

Chelating Ligands and Chelates

A chelating ligand is a bidentate or polydentate ligand which is attached to the same central metal atom by two or more of its donor atoms resulting in the formation of a complex having a strain-free ring structure. The complex having the ring structure is called *chelate* or *chelated complex*. The chelate is also called by various other names like *cyclic complex*, *ring-type complex* etc. The formation of a chelate is called *chelation* or *cyclisation*.

Examples of the formation of chelates

(i) When two molecules of ethylene diamine, $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ (*en*) which is a bidentate ligand, get attached with one Cu^{2+} ion through its two N-donor atoms of each molecule, complex ion viz. $[\text{Cu}(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2)_2]^{2+}$ or $[\text{Cu}(\text{en})_2]^{2+}$ which contains two 5-membered rings is obtained. In the formation of this complex ion, ethylene diamine molecule (bidentate ligand) acts as a chelating ligand and the complex ion thus formed is called a chelate [see Fig. 1.56 (a)].

(ii) When three oxalate ions, $\begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$ or $\text{C}_2\text{O}_4^{2-}$ or ox^{2-} get attached with one Fe^{3+} ion, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ or $[\text{Fe}(\text{ox})_3]^{3-}$ ion is obtained. This complex ion is a chelate. This chelate has three 5-membered rings. In the formation of this chelate, $\text{C}_2\text{O}_4^{2-}$ ion which is a bidentate ligand acts as a chelating ligand [see Fig. 1.56 (b)].

It may be noted that OH^- , Cl^- and NH_2^- ions cannot serve as chelating ligands, because the angle between the lone pairs do not allow them to span adjacent coordination positions of one and the same metal atom. Hydrazine ($\text{H}_2\ddot{\text{N}}\text{—}\ddot{\text{N}}\text{H}_2$) cannot function as a chelating ligand, since a 3-membered ring-type complex formed $\left[\begin{array}{c} \text{H}_2\text{N} \searrow \\ | \quad \nearrow \\ \text{H}_2\text{N} \end{array} \text{M} \right]$ is very strained and hence is unstable.

Thus every polydentate ligand is not necessarily a chelating ligand.

