CHAPTER 1

Introduction

1.1 Introduction.

Recent developments in coordination chemistry are mainly directed towards the study of metal complexes relevant to the function of transition metal ions in catalytic processes, metalloenzyme reactions and many other biochemical processes[1-4]. Under biological and environmental conditions, multiligand multi metal ion equilibria[5] dominate strongly and the simplest of these species, ternary complex [6], consists of a metal and two different ligands, other than the solvent. Such ternary complexes are important in metal ion catalyzed reactions[7-11] which involve catalyst-metal-substrate complexes[12]. They appear in biological fluids [13], create specific structures [14-16] and manifest themselves as enzyme metal ion-substrate complexes [17-30]. Ternary complexes of biochemically important ligands are being considered as models for biochemical processes. However, biomolecules mainly involve N,O and S as the coordinating atoms and have a variety of active metal ion sites showing keen specificity and selectivity. This invokes deeper study of the factors related with the stability of the ternary complexes.

Necessity of such studies has been strongly suggested and by some other observations with enzymes models. It has been observed [31-33] that transition metal catalyzed decarboxylation of dimethyl oxaloacetate could be enhanced by the addition of a π acid ligand such as o - phenanthroline while imonic nitrogen base ligands such as 8 - hydroxy quinoline - 5 sulfonate reduces the catalytic activity of the metal ions [31-33]. Similar effects have been observed with oxaloacetic acid[34-36] and 3 - oxoglutaric acid [37-38]. These observations not only suggest that oxaloacetate decarboxylase forms a mixed ligand complex[39] while decarboxylating the oxaloacetate but also imply the dependence of its activity on the nature of the ligand.

The evolution of the understanding of the astatistical factors influencing the stability of ternary complexes[4, 40–42] has been through several observations. Electrostatic and thermodynamic factors have been found to be invloved in the stabilization of [Cu (en) (OX)] 43–45 compared to [Cu $(OX)_2$] or [Cu $(en)_2$]. Steric factors also have been found to affect the formation of mixed ligand complexes of substituted aliphatic diamines[46–48] and thermodynamics of the formation of the ternary Cu (II) complexes with substituted α- amino-iso-butyric acid and salicylate anion [49] . The steric effect during the formation of mixed ligand complexes of copper with 2,2' - bipyridyl or 1,10 - phenanthroline as one of the ligands has been discussed by Martin and coworkers [40].

It has been observed that the sizes of the chelate rings also affect the formation of the mixed ligand complexes(Table 1.1). Sigel and coworkers [51,52] formulated the following tentative rule for the order of formation constants in ternary complexes containing two chelate rings : one five membered and one six membered ring > two six membered rings > two five membered rings.

π - bonding ligands like aromatic tertiary diimines have marked influence on the stability and reactivity of the ternary complexes and has been a subject of four recent reviews[55–58] . Ternary complexes involving 2,2' - bipyridine and 1,10 - phenanthroline and hydroxy derivatives of benzene or naphthalenes [59], γ- picoline, methyl-α - picolyl sulphide and 2 - acetyl - 3 - hydroxy thiophene[6] have been observed to be much more stable than expected because of statistical reasons (Appendix I). Similar observations have been made in the complexes of the type MAL where A = bipy or phen and L = ethylene diamine, glycine, malonic acid and pyrocatechol[60] . This was almost simultaneously, explained by Griesser and Sigel[60]and Bhattacharya and coworkers[61], attributing greater stability of these complexes to the synergic stabilization of $N \rightarrow M$ σ bond and $M \rightarrow N$ π bond formation.

