

FACTORS AFFECTING STABILITY OF COMPLEXES

- 1) Chelate Effect
- 1) Number of chelate rings and their sizes

1) CHELATE EFFECT

The extra stability conferred by the presence of a chelate ring in a metal complex is known as chelate effect.

The important factor for the stability of the chelate complex is the favourable entropy change, that is, there must be an increase in entropy because larger the number of the product species greater is the disorder. This is proved from the relation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ, \dots\dots\dots(i), \quad \text{where,}$$

ΔG° = Free energy change

ΔH° = Free enthalpy change

T = Absolute temperature

ΔS° = Entropy change

Stability constant (K) and ΔG° of a reaction are related as :

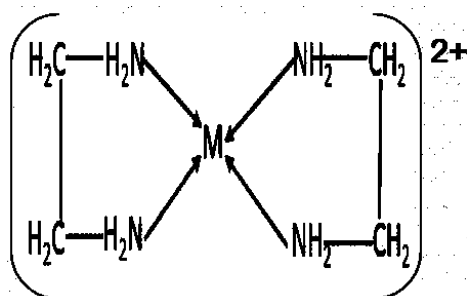
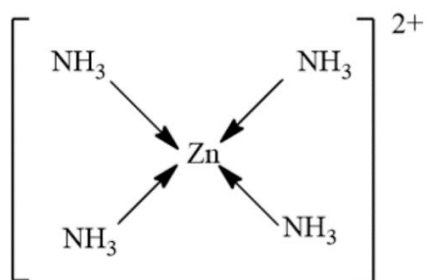
$$\Delta G^\circ = -RT \ln K \dots\dots\dots(ii)$$

Combining equations (i) and (ii) we get :

$$-RT \ln K = \Delta H^\circ - T \Delta S^\circ$$

ΔH remaining constant, for a given system, at a given temperature increase in the value of the ΔS results in negative or decrease in ΔG value and consequently greater will be the stability of the complex.

E.g. Complexes with chelate groups like (en) are more stable than those with unidentate ligands like NH_3 or H_2O because polydentate ligands form heterocyclic rings which are difficult to be ruptured.



Eg : Formation of the complexes $[\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$ from $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ reacted with monodentate NH_3 ligand and bidentate en ligands respectively:

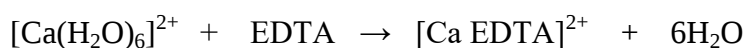


Reactant species = Product species $\rightarrow$ No increase in entropy



Increase in product species $\rightarrow$ Increase in entropy $\rightarrow$ Greater stability

Another example is that of alkaline earth metals which otherwise do not form stable complexes but do so with EDTA. This is made use of in the quantitative estimation of these ions. This is because EDTA being a strong hexadentate ligand can displace or release in solution as many as six water molecules (or any other monodentate ligand) from the original complex. This increases the entropy of the system tremendously which accounts for the stability.

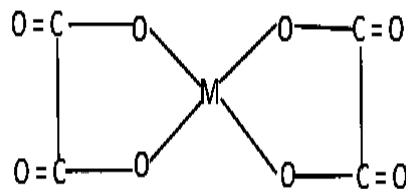
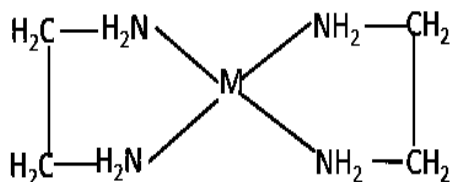


2) Number of chelate and their sizes

The stability of metal chelates depends upon the total number of chelate rings in the complex and the number of atoms in each ring. It is observed that larger the number of chelate rings greater is the stability of the complex. With respect to the number of atoms in each ring, chelate rings of greater stability are the five or six-membered ones because such rings cause less strain to the molecules.

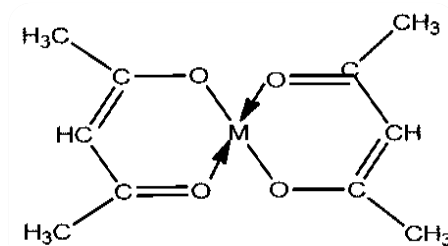
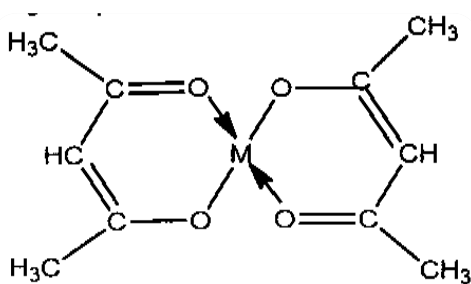
Chelate rings with four or more than six atoms are observed but are uncommon and unstable due to strain set up in the heterocyclic ring; and possibility of a long chain multidentate ligand bonding to more than one metal ion which may give rise to a polynuclear complex rather than a metal chelate.

In general, it has been observed that for saturated ligands, those that form five membered rings ,give the most stable products (en, oxalate).



However, unsaturated ligands also form stable complexes containing six membered rings because in such complexes the i.e. electron density is delocalised and spread over the ring which is thus stabilised by resonance.

E.g. Acetyl acetate complexes.



END