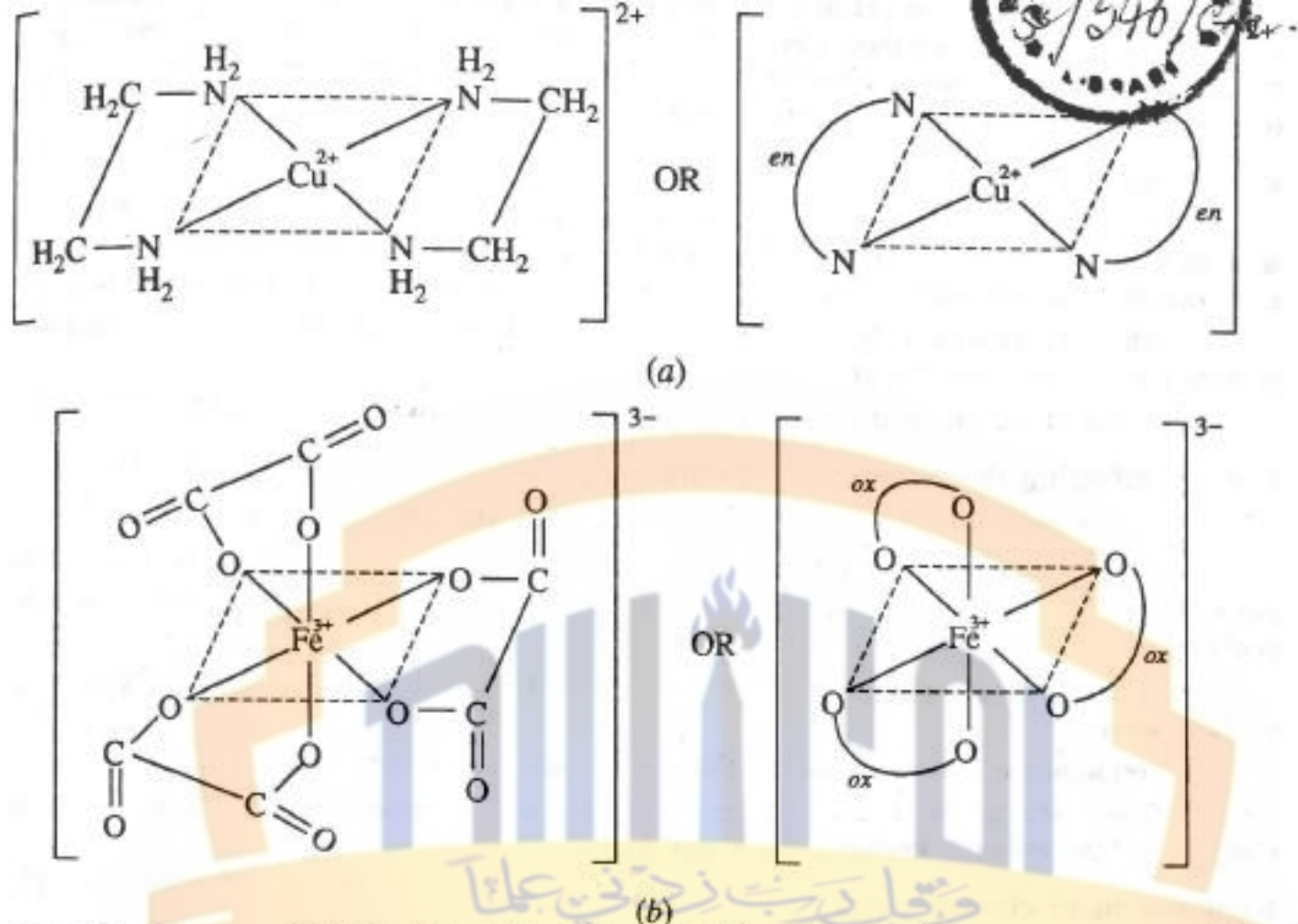


Fig. 1.56. Structure of (a) $[\text{Cu}(\text{NH}_2\text{---CH}_2\text{---CH}_2\text{---NH}_2)_2]^{2+}$ or $[\text{Cu}(\text{en})_2]^{2+}$ and of (b) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ or $[\text{Fe}(\text{ox})_3]^{3-}$ chelated complex ions.

Classification of chelates

Chelates which do not carry any charge are called *inner metallic complexes of the first order*. These chelates are neutral (non-electrolyte) in nature. Examples of such chelates are $[\text{Cr}^{3+}(\text{gly})_3]^0$, $[\text{Co}^{3+}(\text{acac})_3]^0$, $[\text{Cu}^{2+}(\text{big})_2]^0$ etc.

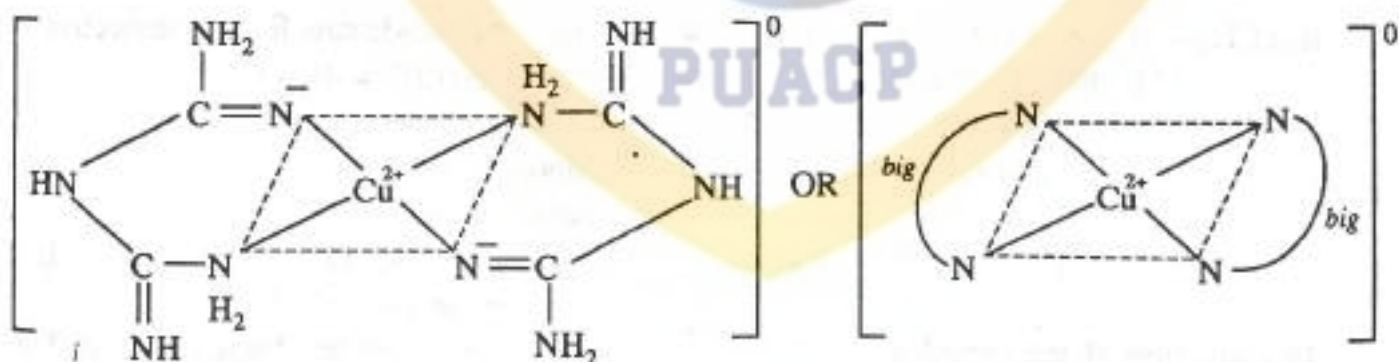


Fig. 1.57. Structure of $[\text{Cu}^{2+}(\text{big})_2]^0$. Here big is the abbreviation for biguanide ion which is a bidentate ligand.

The chelates which carry some charge are called *inner-metallic complexes of the second order*. These chelates are ionic in nature. Examples of such chelates are $[\text{Co}^{3+}(\text{en})_3]^{3+}$, $[\text{Co}^{2+}(\text{acac})_3]^-$ etc. The structure of $[\text{Cu}^{2+}(\text{big})_2]^0$ is shown in Fig. 1.57.

