CHAPTER - I

INTRODUCTION

Mixed ligand complex chemistry has attained a considerable significance in the recent development of co-ordination chemistry. The mixed ligand complexes are formed by the binding of two or more types of ligands in the co-ordination sphere of a metal ion. The ligands may be unidentate or polydentate. If only two types of ligands are co-ordinated to the metal ion, a ternary complex is formed.

Considerable amount of experimental research has been done on ternary complexes, because the mixed ligand complexes play a predominent role as reaction intermediates in catalytical reactions and in analytical chemistry. The relevance of the study of ternary complexes is also because of their role as intermediates in the metalloenzyme substrate reactions in biological systems.[1-8] Thus the ternary complexes provide simpler models to understand more complicated biological reactions. It has also been found interesting to study the stability constants and structures of such ternary complexes in order to investigate the role of the nature of the metal ion and the two ligands on the stability of the ternary complex. Much of the work done in this field has been excellently reviewed by various workers.[9-16]

In a system containing one metal ion (M^{n+}) and two bidentate ligands, the stepwise constants usually decrease as the number of ligands on the complex increases. Thus K^{M}_{MA} is greater than $K^{MA}_{MA_2}$ for the following complexation equilibrium.

$$M + A \rightleftharpoons MA \qquad K^{M}_{MA}$$

$$MA + A \rightleftharpoons MA_2 \qquad K^{MA}_{MA_2}$$

This trend is expected on the basis of statistical, steric and electrostatic considerations.

In a system containing one metal ion (M^{n+}) and two different bidentate ligands AH_2 and LH_2, the formation of the mixed ligand complex $[MAL]$ is more favoured, on a statistical basis, than the formation of binary complexes $[MA_2]$ and $[ML_2]$.[17-19] It was suggested by Dewitt and Watters[17] and later by Kida[20] that the tendency of mixed ligand complex formation is determined by the reproportionation constant for the reaction,

$$MA_2 + ML_2 \rightleftharpoons 2MAL$$

$$K_{reprop} = \frac{[MAL]^2}{[MA_2]\,[ML_2]} \quad \ldots\ldots (1)$$

Under purely statistical conditions, when there is no interaction between MAL, MA_2 and ML_2, there is possibility of 50% formation of MAL, while binary complexes MA_2 and ML_2 are formed to the extent of 25% each.

$$K_{reprop} = \frac{[0.5]^2}{[0.25]\,[0.25]} = 4$$

and $\log K_{reprop} = 0.6$

This leads to the conclusion that log K_{reprop} will be 0.6 if only statistical factors were responsible for the formation constant.

Bonnett and Paris[21] have rearranged the equation (1) to show that,

$$\log K_{reprop} = 2\log K^{M}_{MAL} - \left(\log K^{M}_{MA_2} + \log K^{M}_{ML_2}\right)$$

$$= \left(\log K^{M}_{MAL} - \log K^{M}_{MA_2}\right) + \left(\log K^{M}_{MAL} - \log K^{M}_{ML_2}\right) \qquad \ldots\ldots(2)$$

However, the experimental values of K_{reprop} differ from the statistical expectation.[18,19] The value of K_{reprop} is either more or less than 4. It shows that factors other than statistical are operative. As proposed by Bjerrum[22] in the case of binary complexes, this may be because of the electrostatic effect or rest effect, the latter constituting all contributions to the formation constant which can not be explained either statistically or electrostatistically.

Another way of showing, that the formation of the mixed ligand complex is favoured, is to compare the stability of a binary complex (equation-3) with the corresponding ternary complex (equation-4).

$$M + L \rightleftharpoons [ML]$$

$$K^{M}_{ML} = \frac{[ML]}{[M]\,[L]} \qquad \ldots\ldots (3)$$

$$MA + L \rightleftharpoons MAL$$

$$K_{MAL}^{MA} = \frac{[MAL]}{[MA]\ [L]} \quad \ldots\ldots (4)$$

$$\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^{M} \quad \ldots\ldots (5)$$

