

Class 'b' metals are :

$\text{Cu}^+, \text{Ag}^+, \text{Au}^+, \text{Tl}^+, \text{Cd}^{2+}, \text{Hg}_2^{2+}, \text{Hg}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}, \text{Pt}^{4+}, \text{Tl}^{3+}$, etc.

(iii) Borderline Metals : Borderline metals include dipositive metal ions of 3d-series which are $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$. For a given ligand order of stability of complexes is :

$\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ (Irving-Williams series)

According to Pearson hard metals or acids prefer to bind to hard bases or hard ligand and soft acids or metals prefer to bind to soft bases or ligand.

(2) Nature of Ligands

(i) Basic Character of Ligands : In general, more is the basic character of ligands, more easily it can donate its lone pair of electrons to the central metal ion and hence greater is the stability of the complex formed. For example, for a given dipositive (M^{2+}) 3d-series transition metal ion, order of stability of complex with $\text{NH}_3, \text{H}_2\text{O}$ and F^- is :

$\text{NH}_3 > \text{H}_2\text{O} > \text{F}^-$

(ii) Covalent Character : Higher the covalent character, higher will be the stability of the complex. For example, order of stability and covalent character of complexes of Ag^+ with halogen is :

$\text{AgI}_2^- > \text{AgBr}_2^- > \text{AgCl}_2^- > \text{AgF}_2^-$

— Decreasing order of covalent character →

— Decreasing order of stability of complex →

(iii) π - Bonding Capacity of Ligands : The ligands like CO, CN^- , alkenes, phenanthroline, bipyridyl, $\text{R}_3\text{P}, \text{R}_2\text{S}$, etc have vacant π - or d -orbital to form π - bond and hence form stable complexes with metals.

(iv) Dipole Moment of Ligands : For neutral ligands, higher the magnitude of dipole moment, higher will be the stability of the complex. For example, the order of stability of complexes of ligands having N as donor atom is :

ammonia > ethylamine > diethylamine > triethylamine

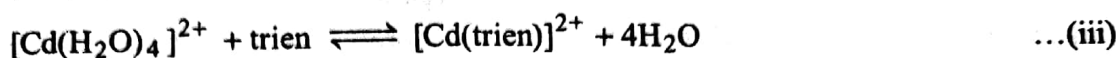
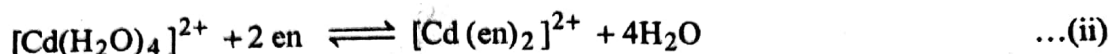
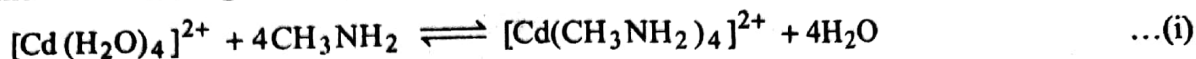
(3) The Chelate Effect

The polydentate ligands (with more than one donor atoms) have geometries such that they can form more than one coordinate bond to the same metal cation, such ligands are called chelating ligands. These ligands, generally are non-linear. The complex formed by the coordination of a polydentate ligand to a metal cation is called a chelate complex or a chelate.

Chelating ligands form more stable complexes than the analogous monodentate ligands (containing the same donor atom). It means that chelated complexes are more stable than their non-chelated analogs. This effect is called as chelate effect.

Let us consider the formation of complexes from hydrated cadmium ion, $[\text{Cd}(\text{H}_2\text{O})_4]^{2+}$ with methylamine (CH_3NH_2), ethylenediamine (en) and triethylenetetraamine (trien) ligands. Where methylamine (CH_3NH_2), ethylenediamine ($\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$) and triethylenetetraamine

(H₂N — CH₂ — CH₂ — NH — CH₂ — CH₂ — NH — CH₂ — CH₂ — NH₂) are monodentate, bidentate and tetradentate ligands respectively.



Structures of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$, $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ are shown in Figure 7.2.