Detection of chelate formation

Since the formation of a chelate is also complex formation, the formation of a chelate may be detected by all those methods that are used for the detection of complex formation. Thus the formation of a chelate may lead to the changes namely (i) the change in the colour of the metal ion (ii) the dissolution of the precipitate (iii) the enhancement of the stability of

the complex (iv) the drop in pH of the solution (v) the change in the electrical conductivity of the solution. These changes show the formation of complex. In order to prove the presence of ring structure, it is necessary that the complex is isolated. Chemical tests and physical measurements (e.g., X-ray diffraction) may prove the presence of the ring in the complex.

Properties of inner metallic complexes

(i) Neutral inner metallic complexes are usually insoluble in water but dissolve in organic solvents immiscible with water. This property has been used for the separation of metals by solvents extraction method. See *Applications of the formation of chelated complexes* discussed on page 34.

(ii) The formation of a chelated complex may lead to the change in colour. This property permits colourimetric estimation.

(iii) Most of the chelated complexes have low melting points and are volatile.

Factors affecting the stability of chelates

Following are important factors which influence the stability of chelates.

1. **Size of the chelate ring.** Chelates having 6-membered rings including the metal atom are more stable than those having 5-membered rings which in turn, are more stable than the chelates with 4-membered rings and so on.

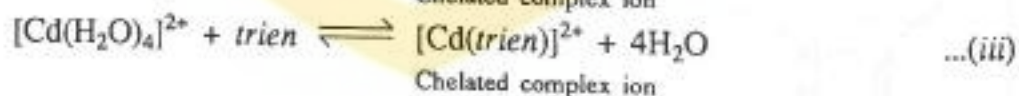
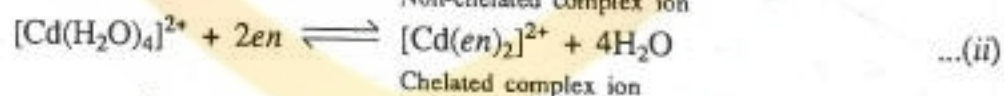
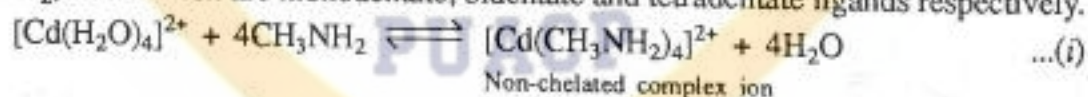
2. **Number of chelate rings.** Greater in the number of chelate rings, greater is the stability of the chelate.

3. **Resonance effects.** Resonance enhances the stability of the chelate.

4. **Chelate effect.** The chelated complexes are known to be more stable than the non-chelated complexes. This effect is known as **chelate effect**.

Explanation of chelate effect

Chelate effect can be explained by considering the formation of some non-chelated and chelated complex ions of the same metal. Hydrated cadmium ion, $[\text{Cd}(\text{H}_2\text{O})_4]^{2+}$ forms 4-coordinated complex ions with methyl amine ($\text{CH}_3\text{—}\ddot{\text{N}}\text{H}_2$), ethylene diamine ($\ddot{\text{N}}\text{H}_2\text{—CH}_2\text{—CH}_2\text{—}\ddot{\text{N}}\text{H}_2$ or *en*) and triethylene tetramine ($\ddot{\text{N}}\text{H}_2\text{—CH}_2\text{—CH}_2\text{—}\ddot{\text{N}}\text{H—CH}_2\text{—CH}_2\text{—}\ddot{\text{N}}\text{H—CH}_2\text{—CH}_2\text{—}\ddot{\text{N}}\text{H}_2$ or *trien*) which are formulated as $[\text{Cd}(\text{CH}_3\text{—NH}_2)_4]^{2+}$, $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ respectively. Note that $\text{CH}_3\text{—NH}_2$, *en* and *trien* are monodentate, bidentate and tetradentate ligands respectively.



The structure of the complex ions formed in the above reactions has been shown in Fig. 1.58. These structures show that (i) $[\text{Cd}(\text{CH}_3\text{—NH}_2)_4]^{2+}$ ion has no rings while $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ ions have two and three 5-membered rings including Cd^{2+} ion. (ii) The number of coordination centres of one molecule of CH_3NH_2 , *en* and *trien* (ligands) is equal to 1, 2 and 4 respectively. In each complex ion the coordination number of Cd^{2+} ion is equal to 4.

