****

****

CHAPTER I

INTRODUCTION

****

****

The complexes, in which metal ion has two or more types of ligands in its coordination sphere, are termed mixed-ligand or ternary complexes. The ligands may be unidentate or polydentate. In the latter case the complex is known as heterochelate.

There has been a growing interest in the study of the ternary complexes, because of the predominant role that they play as reaction intermediates in catalytic reactions and in analytical chemistry. Further, the biological reactions have been shown to proceed through the formation of ternary complexes between the metalloenzyme and the substrate.[1-8] Thus, the ternary complexes provide simpler models to understand more complicated biological reactions. It has, therefore, been found worthwhile to study the stability constants and structures of various ternary complexes to investigate the role of the metal ion and the nature of the two ligands in determining the stability of the ternary complex. The outcome of such studies have been excellently reviewed by various workers.[9-16]

In a solution containing a metal ion and two ligands A and L, 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 :

$$MA_2 + ML_2 \rightleftharpoons 2MAL \; ; \quad K_{reprop} = \frac{[MAL]^2}{[MA_2]\,[ML_2]} \qquad \text{------(1)}$$

K_{reprop} should have a value 4 from purely statistical consideration, presuming no interaction between $[MAL]$, $[MA_2]$ and $[ML_2]$. This is because $[MAL]$ is formed by two paths MA + L and ML + A, whereas $[MA_2]$ and $[ML_2]$ are formed by one path only i.e. MA + A and ML + L, respectively. The concentration of $[MAL]$ is, therefore, double that of $[MA_2]$ and $[ML_2]$.

$$K_{reprop} = \frac{[0.50]^2}{[0.25]\,[0.25]} = 4 \text{ and } \log K_{reprop} = 0.60$$

The equation (1) for log K_{reprop} can also be expanded as follows :

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

$$= \left(\log K^{MA}_{MAL} - \log K^{ML}_{ML_2}\right) + \left(\log K^{ML}_{MLA} - \log K^{MA}_{MA_2}\right)$$

$$\text{------(2)}$$

However, it is generally observed that the value of K_{reprop} is either more or less than 4, showing that factors other than statistical are operative.

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

$$M + L \rightleftharpoons ML \; ; \quad K^{M}_{ML} = \frac{[ML]}{[M][L]} \qquad \text{------}(3)$$

$$MA + L \rightleftharpoons MAL \; ; \quad K^{MA}_{MAL} = \frac{[MAL]}{[MA][L]} \qquad \text{------}(4)$$

$$\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML} \qquad \text{------}(5)$$

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

Since more coordination positions are available for bonding of the first ligand to a given multivalent metal ion than for the second ligand, the stability constant for the formation of 1 : 1 complex is usually greater than that for the 1 : 2 complex and one would expect to observe negative values for $\Delta \log K$. However, the values of $\Delta \log K$ for ternary complexes are also generally higher or lower than expected from statistical considerations alone.

As proposed by Bjerrum[21] in case of binary complexes, this may be because of the electrostatic effect or rest effect, the latter constituting all contribution to the formation constant which can not be explained either statistically or electrostatically.

Watters and Dewitt[18,19] observed that in the mixed-ligand complex $[MAL]$, where A = ethylenediamine (en) and L = oxalate ion (ox), K^{MA}_{MAL} is lower than K^{M}_{ML}. This is expected because en molecule has greater bonding tendency than water molecule and will increase the concentration of electrons around the metal ions. Therefore, the tendency of the oxalato ion to get bound with $[M.en]^{2+}$ is less than its tendency to get bound with aquated metal ion.

It has, however, been observed[18,19] that the mixed-ligand formation constant K^{MA}_{MAL} is significantly larger than would be expected from statistical considerations. $K^{M.en}_{M.en.ox}$ has much higher value than $K^{M.ox}_{M.ox_2}$. This can be explained by the consideration of electrostatic factor which affects the enthalpy change and also the entropy factor. In the formation of $[Cu.ox_2]^{2-}$, from $[Cu.ox]$, the incoming second ox^{2-} ion is repelled by the existing ox^{2-}. In other words, $[Cu.en]^{2+}$ has more attraction for ox^{2-} than that of neutral $[Cu.ox]$. The enthalpy change in the formation of $[Cu.en.ox]$ is more negative than in the formation of $[Cu.ox_2]^{2-}$. Further, since the molecule $[Cu.ox.en]$ is neutral, there is less solvation of the molecule and, therefore, the solvation entropy is more positive than in the formation of negatively charged $[Cu.ox_2]^{2-}$. Thus, both enthalpy and entropy factors favour the formation of [Cu.en.ox], resulting in more negative ΔF value and a higher value of $K^{Cu.en}_{Cu.en.ox}$. This explains why $K^{Cu.en}_{Cu.en.ox} > K^{Cu.ox}_{Cu.ox_2}$.

