CHAPTER - VI

Isolation and Spectral Studies

Different types of mixed ligand complexes have been prepared in solid state and characterized by various workers.[238-243] Herzog and coworkers[244] reported the formation of [(diacetato)(2,2'-dipyridyl)Cu(II)] complexes. Sarkar and Dutta[245] have isolated the ternary complexes by mixing [cis diamine Co(II)] with ethylenediamine, 2,2'-dipyridyl or 1,10-phenanthroline. The complexes of 2,3-dihydroxynaphthalene and 2,2'-dipyridyl or 1,10-phenanthroline have been studied with a series of oxycations.[246] Yamamoto and coworkers[247] synthesized [diethyl-bis-dipyridyl Fe(III)] and [ethyl 2,2'-dipyridyl Ni(II)] complexes. Mixed ligand complexes containing Co(III), paludrine and 2,2'-dipyridyl or 1,10-phenanthroline have been described by Gheorghin and coworkers.[248] Dutta and coworkers[249-252] have reported a series of complexes of Vo(II) and Cu(II) having a tridentate ligand and 2,2'-dipyridyl or 1,10-phenanthroline. They[253,254] have also synthesized and characterized mixed ligand complexes of the type $[Cu(A\text{-}A)(X_2)]$, where A-A = 2,2'-dipyridyl, 1,10-phenanthroline or 5-nitro-1,10-phenanthroline, and $X = CNS^-$, NO_2^- or N_3^- and $[Cu(A\text{-}A)(xy)]z$ where A = same as above, xy = glycine or DL-alanine and $Z = Cl^-$, Br^- or I^-. Mixed ligand complexes containing Cu(II), phthalamide and 2,2'-dipyridyl or 1,10-phenanthroline were reported by Narain.[255] Ripan and Saceban[256] reported the synthesis of ternary complexes of Vo(II) with 2,2'-dipyridyl or 1,10-phenanthroline and o-, m- or p-aminobenzoic acids.

Detailed studies were carried out by various workers[20-32] on the mixed-ligand complexes of different metal ions containing β-ketones and another ligand, from the point of view of educidation of structure, kinetics of formation and reactions over the co-ordinated ligands. Solid mixed ligand complexes of the type $[MAL]$, where M = Cu(II) or Ni(II), A = 2,2'-dipyridyl or 1,10-phenanthroline and L = amino acids, mercaptoacids, polyphenols or o-hydroxy aromatic aldehydes and ketones have been reported from our laboratory.[33-36]

Bis complexes of β-ketoanilides and salicylamide derivatives with different metal ions have been isolated by various workers[37-48] to ascertain the structure, and co-ordination sites. The adduct compounds of composition $[ZnL_2X]$, where L = acetoacetanilide and X = pyridine, 2-, 3-, 4-picoline or quinoline were reported by Syamal.[49] Syamal[50-52] and Ghanekar have synthesized and characterized complexes of the formula $[Co(III)(B)(A)]$, where B are different tetradentate Schiff bases and A = acetoacetanilide or other bidentate ligands. Mixed-ligand complexes of the composition $[ML(OAc)_2]$, where L = acetoacetanilide or other bidentate ligands have also been prepared.[53]

The isolation of mixed-ligand Cu(II) amino acid complexes from human serum by Sarkar and Kruck[54] has generated considerable interest in the study of mixed-ligand complexes of Cu(II) with aminoacids and peptides.

Several ternary amino acid Cu(II) complexes have been described and characterized both in solution and in solid state.[55-60]

In the present work isolation of two series of ternary complexes of Cu(II) containing 1,10-phenanthroline or 5-nitro-1,10-phenanthroline and one of the following secondary ligands : ethylenediamine, glycine, phenylalanine, tyrosine, L-dopa, catechol, 2,3-dihydroxy-naphthalene and dopamine have been carried out. The bonding characteristics of these two series of complexes have been studied and compared by the help of IR spectral, electronic spectral and magnetic studies.

Experimental

Copper acetate of A.R. quality (BDH) was used. All other reagents were same as described in earlier chapters. Solvents used were also of analar grade.

Preparation of [CuA(ethylenediamine)] Complex - An aqueous solution of copper acetate (8 mmole) in 20 ml. distilled water was slowly added to an ethanolic solution of 1,10-phenanthroline or 5-nitro-1,10-phenanthroline (8 mmole) in 20 ml ethanol. A blue solid was formed immediately. As the mixture was stirred magnetically the appropriate amount of ethylenediamine (10 mmole) in 10 ml aqueous solution was slowly added, followed by 1M ammonium hydroxide solution until a clear solution was obtained. The solution was warmed and stirred for a further 45 min., heated till its volume was reduced by approximately half and then 0.1M solution of sodium tetraphenyl borate was added. Immediately solid separated out. This was filtered, washed with small prortions of cold water followed by ethanol and then dried in vacuo.