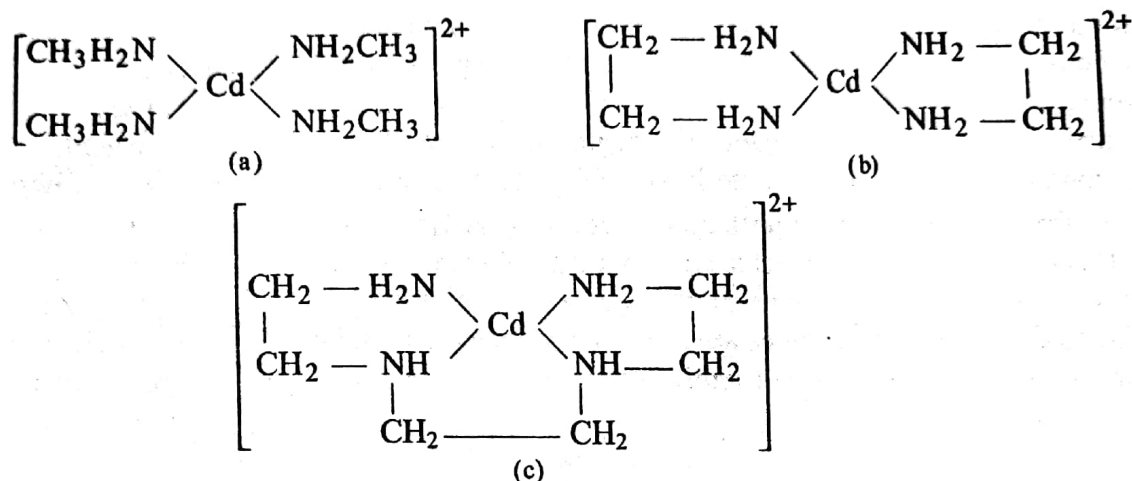
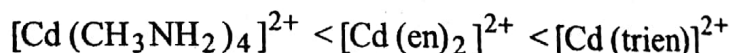


Figure 7.2 Structures of: (a) $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$, (b) $[\text{Cd}(\text{en})_2]^{2+}$, (c) $[\text{Cd}(\text{trien})]^{2+}$

$[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ is a non-chelated complex ion whereas $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$ are chelated complex ions. Thus, $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ is less stable than $[\text{Cd}(\text{en})_2]^{2+}$ and $[\text{Cd}(\text{trien})]^{2+}$. It is also observed that $[\text{Cd}(\text{trien})]^{2+}$ is more stable than $[\text{Cd}(\text{en})_2]^{2+}$ chelate ion. Therefore, order of stability of these complex ions is :



The above order of stability of complexes can be explained in two ways :

1. In reaction : (i) a non-chelated complex ion $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ is formed and there is no net change in the number of molecules and entropy of reaction. On the other hand, in reaction (ii) and (iii) there is an increase in number of molecules and hence there is an increase in entropy of reaction. Since increase in number of molecules in reaction (iii) is greater than that of reaction (ii) Therefore, the increase in entropy is greater in reaction (iii) than reaction (ii). Since bonding in all the above three reactions is same, (i.e., $\text{Cd}^{2+} - \text{N}$ bond) thus, ΔH° in all the three reactions is same and negative in sign.

Thermodynamically, the stability of a complex is expressed in terms of ΔG° . For a stable complex ΔG° is negative and large.

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

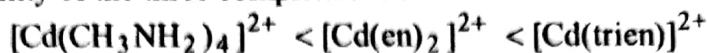
Since ΔH° in all the above three reactions is same and entropy increases from reaction (i) to (ii) to (iii) and thus, free energy change will be negative in the three reactions and increases from reaction (i) to (ii) to (iii).