Schaap and McMaster[22] observed the tendency of the neutral en molecule to combine as second ligand with [Cu.ox] and to $[Cu.en]^{2+}$ and the formation constants obtained were in agreement with the prediction based on statistical factor alone. This is because there is no additional electrostatic repulsion or charge neutralisation effect involved in the formation of [Cu.ox.en] or $[Cu.en_2]$, as en is a neutral molecule.

However, 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 statistical considerations.[9,23,24] K^{MA}_{MAL} is greater than $K^{ML}_{ML_2}$ and is close to K^{M}_{ML}. Thus, the value of Δlog K is less negative.

An explanation was extended by Griesser and Sigel[25] and Chidambaram and Bhattacharya,[26] almost simultaneously, attributing lower negative or positive values of Δlog K to the special behaviour of 2,2'-dipyridyl or similar tertiary amines. These ligands are bound to the metal ion by $N \longrightarrow M$ σ bond. Besides this, there is also $M \longrightarrow N$ π bond formation by the back donation of electrons from the metal dπ orbitals to the vacant delocalized pπ

orbitals of the ligand. This $d\pi - p\pi$ interaction does not allow the concentration of electrons on the metal ion to increase significantly. In other words, the electronegativity of the metal ion in [M.dipyridyl] is almost same as in $[M(H_2O)_x]$ and hence, the tendency of L to coordinate with [M.dipyridyl] is comparable with $[M(H_2O)_x]$ and $K^{M.dipyridyl}_{M.dipyridyl.L} \approx K^{M}_{M.L}$.

Further, it has been observed by Sigel and coworkers[25,27-33] and also by Bhattacharya and coworkers[26,34-42] that the values of $\Delta \log K$ are more negative when in the secondary ligand (L) the coordination is from two nitrogen atoms (aliphatic diamines). It is less negative when the secondary ligand coordinates through one oxygen and one nitrogen atoms as in amino acid ions or through two oxygen atoms, as in the case of catecholate, oxalate or salicylate ions. It was also observed that in case of complexes of the type [CuAL] where A = dipyridyl or o-phenanthroline and L = ligands coordinating through two O^-, $\Delta \log K$ is positive.

Sigel[25] has put forth two explanations for the positive value of $\Delta \log K$ in [Cu.dipyridyl.catecholate] complex. The distorted octahedron of $[Cu(H_2O)_6]^{2+}$, due to Jahn Teller effect, is some what more strongly distorted towards a square planar structure by the coordination of strongly binding 2,2'-dipyridyl, thus creating the right geometry for the coordination of the secondary ligand in the square plane. This increases the stability of the 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 overall delocalization, i.e. a cooperative interaction, will stabilize the ternary complex to a greater extent. The two factors in association make $K^{Cu.dipy}_{Cu.dipy.cat} > K^{Cu}_{Cu.cat}$.

The effect of π accepting capacity of the different tertiary amines on increasing the stability of the mixed-ligand complexes has been reported.[43,44] In a detailed solution study[44] of the stability of mixed-ligand complexes of the type [M.A.catecholate], where M = Co(II), Ni(II), Cu(II) or Zn(II) and A = bis(2-pyridyl)ketone (dpk), bis(2-pyridyl)-methane (dpm) or bis(2-pyridyl)amine (dpa), it has been shown that the $\Delta \log K$ values decrease in the following order dpk > dpm > dpa. This has been explained to be due to the positive or negative inductive effects of the additional groups on the tertiary amine. 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 acceptor of π back bonding electrons from a d metal ion than a moiety with a higher electron density, π acceptor ability decreases in the order dpk $\rangle$ dpm $\rangle$ dpa, same as the order of stabilization of the ternary complexes with these tertiary amines.

By an analogy with the stabilization of ternary complexes with tertiary diamines, Sigel[12] has explained the greater stability of mixed-ligand complexes in biochemical systems involving imidazole. However, in a recent publication, Abbott and coworkers[45] have shown that ternary complexes containing imidazole do not exhibit as much astatisticality, as those containing tertiary diamines, since imidazole is a monodentate ligand. The lack of planarity, between the two imidazole groups occupying cis positions on Cu(II), does not allow sufficient π bonding between the d_{xy} orbital of metal ion with imidazole resulting in negative $\Delta \log K$ values in [Cu.imidazole.L] complexes (L = glycine, aspartic acid, dipyridyl, malonic acid, 5-sulfosalicylic acid, histamine).