The difference in stability, $\Delta \log K$, characterizes the tendency towards formation of mixed ligand complexes.[9]

From the statistical consideration, stepwise stability constants usually decrease as the number of ligands in the complex increases. The tendency of L to bind itself to $[MA]$ is less than its tendency to get bound with free metal ion M^{n+}. Hence, K_{MAL}^{MA} should be less than K_{ML}^{M} and should be comparable with $K_{ML_2}^{ML}$. However, with greater contribution from nonstatical factors, $\log K_{MAL}^{MA}$ has much greater value than $\log K_{ML_2}^{ML}$ and $\log K_{MAL}^{M} - \log K_{ML}^{M}$ becomes less negative.

Watter and Dewitt[18,19] observed that in the mixed ligand complex $[MAL]$, where A = ethylenediamine (en) and L = oxalate ion (ox), K_{MAL}^{MA} is lower than K_{ML}^{M}. However, the value of the mixed ligand formation constant K_{MAL}^{MA} is significantly larger than would be expected from statistical consideration. $K_{M.en.ox}^{M.en}$ has much greater value than $K_{M.ox_2}^{M.ox}$. This can be explained by the consideration of electrostatic factor which affects the enthalpy change and entropy factor.

During the formation of $[Cu(ox)]$, the incoming second ligand ox^{2-} is repelled by the existing ox^{2-}. In other words $[Cu(en)]^{2+}$ has more attraction for ox^{-2} than the neutral $[Cuox]$. The enthalpy change in the formation of $[Cu.en.ox]$ is more negative than that in the formation of $[Cu(ox)_2]^{2-}$. Further, molecule $[Cu.ox.en]$, being neutral, is less prone to solvation and therefore, the value of solvation entropy is more positive than that in the formation of negatively charged $[Cu(ox)_2]^{2-}$. Thus, both enthalpy and entropy factors favour the formation of $[Cuenox]$, resulting in a more negative value of ΔF and a higher value of K^{Cuen}_{Cuenox}. This leads to the conclusion that $K^{Cuen}_{Cuenox} > K^{Cuox}_{Cuox_2}$.

Schaap and Mcmaster[23] observed that the tendency of the neutral en molecule to combine as second ligand with $[Cu.ox]$ and to $[Cu(en)]^{2+}$ and the related formation constants are in agreement with the predictions based on statistical factor alone. This is because there is no additional effect involved in the formation of $[Cu.ox.en]$ or $[Cu(en)_2]$ as en is a neutral molecule.

Further, it has been observed that in ternary complexes of the type $[M.dipyridyl.L]$, the mixed ligand formation constant is much higher than expected from statiscal consideration.[9,24,25] K^{MA}_{MAL} is greater than $K^{ML}_{ML_2}$ and is close to K^{M}_{ML}. Thus, the value of $\Delta \log K$ is less negative.

An explanation was extended by Griesser and Sigel[26] and Bhattacharya and coworkers[27] simultaneously, attributing lower negative or positive values of Δ log K to the special behaviour of dipyridyl or similar tertiary amines. These ligands are bound to the metal ion by N ----→ M σ bond. Besides this, there is also M ---→ N π bond formation by the back donation of electrons from the metal dπ orbitals to the vacant delocalized pπ orbitals over the ligand.

The dπ - pπ interaction does not allow the concentration of electrons on the metal ions to increase significantly. In other words, the positive charge on the metal ion or its electronegativity in $[M\ (dipy)]^{2+}$ is almost same as in $[M\ (H_2O)_n]^{2+}$, and hence $K^{Mdipy}_{MdipyL} \approx K^{M}_{ML}$. The value of K^{Mdipy}_{MdipyL} is much higher than $K^{M}_{ML_2}$, as is expected from the effect of π bonding, electrostatic repulsion and charge neutralization in the formation of $[M.dipy.L]$ and $[ML_2]$.