A large negative value of ΔG° indicates the large value of stability constant (K)

because

$$\Delta G^\circ = -RT \ln K$$

Thus, order of stability of the three complexes is :



2. CH_3NH_2 , *en* and *trien* ligands are competing for the formation of complexes with Cd^{2+} ion in aqueous solution, the probability of either of them coordinating to the first site may be taken as equal. Once one end of *en* or *trien* is attached to Cd^{2+} ion, it is seen that the second amine group of *en* and *trien* is now greater in vicinity of Cd^{2+} ion than the second CH_3NH_2 ligand which is free to move randomly in the solution. Thus, probability of second amine group of *en* or *trien* to attach to Cd^{2+} ion is greater than that of monodentate ligand CH_3NH_2 . This indicates that formation constant is larger for the formation of chelates.

Further, the third and fourth donor atoms (amine groups) of *trien* are now greater in vicinity whereas the second *en* and the monodentate ligand CH_3NH_2 are moved freely and randomly in the solution. Thus, probability of third and fourth amine groups of *trien* to attach to Cd^{2+} ion is greater than that of *en* and CH_3NH_2 ligands. This indicates that stability of complex increases with the denticity of the ligand (denticity of a ligand is the number of donor atoms). In other words, we can say that the chelates in which one ligand form two or more rings are more stable than the complex in which one ligand form only one ring or no ring. The dependence of stability of chelates on the size of chelate ring is shown in Figure 7.3.