Table 1.1 Effect of Ring size on the stability of ternary complexes

Values of $\Delta \log K$ and log x of some ternary Cu^{2+} complexes containing two-five membered or two six membered chelate rings or a five and a six membered chelate ring (I=0.1; 25^{O})

	L^1	L^2	size of the chelate ring	$\Delta \log K$	log x	Ref.
1.	1,3 - pn	mal	6,6	- 1.30	2.55	52
2.	1,3 - pn	β - al	6,6	- 1.18	1.70	52
3.	1,3 - pn	ox	6,5	- 0.35	3.14	52
4.	1,3 - pn	gly	6,5	- 0.79	2.37	52
5.	1,3 - pn	1,2 - pn	6,5	- 1.46	1.13	52
6.	1,3 - pn	en	6,5	- 1.49	1.00	52
7.	en	β - al	5,6	- 0.93	0.88	52
8.	en	mal	5,6	- 0.76	2.31	52
9.	en	1,2 - pn	5,5	- 1.26	0.31	52
10.	en	gly	5,5	- 0.80	1.03	52
11.	en	ox	5,5	- 0.79	0.94	52
12.	bipy	1,3 - pn	5,6	- 2.47	0.06	51
13.	bipy	β - al	5,6	- 0.59	2.68	51
14.	bipy	mal	5,6	+ 0.27	5.49	60
15.	bipy	en	5,5	- 1.29	1.10	60
16.	bipy	gly	5,5	- 0.35	3.05	60
17.	bipy	ox	5,5	+ 0.7	4.9	51

en = ethylene diamine ; 1,2 - pn = 1,2 - propylene diamine; 1,3 - pn = 1,3 - propylene diamine ; gly = glycinate ; β-al = β-alaninate ; ox = oxalate ; mal = malonate and bipy = 2,2' - bipyridyl.

Another interesting observation has been made by Sigel and coworkers [60-62] and Bhattacharya and coworkers [63,64] about the selective binding of ligands in ternary metal complexes. They have observed that the metal bound to a heteroaromatic N base (tertiary diimine), like 2,2' - bipyridine, discriminates between the ligands containing N-N, $\bar{O}$-N and $\bar{O}$-$\bar{O}$ coordinating sites (Table 1.2). Further it has been shown that the ternary complexes involving tertiary diimines and $\bar{O}$-$\bar{O}$ coordinating ligand are most stabilized[60].

Varying geometries and electron densities at the coordinating sites can bring in difference in the stabilities of the respective complexes. These changes in the geometry or electron density are invariably related with the groups or substituents present on the ligand molecule. Recently, it has been shown that the electrochemical properties of some complexes containing ligands derived from salicylaldehyde are strongly influenced by the substituents present on the ligand [65-67]. The non - interacting groups present over the ligand have also been observed to affect the catalytic activity of the complexes and the catalyst decomposition [68]. From this point of view systematic study of the effect of substituents on the ligand on stability and behaviour of the complexes becomes important. Such kind of studies have been reported with series of aliphatic and aromatic diamines [46, 50, 69, 70] tertiary diimines [63, 64, 71-78], amino acids [79], catechol derivatives [76, 77, 80] with non π bonding $\bar{O}$-$\bar{O}$ coordinating sites and several other ligands. These will be briefly reviewed in the beginning of the following chapter.

A part of the current activity is devoted to the study of non-covalent interaction[81, 82] in ternary complexes as a source of ligand discrimination that leads to specificity or selectivity of ternary complex formation. The intramolecular ligand-ligand interactions can be classified as :

(i) Steric hindrance due to bulky side groups ;

(ii) electrostatic interactions and hydrogen bonds between charged and/or polar side groups ;

(iii) hydrophobic interactions between aromatic and/or aliphatic side chains ; and

Table 1.2 The discriminating qualities of Cu (tertiary diimine) $^{2+}$

Ligand A	Ligand L	Coordinating sites.	ΔLog K	Log x	Ref.
bipy	pyr	O - O	+ 0.43	6.15	60
			+ 0.84		63
	OAP	O - N	- 0.31	3.14	62
			- 0.63		63
	OPD	N - N	- 1.18	1.06	62,63
phen	pyr	O - O	+ 0.67		63
	OAP	O - N	- 0.66		63
	OPD	N - N	- 1.22		63
N - phen	pyr	O - O	+ 0.94		
	OAP	O - N	+ 0.63		
	OPD	N - N	- 0.36		
pybzim	pyr	O - O	+ 1.32		63
	OAP	O - N	+ 0.05		63
	OPD	N - N	- 0.75		63
pyim	pyr	O - O	- 0.47		63
	OAP	O - N	- 0.97		63
	OPD	N - N	- 1.37		63
bipy	ox	O - O	+ 0.7	4.9	51
	gly	O - N	- 0.35	3.05	60
	en	N - N	- 1.29	1.10	60
en	ox	O - O	- 0.79	0.94	52
	gly	O - N	- 0.80	1.03	52
	N - Me en	N - N	- 1.26	0.31	52