However, it has been pointed out by Sigel[15] in a recent communication that a negative $\Delta \log K$ does not exclude a stability increasing influence of imidazole, and a less negative value of $\Delta \log K$ indicates that the ternary complexes containing imidazole are also stabilized. Although not positive, $\Delta \log K$ is not as negative as expected from statistical considerations. However, it can be seen that the monodentate imidazole does not bring as much stabilization to the ternary complex as the bidentate tertiary amines like dipyridyl. It is, therefore, interesting to study mixed-ligand complexes involving bidentate tertiary amines with a combination of imidazole and pyridyl rings and to see the effect on the stability of the ternary complex. In the present work the primary ligands selected are 2,2'-dipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline.

The observation that there is an increase in stabilization of [M.tertiary amine.L] complexes, where L coordinates through two oxygen atoms has led the workers to the study of [M.tertiary amine. β-diketonate] complexes. β-diketones are strongly chelating ligands forming pseudoaromatic chelate rings with the metal ion. There has been a controversy[46] about the extent of π interaction between the metal $d\pi$ electrons and the $p\pi$ electrons of the coordinating oxygen atoms and the carbon chain, and its contribution to the stability of the β-diketonate complexes. However, there are strong evidences[47-54] to show that the metal $d\pi$ orbitals interact with the π molecular orbitals over the enolate ion, thus forming bonding and antibonding π molecular orbitals. The electrons present in the bonding molecular orbitals are delocalized over the whole chelate ring. This accounts for the stability of the ring and the shortening and equality of the pair of bonds (distance measured as 1.39 A^{o}, thus being intermediate between single and double bond distances[50]).

Orgel and coworkers[51] in their NMR studies of [VO(III).acetylacetonato] complex observed a lowering in the chemical shifts for the ring protons. This contact shift has been attributed to the delocalization of unpaired π electron density of the metal electrons over the ligand atoms thus bringing in a shielding effect. Collman and coworkers[52-54] have indicated the presence of ring current in β-diketonate chelate ring on the basis of studies on mixed β-diketonate complexes of Co(III) and Rh(III) by PMR spectroscopy.

The chemical evidences[54-60] also support pseudo-aromaticity in the [M. β-diketonato] complexes. The proton on the chelate ring is very labile and can be replaced by several groups under electrophilic substitution reactions viz. halogenation, nitration, formylation etc. These studies unambiguously show that chemically speaking the chelate ring is aromatic.

Orthohydroxy aromatic aldehydes and ketones also coordinate through two oxygen atoms with a possible π interaction between metal dπ orbitals and the ligand atom orbitals.[42,61] It has been observed in our laboratory that in the complexes of the type $[Cu.dipy.L]^+$, where L = β-diketonates[48] or anions of o-hydroxy aromatic aldehyde and ketones[42,61] Δ log K is zero or positive. This naturally leads one to think of stabilization due to inter-ligand π interaction.

Since in all these systems the secondary ligands coordinate through oxygen atoms involving π interaction, it has led the workers to believe that oxygen coordination is a must for greater stability of mixed-ligand complex. This has also given a support to the concept of inter-ligand π interaction stabilizing the ternary complex. The existence of a cooperative π interaction between the two ligands in [Cu(II).dipy.cat] complex has been further supported by Sigel and coworkers,[62] through ESR studies. However, they feel that it is not wise to rely heavily on the ESR parameters.

However, Δ log K has been observed to be positive in the complexes [Cu.dipy.L], where L = malonate[29a] with no π electrons and to be zero where L = a ligand coordinating through oxygen and nitrogen atoms.[42] Hence inter-ligand π interaction may not be the factor responsible for the additional stabilization of the ternary complexes. With the aim of investigating this fact, work is going on in our laboratory on the complexes of the type [CuAL], where A = 2,2'-dipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)-benzimidazole or 2-(2'-pyridyl)imidazoline and L = ligands with different substitutions over them.

β-ketoanilides are similar to β-diketones in the fact that they coordinate through two oxygen atoms with a possible pseudoaromatic chelate ring formation. The lone pair of electrons present over the nitrogen atom of the anilide group can influence the nature of bonding between the metal and the ligand. In the present study, therefore, the secondary ligands selected are acetoacetanilide, acetoacet-o-toluidide, acetoacet-o-anisidide and benzoatoacetanilide. Studies have also been carried out on ternary complexes of the type $[CuAL]^+$ where L = anion of salicylamide, salicylanilide, 5-bromosalicylamide and 5-bromosalicylanilide. The presence of an aromatic ring in the salicylamide derivatives and the substitution over the aromatic ring will throw some light on how the stability of the mixed-ligand complexes is affected by the electron density on the secondary ligand L and how the substituent groups not directly linked to the metal ion affect the formation constant values.

In the succeeding chapters the studies of the formation constants of the binary and ternary complexes, isolation of the solid complexes and their magnetic and spectral properties, have been presented.