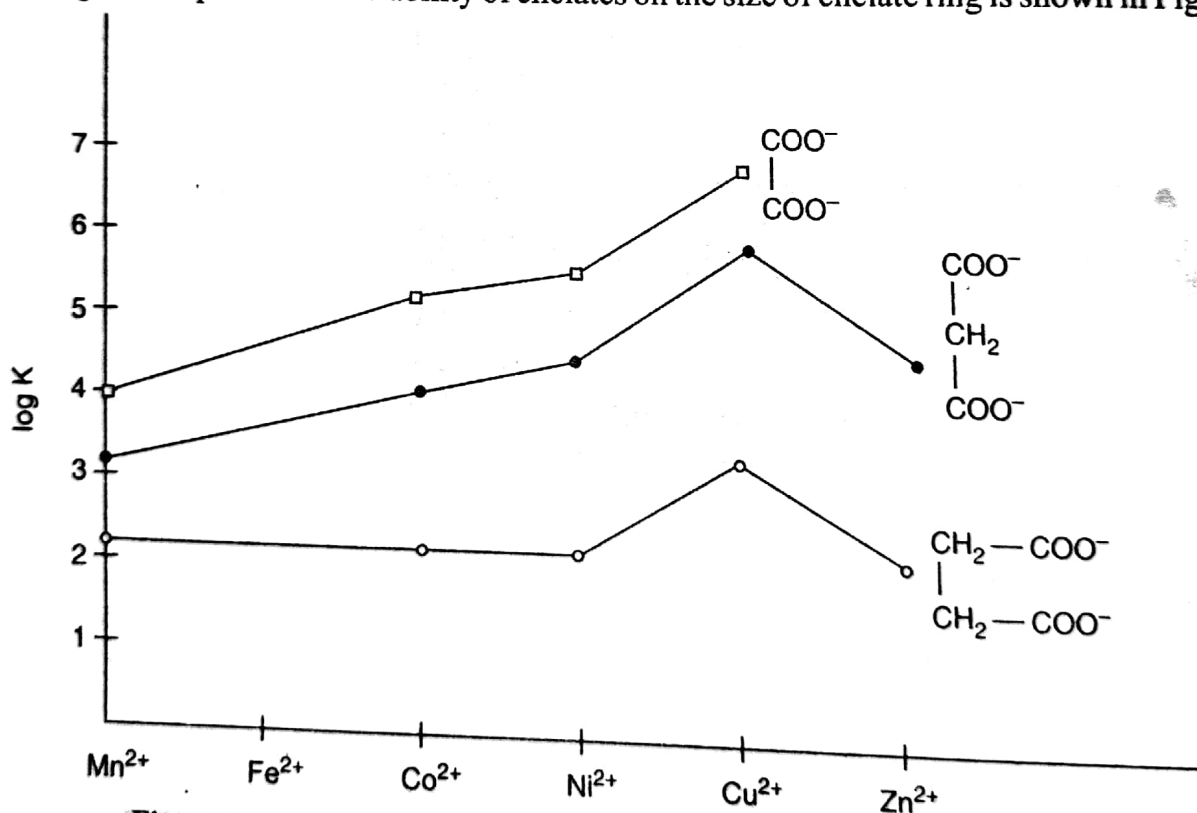


Figure 7.3 Dependence of complex stability on the size of the chelate ring.

In general, the chelates having five membered rings (including the metal) are more stable than six membered rings which are in turn more stable than the seven membered rings. Thus, the chelate effect weakens as the ring size increases. The chelate effect is usually most pronounced for 5 - and 6 - membered rings. Smaller rings generally involve excessive strain and become less stable. When the

chains and rings become much larger, the enhancement of local concentration (*i.e.*, vicinity of second donor atom of bidentate ligand) decreases and the resulting complex becomes less stable.

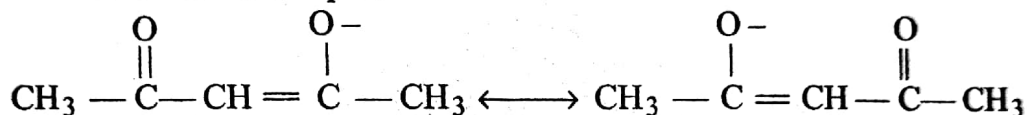
Furthermore, for the chelates formed by different bidentate ligands of same size with the same metal, the stability will be in the order, for example, oxalate < glycinate < ethylenediamine.

(4) Macrocyclic Effect

Macrocyclic ligands are large ring size compounds even without a metal atom present and these ligands have several donor atoms inside their rings to form coordinate bonds with a metal ion. Chlorophyll, heme and vitamin B₁₂ all contain tetradentate macrocyclic ligands. As stated earlier the chelating ligands form more stable complexes than analogous monodentate ligands and the macrocyclic ligands of appropriate size form more stable complexes than chelating ligands. There is a competition between a non-cyclic ligand and a macrocyclic ligand (a cyclic multi dentate ligand) having the same type of donor atoms and the complex formed by macrocyclic ligand will be more stable. This effect is called as macrocyclic effect. Chlorophyll, heme and vitamin B₁₂ all contain tetradentate (four N-donor atoms) macrocyclic ligands.

(5) Resonance Effect

Resonance enhances the stability of complexes. For example, acetylacetonate anion ligand shows resonance and form stable chelated complex.



As a result of resonance the M—O bonds are equal in length and strength.

(6) Steric Effect or Steric Hindrance

If a bulky group is either attached to donor atom or to the atom adjacent to donor atom, the metal-ligand bond becomes weak and the stability of the complex decreases. This effect is called steric effect. For examples :

(i) Ethylene diamine (H₂N—CH₂—CH₂—NH₂) and N—tetramethyl ethylenediamine (CH₃)₂N—CH₂—CH₂—N(CH₃)₂ both are bidentate ligands and form chelates with Ni²⁺ ion as shown in Figure 7.4.

