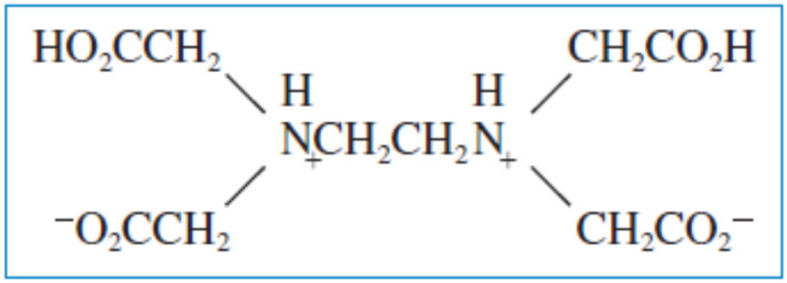
Complexometric titration

- The formation of complexes can also serve as the basis of accurate and convenient titrations for metal ions in which the titrant is a complexing agent.
- Selectivity can be achieved by appropriate use of *masking agents* (addition of other complexing agents that react with interfering metal ions, but not with the metal of interest) and by pH control, since most complexing agents are weak acids or weak bases whose equilibria are influenced by the pH.
- The EDTA titration of calcium plus magnesium is commonly used to determine water hardness.
- Ligands: variety of substances that have a pair of unshared electrons (e.g., on N, O, S atoms in the molecule) capable of satisfying the coordination number of the metal cation.
- Monodentate Ligand: Ligand that contain only one atom that can be attached to central metal. Ex: NH_3 and Cl
- Bidentate Ligand: Ligand that contain two atoms/groups that can be attached to central metal simultaneously. Ex: ethylenediamine $H_2NCH_2CH_2NH_2$

Chelating agent

An organic agent that has two or more groups capable of complexing with a metal A negatively charged chelate results. ion is called a **chelating agent**. The complex formed is called a **chelate**. The chelating agent is called the *ligand*. Titration with a chelating agent is called a **chelometric titration**, perhaps the most important and practical type of complexometric titrations. For example EDTA or **ethylenediaminetetraacetic acid**

EDTA is most commonly available as the disodium salt, where the two ionized carboxylic acid groups form the salt. Each of the two nitrogens and each of the four carboxyl groups contains a pair of unshared electrons capable of complexing with a metal ion. Thus, EDTA contains six complexing groups.



EDTA represented as H_4Y

Chelate Effect

- A chelated complex, i.e. one formed by a bidentate or a multidenate ligand, is more stable than the ***corresponding*** complex with monodentate ligands: the greater the number of points of attachment of ligand to the metal ion, the greater the stability of the complex. This is known as chelate effect. For example, the complexes formed by the nickel(I1) ion with (a) the monodentate NH_3, molecule, (b) the bidentate ethylenediamine (1,2-diaminoethane), and (c) the hexadentate ligand 'penten' $\{(H_2NCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2\}$an overall stability constant value for the ammonia complex of 3.1×10^8, which is increased by a factor of about 10^{10} for the complex of ligand (b), and is approximately ten times greater still for the third complex. The chelate effect is an entropy effect.

- Steric Effect: inhibition of complex formation owing to the presence of a large group either attached to, or in close proximity to, the donor atom.

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = -RT\mathrm{Ln}\ K$$