⊛ Stepwise formation constants and overall formation constants:

Formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex, ML_n (M = central metal ion, L = monodentate ligand and n = co-ordination no. of the metal ion for the ligand L) may be supposed to take place by the following 'n' consecutive steps and equilibrium constan-

$M + L \rightleftharpoons ML$; $K_1 = \frac{[ML]}{[M][L]}$

$ML + L \rightleftharpoons ML_2$; $K_2 = \frac{[ML_2]}{[ML][L]}$

$ML_2 + L \rightleftharpoons ML_3$; $K_3 = \frac{[ML_3]}{[ML_2][L]}$

. . . . . .

$ML_{(n-1)} + L \rightleftharpoons ML_n$; $K_n = \frac{[ML_n]}{[ML_{(n-1)}][L]}$

The equillibriem constants K_1, K_2, K_3 . . . K_n are called stepwise formation constants or stepwise stability constants.

The formation of the complex ML_n may also be expressed by the following steps and the equm constants;

$M + L \rightleftharpoons ML$; $\beta_1 = \frac{[ML]}{[M][L]}$

$M + 2L \rightleftharpoons ML_2$; $\beta_2 = \frac{[ML_2]}{[M][L]^2}$

$M + 3L \rightleftharpoons ML_3$; $\beta_3 = \frac{[ML_3]}{[M][L]^3}$

. . . . . .

$M + nL \rightleftharpoons ML_n$; $\beta_n = \frac{[ML_n]}{[M][L]^n}$

The equillibriem constants β_1, β_2, β_3 . . . β_n are called overall formation constants or overall stability constants

Relation betⁿ β_n and K_1, K_2 . . . K_n

Stepwise formation constants (K_1, K_2 . . . K_n) and overall formation constants (β_1, β_2 . . . β_n) are related to one-another.

Consider for example; the expression for β_3

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

We know;

$$K_1 = \frac{[ML]}{[M][L]}, \quad K_2 = \frac{[ML_2]}{[ML][L]}, \quad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\therefore K_1 \times K_2 \times K_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} = \frac{[ML_3]}{[M][L]^3}$$

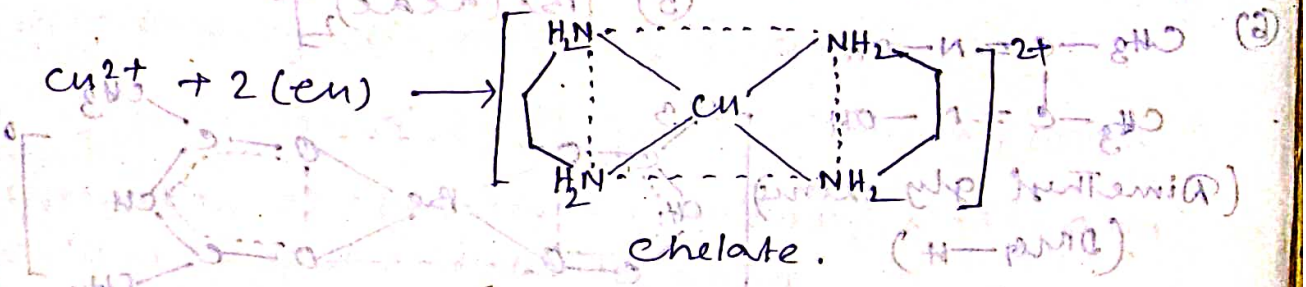
$$= \beta_3$$

Therefore we write $\beta_n = K_1 \times K_2 \times K_3 \ldots K_n$. From the above relation it is evident that the overall stability constant (β_n) is equal to the product of the stepwise stability constants ($K_1, K_2 \ldots K_n$)

Chelated complex or chelate

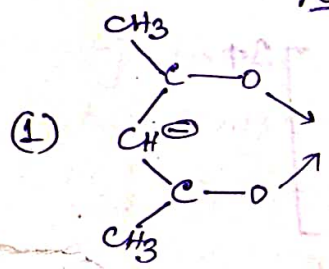
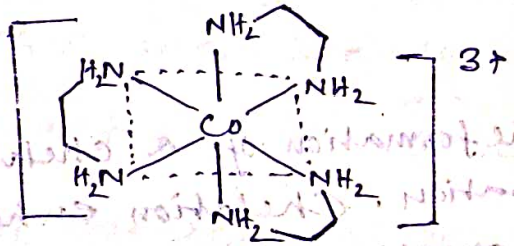
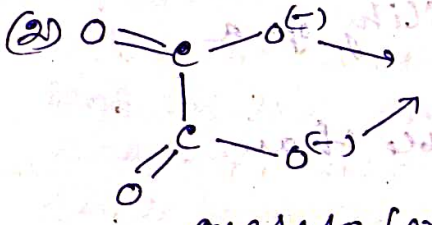
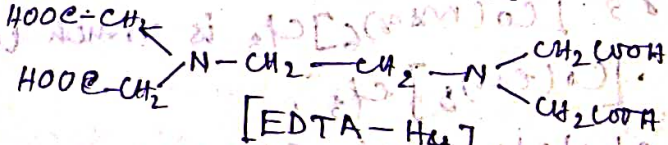
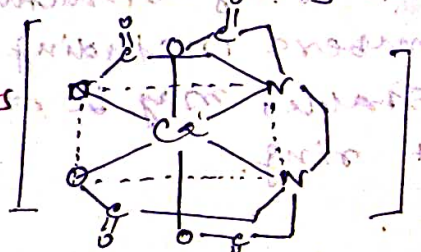
When a bidentate or polydentate ligand simultaneously occupy two or more co-ordination positions of the same central metal ion. A complex is formed containing a ring str. Such ligands are called chelating ligands and the complex is called chelate complex or chelate.