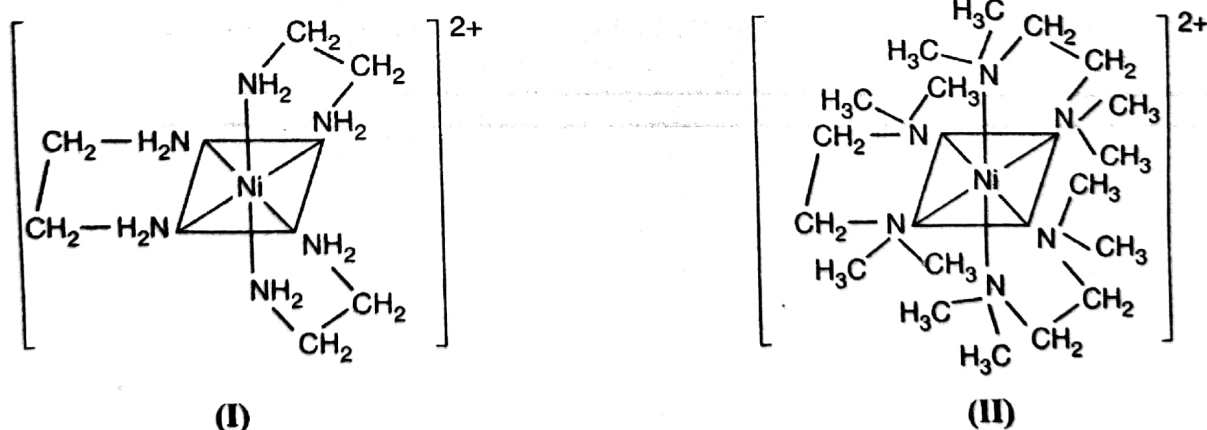


Figure 7.4

The complex (II) is less stable than (I) because in complex (II) the methyl groups attached to donor atoms create steric hindrance and decrease the stability of complex.

(ii) 8-hydroxy quinoline and 2-methyl-8-hydroxy quinoline both are bidentate ligands and form chelated complexes with Ni^{2+} ion as shown in Figure 7.5.

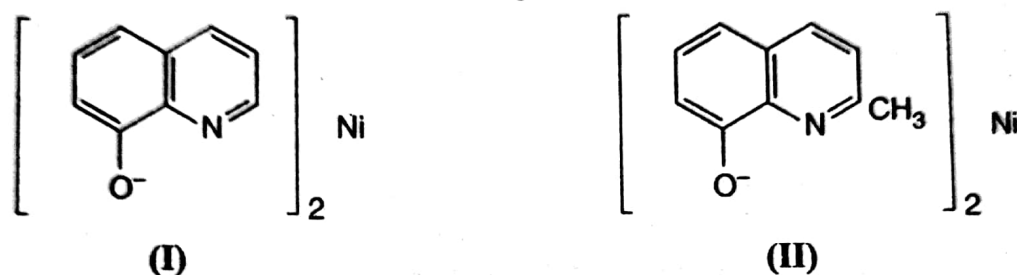


Figure 7.5

The complex (II) is less stable than complex (I) because in complex (II) a bulky group is attached to an atom adjacent to donor atom which causes a steric hindrance and lowers the stability of the complex.

The chelates containing chelating ligands with delocalized electronic structures are also stabilized by electronic effect in addition to entropy effect. The examples of such type of ligands are diimine ligands such as bipyridine and *o*-phenanthroline. These ligands stabilize the complexes because of their ability to act as σ -donors as well as π -acceptors. These ligands form π -bonds by overlapping their empty ring π^* orbitals with filled metal d -orbitals. An important example of such type of complexes is $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 7.6).

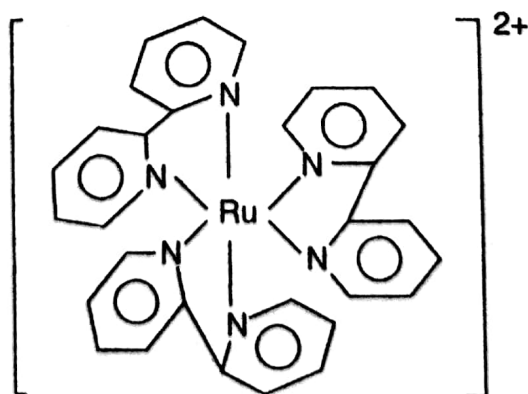


Figure 7.6