bipy = 2,2' - bipyridyl , phen = 1, 10 - phenanthroline, pybzim = 2 - (2' - pyridyl) benzimidazole, pyim = 2 - (2' - pyridyl) imidazoline, pyr = pyrocatecholate, OAP = O - aminophenolate , OPD = O - phenylene diamine, ox - oxalate, gly=glycinate, en = ethylene diamine , N - Meen = N - methyl ethylene diamine.

(iv) metal ion mediated electrostatic interactions between coordinated π donor and π acceptors.

Initial support of ligand-ligand interactions is furnished by facile synthesis of ternary complexes involving two amino acid ligands, one with negatively charged side chain and one with free monoprotonated basic site or polar side chains which can lead to electrostatic interactions between the two ligands [83-88]. Such complexes have no marked influence of the solvent dielectric constant on their stability [89], where as the hydrophobic [90-93] and aromatic ring stacking [94] interactions are solvent depedant [93, 95-97]. There is also evidence that both aromatic and aliphatic hydrocarbon portions of ligands tend to occupy space near the metal ion rather than out in solution [98-110]. Some authors have referred this tendancy as ligand — metal interaction [100] though a direct favourable hydrocarbon metal interaction by less than van der waals distances has been shown only for aromatic rings with metal ions in several crystal structure determinations. Extensive work has been reported on the non covalent interactions in ternary complexes consisting of biologically important amino acids with side groups and nucleotides [105, 111-120]. However, there exist controversial views [93, 95-97, 109, 112] about the contribution of the kinds of the above interactions to the stability of the complexes and no definite conclusion can be drawn on the basis of the studies reported so far.

Although, extensive comparative studies have been made using potentiometric techniques for the determination of the formation constants and various computer programs have been developed (Table 1.3) several other methods have also been reported for the study of complexes. These include various electrometric and spectroscopic techniques. Polarographic and cyclic voltammetric studies provide information about the ease of reduction/oxidation of a metal ion under the influence of the ligand field and hence about the effective electron density over the metal ion [45, 134-137]. The d-d transistions in the metal ion and charge transfer bands resulting from electronic transistions between the metal ion and the ligand in the electronic absorption spectra of the complexes provide useful

Table 1.3 Summary of some published non-linear least-squares programs for calculation of formation constants.

Program	Data treated	Sum of squared residuals minimized	Iterative method used	Ref.
GAUSS	Potentiometric	Analytical hydrogen ion concentration	Gauss-Newton	121–123
LETAGROP	Potentiometric	Several ($\bar{n}$, analytical hydrogen ion concentration e.m.f.)	Pitmapping (Newton - Raphson)	124–127
SCOSUS	Potentiometric	Analytical hydrogen ion concentration		128
COMICS	Potentiometric	Analytical concentrations	Newton - Raphson.	129
SCOGS	Potentiometric	Volume of titrant	Gauss-Newton	130
LEAST	Potentiometric	Analytical concentrations	Gauss-Newton or Newton - Raphson.	
LEASK	Potentiometric	Analytical concentrations	Search	
STEW	Potentiometric	Analytical hydrogen ion concentration	Fletcher - powell.	
MINIQUAD	potentiometric	Analytical concentrations	Gauss-Newton	131,132
SUPERQUAD	Potentiometric	Analytical concentrations		133
SQUAD	Spectrophotometric.	Absorbance	Gauss-Newton	
DALSFEK	Spectrophotometric, potentiometric.	Absorbance, e.m.f.	Marquardt	

information about the M-L interaction[138]. Non-linear least-squares programs like SQUAD and DALSFEK have also been published for the treatment of spectrophotometric data to get formation constants. Much information about the nature of M-L binding can be obtained from ESR[139-142] and NMR[115, 116] measurements. Equilibrium constants of mixed ligand complexes can also be obtained using ESR [143].