When two molecules of ethylene-di-amine (en) which is a bidentate ligand, get attached with one Cu^{2+} ion through its two 'N' donor atoms of each molecule. $[Cu(en)_2]^{2+}$ complex ion which contains two five membered rings is obtained. This complex ion is called chelate.



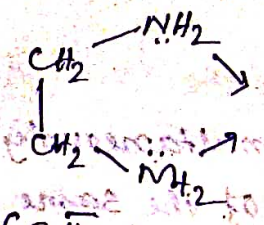
Chelate.

- Some examples of chelating ligands and chelates formed by them are given below;

Ligand	Chelate
(1)  (Acetyl acetonato)	(1) $[Co(en)_3]^{3+}$ 
(2)  Oxalato (ox)	(2) $[Ca(EDTA)]^{2-}$  $[EDTA-H_4]$ 

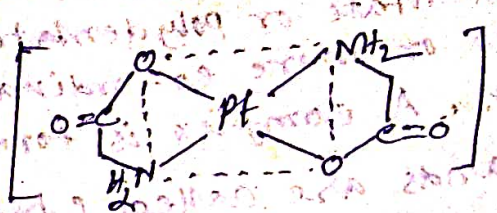
B: Ca(II) at pH=10, forms a chelate with EDTA. State the no. of chelate rings per Ca(II) EDTA complex. Draw the structure of the chelate out of Ca(II)-EDTA

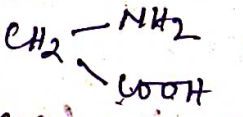
Q. How many chelate rings are formed when EDTA reacts with Mg^{2+} ion?

(3) 

(ethylene-di-amine)
(en)

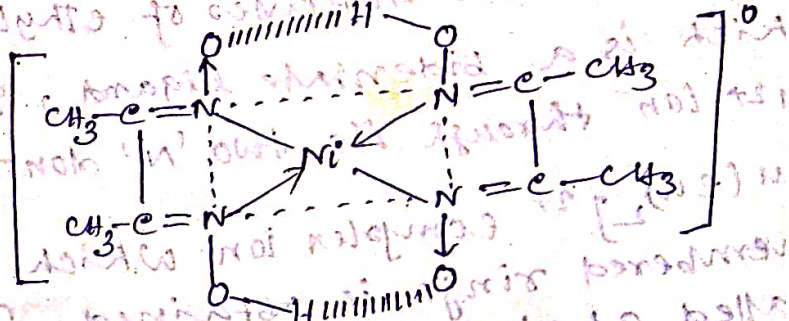
(3) $Pt(gly)_2$

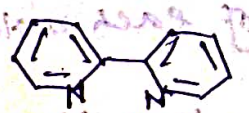


(4) 

(glycine) (gly-H)

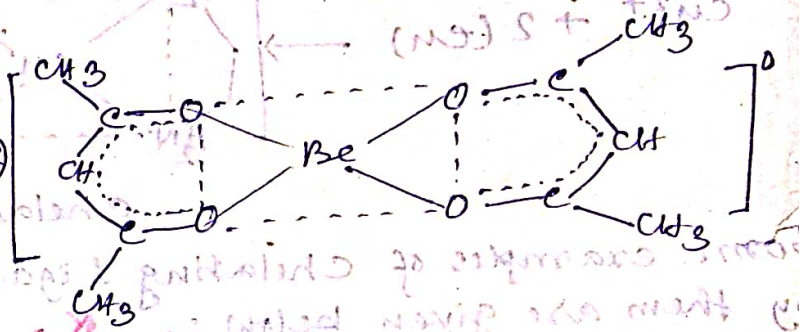
(4) $[Ni(DMG)_2]^0$

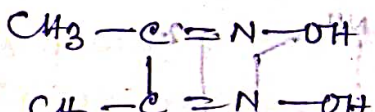


(5) 

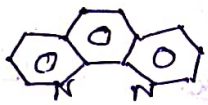
(2,2'-bi Pyridine)
(bpy)

(5) $[Be(acac)_2]^0$



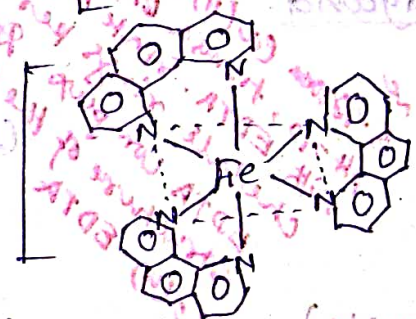
(6) 

(Dimethyl gly oxime)
(DMG-H)

(7) 

(Ortho-phenanthroline)
(o-phen)

(6) $[Fe(o\text{-}phen)_3]^{3+}$



The formation of a chelate is called chelation or cyclisation. Chelation enhances the stability of a complex.

e.g.; $[Co(NH_3)_6]Cl_3$ is much less stable than $[Co(en)_3]Cl_3$.

The chelate ring structures containing five and six members including the metal ion are the most stable; may be due to reduced steric strain in such ring.