Since $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ ions are chelated ions, each of these is more stable than $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ ion which is a non-chelated ion. It has been found that the stability of these ions is in the order:



The above order can be explained on the basis of ΔG° value of reactions (i), (ii) and (iii) which lead to the formation of the complex ions. The value ΔG° for a reaction is given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The value of ΔH° for all the three reactions has been found to be negative. It has been found that larger is the negative value of ΔG° , greater is the stability of the complex ion.

In reaction (i), since the number of molecules on the RHS is the same as that on LHS, there is no change in the randomness or entropy in going from reactants to products, i.e., for reaction (i), $\Delta S^\circ = 0$ and hence

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \times 0 = \Delta H^\circ \\ &= - \text{Negative quantity, since } \Delta H^\circ \text{ is negative.}\end{aligned}$$

In reaction (ii), since four molecules of H_2O are replaced by two molecules of *en*, there is an increase of two molecules on going from reactants to products and hence there is an increase in the value of ΔS° in the same direction. Thus ΔS° would have a large positive value. This implies that since ΔH° is negative, ΔG° would be a large negative quantity.

In reaction (iii), since four molecules of H_2O are replaced by one molecule of *trien*, there is an increase of three molecules on proceeding from reactants to the products and hence there is a greater increase in the magnitude of ΔS° in the same direction. Thus ΔS° would have a larger positive value. This implies that, since ΔH° is negative, ΔG° would be a larger negative quantity. Thus the value of ΔG° would be larger than that (i.e., ΔG°) of reaction (ii).

The above discussion shows that ΔG° has a negative value for all the three reactions and the magnitude of this negative value increases in the order $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+} < [\text{Cd}(\text{en})_2]^{2+} < [\text{Cd}(\text{trien})]^{2+}$. Thus, $[\text{Cd}(\text{trien})]^{2+}$ is more stable than $[\text{Cd}(\text{en})_2]^{2+}$ which is more stable than $[\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}$. It also follows from this discussion that as the number of coordination centres of CH_3NH_2 , *en*, and *trien* (ligands) increases as 1→2→4, the stability of the complexes given by these ligands with the same metal also increases.

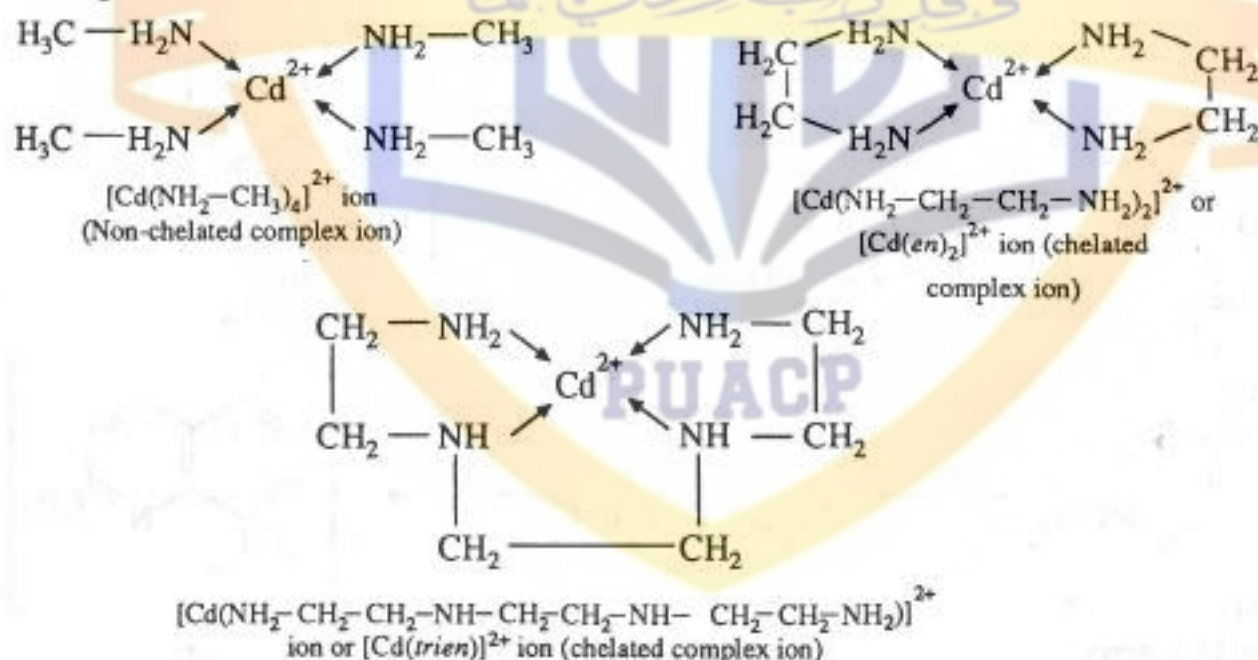


Fig. 1.58. Formation of $[\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}$, $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ ions from $[\text{Cd}(\text{H}_2\text{O})_4]^{2+}$ ion.

