyl alcohol, ether, acetic acid and alkalies.



Use: This reagent precipitates quantitatively cobalt (below pH 8.74) palladium (below pH 11.82), thorium (pH 4.8-5.6), ferric ion (0.95-2) and ferrous ion from alkaline solution. The chief use of the reagent is in the separation of the cobalt from a nickel solution from which iron (III) has been removed.

Salicylaldoxime:

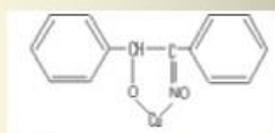
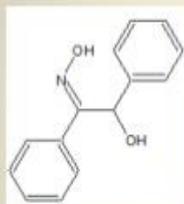
The reagent which is represented by formula $C_7H_7O_2N$, is a white crystalline of MP $57^\circ C$ and is sparingly soluble in water.



Use: The reagent is chiefly employed for the estimation of the bivalent copper. The solution of the reagent is prepared by dissolving 1.0g of the solid in 5ml of 90% ethanol, then adding 95ml water and keeping the temperature at $80^\circ C$, the reagent solution decomposes if kept and hence should be prepared a fresh before use.

Benzoin oxime (cupron):

The reagent is a white crystalline solid with MP $152^\circ C$ and has the molecular formula $C_{14}H_{13}O_2N$. It is sparingly soluble in ethanol.

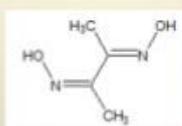


Use: It is specific reagent for copper which is detected as a green precipitate of composition $Cu C_{14}H_{11}O_2N$ from an ammoniacal solution containing some tartarate. It can also precipitate molybdate and tungstate from acid solution quantitatively but precipitation of vanadate and tantate is only partial.

Organic reagents with the donor atoms N,N

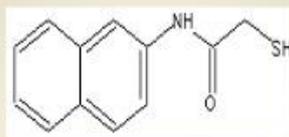
- **Biacetyl dioxime:**

This reagent yields water insoluble chelates with nickel (II) and palladium (II). The palladium chelate is yellow and precipitated from dilute acid medium, whereas the red nickel (II) chelate can be brought down from a neutral medium.



- **Thionalide (2-mercapto-N-naphthylacetamide):**

It is a white to ovy-colour needles like crystals.
It is insoluble in water but soluble in many organic solvents.

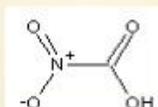


- **Use:** It is reagent use to precipitate copper, mercury, silver, thallium, and bismuth.

Organic reagents used for Masking or Sequestration

- **Nitroacetic acid:**

It is a yellow crystalline solid. It is insoluble in water but soluble in organic solvents.

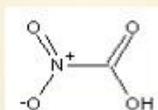


Use: It is a polydentate ligand and forms complexes with metals like Ca, Sr, Ba and Mg. These complexes are stable hence precipitated out.

Organic reagents used for Masking or Sequestration

- **Nitroacetic acid:**

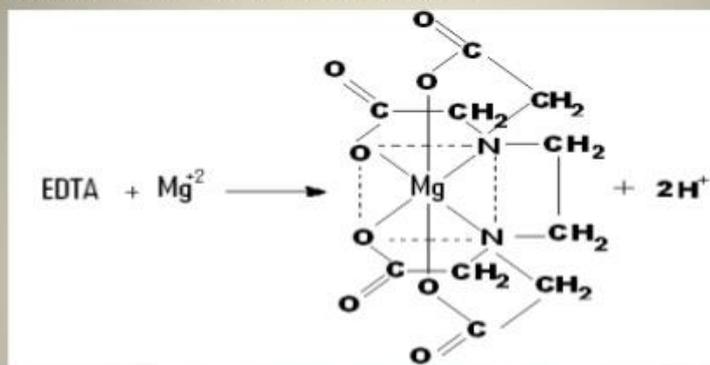
It is a yellow crystalline solid. It is insoluble in water but soluble in organic solvents.



Use: It is a polydentate ligand and forms complexes with metals like Ca, Sr, Ba and Mg. These complexes are stable hence precipitated out.

EDTA (Ethylene diaminetetracetic acid):

It is a polyamino carboxylic acid and is a colourless compound. It is a water soluble acid.



Use: It is used in colorimetric analysis and for the titration of metallic ions. It is also used as masking agent as it is a polydentate ligand and form complexes with metals like calcium, barium, and magnesium. It also used for the determination of ions.