It has been observed by Sigel[26,28-35] and coworkers and also by Bhattacharya and coworkers,[27,36-44] that $[MA]$ complexes, where A = heteroaromatic N-bases, show discriminating effect towards secondary ligand L co-ordinating through N-N, N-O^- or O^--O^-. In case of ternary complexes in which L co-ordinates through two nitrogen atoms, Δ log K is more negative. The value of Δ log K is less negative when secondary ligands co-ordinate through one nitrogen atom and one O^- as in aminoacid ions. When L co-ordinates through two O^- as in malonate or catecholate, Δ log K is still less negative. The effect is more significant in Cu(II) complex and the value of Δ log K in $[CuA\ O^-$-$O^-]$ complex is positive.

Sigel[26] has put forth two explanations for the positive values of Δ log K in [Cu.dipy.catecholate] complex. The distorted octahedral structure of $[Cu(H_2O)_6]^{2+}$, due to Jahn-Teller effect, is some what strongly distorted towards a square planar structure by the co-ordination of strongly binding 2,2'-dipyridyl, thus creating the right geometry for the co-ordination of secondary ligand in the square plane. This increases the stability of ternary complexes. Another explanation is in terms of the existence of a π interaction between metal dπ orbitals, π orbitals over dipyridyl and the delocalized π electron cloud over catecholate ion. This over all delocalization, i.e. a co-operative interaction is supposed to stabilize the ternary complex to a greater extent. The two factors in association make

$K^{Cudipy}_{CudipyCat} > K^{Cu}_{CuCat}$.

However, it has been shown by Bhattacharya and coworkers that interligand π interaction is not significant[45] and an alternate explanation has been extended in terms of electron repulsion. In the formation of binary complexes, there is electron repulsion between the metal dπ electrons and the additional lonepair of electrons present over co-ordinated O^--O^-. However, in the ternary complexes, due to M -----> A back donation of electron through π bonding, electron density is reduced over the metal ion in $[MA]^{2+}$. Hence, the repulsion between the metal dπ electrons and the additional lone pair of electrons over the secondary ligand (L) is less in the ternary complexes.

The effect of increase in the π accepting capacity of the tertiary amines on the stability of the mixed ligand complexes has also been reported.[44] It has been pointed out by Sigel[27] that in case of [CuAL] complexes where A = en, histamine or dipyridyl and L = pyrocatechol, the π system of A is important for the higher stability of the ternary complex. Histamine has only one aromatic N for the M ---> A back donation and hence the value of Δ log K is less positive in [Cu His O^{-}-O^{-}] and hence the value of Δ log K is less positive than [Cudipy O^{-}-O^{-}] system.

It has been observed by Bhattacharya and coworkers that the order of formation constants of mixed ligand complexes of the different tertiary diamines is as follows : 2(2'-pyridyl)benzimidazole > 2,2'-dipyridyl ≈ 1,10-phenanthroline > 2(2'-pyridyl)imidazoline.[45] The order is due to the extent of M -----> A π interaction. In case of bipyridyl or 1,10-phenanthroline the extent of Cu -----> A π interactions are almost same. However, in 2(2'-pyridyl)benzimidazole, the co-ordination is from pyridine N and one benzimidazole ring N and hence the Cu -----> A π interaction is greater, resulting in greater stabilization of ternary complexes. In case of 2(2'-pyridyl)imidazoline, the ligand co-ordinates from one pyridine N and one imidazoline ring N. The possibility of the π interaction is only with the pyridine ring. The imidazoline ring is saturated and has no delocalized π electron cloud and therefore results in less stable ternary complexes.

In a recent study[46] of the stability of the mixed ligand complexes of the type [MA Catecholate], where M = Co(II), Ni(II), Cu(II), or Zn(II) and A = bis (2-pyridyl)ketone (dpk), bis(2-pyridyl)amine (dpa), it has been shown that the Δ log K values decrease in the following order dpk > dpm > dpa. This has been explained to be due to the positive or negative inductive effect of the additional groups on the tertiary amines. The carbonyl group in dpk reduces the electron density on the ring due to its electron withdrawing effect. Contrary to this, the amino group in dpa increases the electron density on the ring due to the interaction of nitrogen lone pair with the π system of aromatic moiety. As a pyridyl moiety with a lower electron density can act as a better π acceptor of π back bonding electrons from the d orbital of a metal ion than a moiety with a higher electron density, the π accepting ability decreases in the order dpk > dpm > dpa, same as the order of stabilization of the ternary complexes with these tertiary amines.