5. Steric effect (Also called steric hindrance or steric strain). When a group is either attached with the donor atom of the ligand or is present near the donor atom, the metal-ligand bond gets weakened and hence the stability of the complex is lowered. This effect is called steric effect. This effect can be illustrated by the following examples.

(a) Ethylene diamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (*en*) and its N-tetramethyl derivative viz. N-tetramethyl ethylene diamine, $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (*tetrameen*) both form chelated octahedral complex ions with Ni^{2+} ion. These complex ions are formulated as $[\text{Ni}(\text{en})_3]^{2+}$ and $[\text{Ni}(\text{tetrameen})_3]^{2+}$, since both the ligands are bidentate ligands. The structure of these complex ions is given below in Fig. 1.59 and 1.60 respectively.

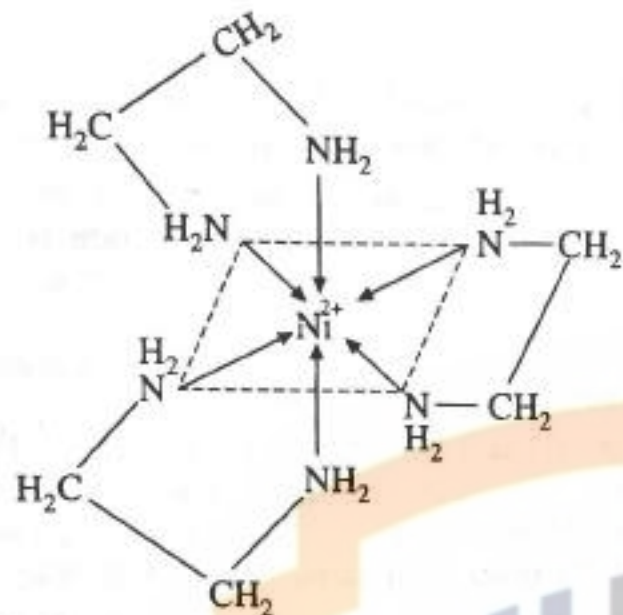


Fig. 1.59. Structure of $\text{Ni}(\text{NH}_2\text{---CH}_2\text{---CH}_2\text{---NH}_2)_3^{2+}$ or $[\text{Ni}(\text{en})_3]^{2+}$ ion (I).

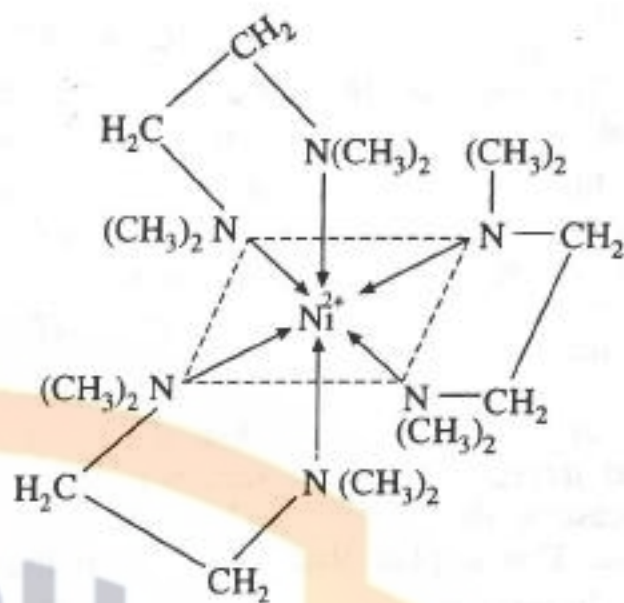


Fig. 1.60. Structure of $[\text{Ni}\{(\text{CH}_3)_2\text{N---CH}_2\text{---CH}_2\text{---N}(\text{CH}_3)_2\}]^{2+}$ or $[\text{Ni}(\text{tetrameen})_3]^{2+}$ ion (II).