Various methods have been used for the study of the complexes in solid state. Diffuse reflectance electronic spectral, I.R. Spectral and magnetic studies help in assigning structure to the complex. X-ray crystallography is considered to be the most powerful technique for structure determination. EXAFS is also being used to provide precise data on the metal coordination sphere and bond distances in complexes of unknown crystal structure[144]. EXAFS can distinguish very small changes in the coordination sphere of the metal ion and hence allows comparative studies[145].

Since the beginning of the coordination chemistry, increasing attention is being paid to the chemistry of copper complexes. This is because of the special properties[146] associated with copper. Number of reviews pertaining to copper (II) complexes have appeared in the last decade[147-150]. Also the interest in copper coordination chemistry is because of the biochemistry of copper [146, 147], [151-154], which has evolved rapidly with the development of various instrumental techniques. ESR has been one of the most versatile techniques used for the detection of biological copper and the study of the nature of the active sites [29, 152, 155]. Detection of 'EPR inactive' sites[150] in some copper proteins like haemocyanine[156] and tyrosinase[157] motivated research in the area of antiferromagnetic interaction in binuclear (multinuclear) complexes. A number of articles and reviews pertaining to the magnetic exchange interactions in binuclear complexes have appeared and now the research in this area is directed towards definite understanding of the mechanisms of such interactions and designing of model

systems on the basis of this knowledge, to mimic the active bio-sites. A short account of this work is included in the beginning of the last chapter of this thesis.

Present work involves a comparative study of the ternary copper (II) complexes of tertiary diimines and the compounds containing $\bar{O}$-O bidentate coordinating sites as secondary ligands. General structures and description of the ligands used is given on p. 29 . The formation constants of these complexes have been determined potentiometrically and their stabilities are compared on the basis of the electronic characteristics of the ligands. The complexes have been isolated in the solid state and characterized by spectral and magnetic measurements. Finally, reactions of some aldehyde containing complexes have been carried out with aromatic diamines. The binuclear complexes, thus obtained, have been characterized by spectral and magnetic studies.

1.2 References

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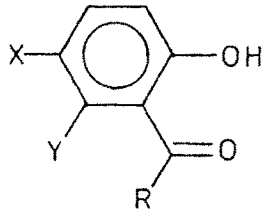
Ligands and abbreviations.

Symbol	abbreviation	ligand.
A^1	dpa	bis (2-pyridyl) amine
A^2	N-phen	5-nitro (1, 10 - phenanthroline)
A^3	bipy	2,2' - bipyridyl
A^4	phen	1, 10 - phenanthroline
HL^1	sal	salicylaldehyde
HL^2	B-sal	5-bromo salicylaldehyde
HL^3	N-sal	5-nitro salicylaldehyde
HL^4	naph	2-hydroxy naphthaldehyde
HL^5	acph	2-hydroxy acetophenone
HL^6		aceto acetanilide
HL^7		aceto acet-o-toluedide
HL^8		aceto acet-o-anisidide
HL^9		benzoyl acetanilide
HL^{10}		salicyl amide
HL^{11}		salicyl anilide
HL^{12}		5-bromo salicyl amide

Structures of the ligands.



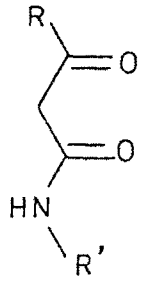
HL^1 X = H Y = H R = H

HL^2 X = Br Y = H R = H

HL^3 X = $-NO_2$ Y = H R = H

HL^4 XY = $-(CH)_4-$ R = H

HL^5 X = H Y = H R = CH_3

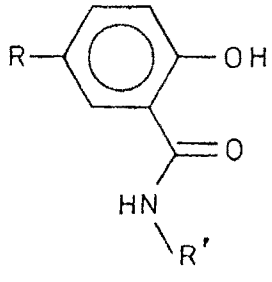


HL^6 R = CH_3 R' = C_6H_5

HL^7 R = CH_3 R' = o - Me C_6H_4

HL^8 R = CH_3 R' = o - MeO C_6H_4

HL^9 R = R' = C_6H_5



HL^{10} R = R' = H

HL^{11} R = H , R' = C_6H_5

HL^{12} R = Br R' = H