The substituents over the secondary ligands, though not co-ordinated to the metal ion, also affect the stability of the ternary complex. It has been observed[26,30-35] that electron withdrawing substituents decrease the stability of the ternary complex and electron releasing substituents increase the stability of the ternary complexes.

It will be interesting to see the effect of the electron withdrawing groups over the primary ligand A. This should increase the π accepting tendency. In order to further investigate the effect of the substitution on the two ligands in the present thesis, the mixed ligand complexes [MAL] where M = Cu(II) or Ni(II), A = 5-nitro-1,10-phenanthroline (A^1), 2,2'-dipyridylketone (dpk) (A^2) or 2,2'-dipyridylamine (dpa) (A^3) and L = various N-N, $N-O^-$ and O^--O^- co-ordinating ligands have been studied.

In the second chapter of the thesis the SCOGS programme has been used for computer calculation of the formation constant of complexes [MAL] where M = Cu(II), Ni(II), A = A^1 and L = ethylenediamine (L^1), 1,2-propylenediamine (L^2), N-methylethylenediamine (L^4), glycine (L^6) α-alanine (L^7) β-alanine (L^8) or malonate (L^9). It is observed that Δ log K is more positive or less negative in the following order for the complexes with L = $N-N < N-O^- < O^--O^-$. The effect is more pronounced when the co-ordinating atoms are on the aromatic rings. This has been explained in terms of release of electron repulsion in the ternary complexes. In cases of catechol derivatives, it has been observed that the ternary complex stability is also dependent on the effect of substitution on the ring.

The third chapter presents an account of [MAL] complexes where M = Cu(II), Ni(II), A = dpk or dpa and L = same ligands as in the second chapter. Dpk is known to co-ordinate with Cu(II) at low pH from N-N end and at higher pH from $N-O^-$ end by the dissociation of one -OH of the diol form. It has, however, been observed that in cases of the ternary complexes [M dpk L] where L = catechol and its derivatives, dpk co-ordinates from N-N end over the whole pH range. This is because $O^{-}-O^{-}$ co-ordinating ligand prefer N-N co-ordination of the tertiary amine. In cases of other ligands N-N co-ordination of dpk is only upto pH 5 in ternary system also. It has been observed that [CudpkL] complexes are more stable than [MA^1L] and [MA^3L]. This has been attributed to the existence of co-ordinating dpk in two equilibrium form keto, and gem-diol.

The chapter IV presents an account of the ternary complexes [MAL] where M = Cu(II), Ni(II), A = A^1, A^2, A^3 and L = histidine or histamine. As in the binary complexes in ternary complex [CuA histidine] also, histidine combine from amino acid end in the lower pH range and from histamine end in the higher pH range. In [NiAhistidine] complexes, however, co-ordination is from histamine end over the whole pH range. It has been shown that in [MAL] complexes, histamine or histamine like co-ordinated histidine are occupying one equatorial and one axial position.

It has been observed that the unco-ordinated hydrophobic phenyl or substituted phenyl group of the aromatic amino acid prefer a position near to the metal ion. In the IVB chapter the mixed ligand complexes [MAL] where M = Cu(II), Ni(II), A = A^1, A^2, A^3 and L = 2,3-

dihydroxyphenylalanine, tyrosine, phenylalanine, tryptophan have been studied. The special effect of the free aromatic ring results in astatistical stabilization of these ternary complexes.

The nature of the interligand stacking interaction in the ternary complex has been investigated in the Vth chapter by studying ternary complexes of the type [MA(ATP)] in aqueous-dioxan solvent. The stacking interaction between A and the adenosine base of ATP is found to be solvent dependent.

Chapter VIth deals with the isolation of the ternary complexes in solid state and their characterization by elemental analysis and spectral and magnetic studies.