It has been found that complex ion (II) has lower stability than complex ion (I). Lower stability of (II) is due to the fact that the two bulky CH_3 groups attached with N-atom (donor atom) produces steric overcrowding round the central Ni^{2+} ion. Thus complex ion (II) has lower stability than the complex ion (I).

(b) 8-hydroxy quinoline and its 2-methyl derivative viz. 2-methyl 8-hydroxy quinoline both form chelated complexes with Ni^{2+} ion as shown in Fig. 1.61.

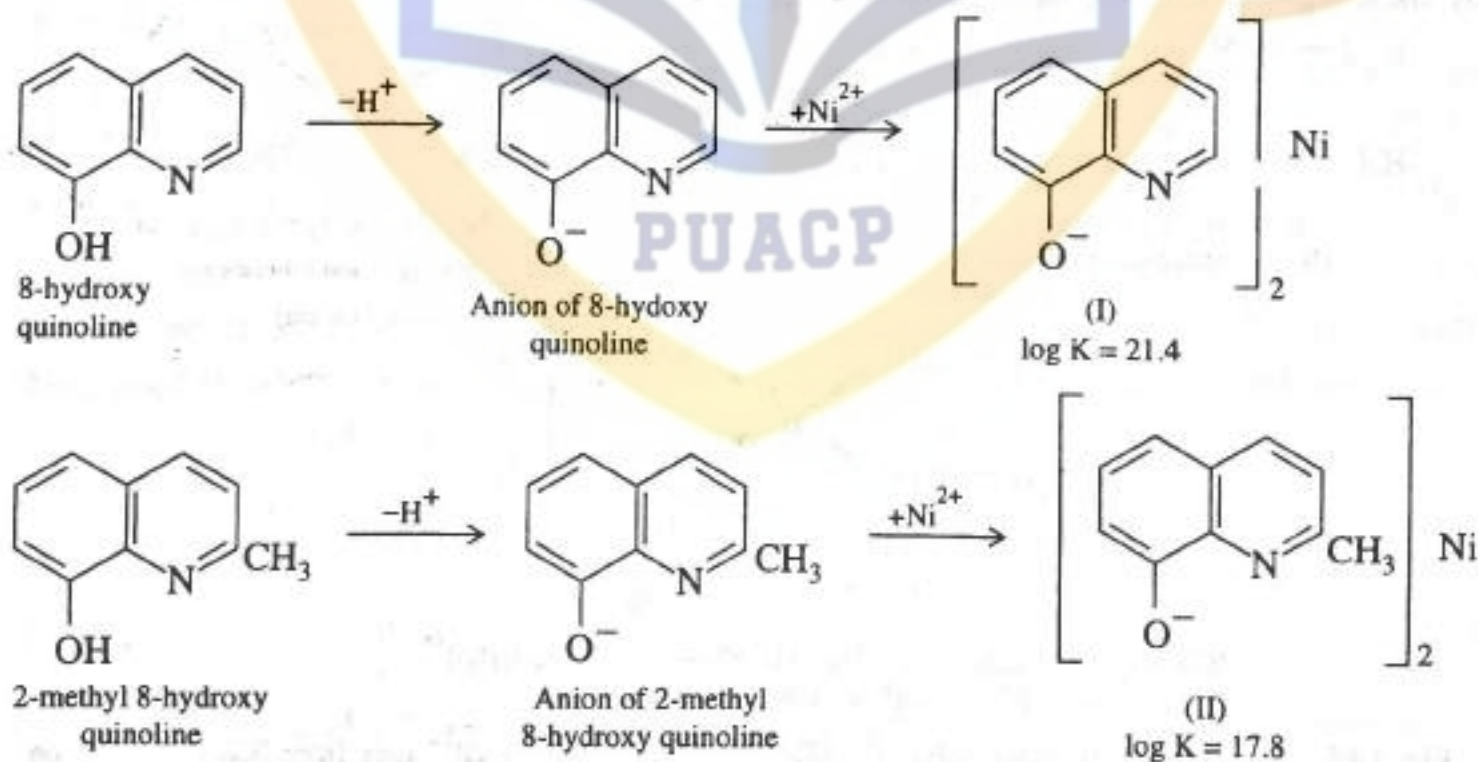


Fig. 1.61. Chelated complexes formed by Ni^{2+} ion with 8-hydroxy quinoline and its methyl derivative.

As is evident from the values of $\log K$ of both the complexes, complex (II) has lower stability than complex (I). Lower stability of (II) is due to the steric overcrowding produced by the presence of CH_3 group near N-atom (donor atom) in the ring in position number 2.