Preparation of [CuAamino acid] Complexes - An aqueous solution of copper acetate (8 mmole) in 20 ml distilled water was slowly added to an ethanolic solution of 1,10-phenanthroline or 5-nitro-1,10-phenanthroline (8 mmole) in 20 ml ethanol. A blue solid was formed immediately. As the mixture was stirred magnetically the appropriate amount of amino acid (10 mmole) in 0.1M hydrochloric acid was slowly added,

followed by 1M ammonium hydroxide solution until a clear blue solution was obtained. The solution was warmed and stirred for further 45 min., heated till its volume was reduced by approximately half and then 0.1M solution of sodium tetraphenylborate was added. The solid immediately separated out. This was filtered, washed with small portions of cold water followed by ethanol and then dried in vacuo.

Preparation of [CuAdianion] Complexes :- An aqueous solution of dianions (10 mmole) in 20 ml distilled water was slowly added to an ethanolic solution of 1,10-phenanthroline or 5-nitro-1,10-phenanthroline (8 mmole) in 50 ml ethanol. This ligand mixture was then slowly added to an aqueous solution of copper acetate (8 mmole) in 20 ml distilled water followed by 1M ammonium hydroxide solution in order to raise the pH to 6.0 whereupon the complex was formed immediately. This was filtered, washed with distilled water followed by ethanol and then dried in vacuo.

Copper(II) was estimated gravimetrically. Percentages of N, C and H were estimated on Coleman Analyzer Models 29 and 33, respectively. TLC analysis were done on a silica gel G (Sichem) plates using ethanol as solvent.

Magnetic Studies

The magnetic susceptibilities of the isolated complexes were determined by Guoy's method using Mettler

balance and electromagnet working at a constant current strength of 3 amps. in all cases. The procedure followed for the measurements of magnetic susceptibilities is as follows :

The compound was finely powdered and was filled in the caliberated tube (with predetermined β values) with Hg $\left[Co(NCS)_4\right]$ upto the caliberation mark with constant tappings. The temperature ($\sim 30^{\circ}C$) was noted and current 3 amps. was fixed in the electromagnet with the help of rheostat connected in series. The tube was suspended with the help of a wire connected to a pan of the balance such that the portion of the tube filled with the compound remained in between two magnetic poles. The weight of the (tube + compound) in the presence of magnetic field and also without field was noted. From the difference in the weight d_w, molar susceptibility of the complexes were determined, using following equation :

$$X_g = \frac{\alpha + \beta d_w}{m}$$

where $\alpha = X_2 \rho_2 V = 0.029V \times 10^{-6}$

β = tube constant

d_w = difference in the weight in the field + tube correction i.e. diamagnetic correction of the glass tube

V = Volume of the tube

m = Weight of the complex taken

β was obtained for the tube by caliberating it with a complex of known molar susceptibility. The compound used was $Hg[Co(CNS)_4]$ and β was found out by using the equation

$$\beta = \frac{(32w - 0.029V) \times 10^{-6}}{d_w}$$

The pascal's diamagnetic correction for the metal and other constituents of the complex was made, and from the value of X_m (corrected), thus obtained, magnetic moment values were calculated using the following equations.

$$X = \frac{(0.029V + \beta.dw) \times 10^{-6}}{W}$$

$$X_m = X.Mol.Wt.$$

$$\mu eff = 2.84 \times \sqrt{X_m \cdot T} \quad B.M.$$

where V = Weight of the tube with water - Weight of empty tube

W = Weight of tube with powder - Weight of the empty tube

0.029V value is due to the air susceptibility which is present in the closed compartment.

The elemental analysis and the magnetic moment values (Bohr Magnetons) of all the complexes have been presented in Table VI 1,2.

Spectral Measurements

IR spectra were recorded from 4000 - 200 cm^{-1} on a 'Perkin Elmer Model 638' Spectrometer. KBr Pellets and Nujol mulls were employed through out and the bands have been presented in Table VI 4 . A Carl Zeiss Specord UV-Visible Spectrophotometer with 1 cm quartz cells was used for the electronic spectral measurements.

Table VI 1

Magnetic susceptibility measurements and analytical Copper(II) ternary complexes

Name of complexes	Obtained				Expected				μ_{eff}
	% C	% H	% N	% Cu	% C	% H	% N	% Cu	
[Cu(5-nitro-phen)(en)]$(Bph_4)_2$	71.76	4.67	7.02	6.2	73.9	5.26	7.09	6.43	1.95
[Cu(5-nitro-phen)(gly)]Bph_4	64.73	6.34	7.8	9.06	65.91	6.3	8.21	9.32	1.92
[Cu(5-nitro-phen)(cat)]	54.36	2.70	11.7	16.4	54.47	2.77	10.59	16.02	1.65
[Cu(5-nitro-phen)(2,3-dihydroxynaphthalene)]	57.22	3.13	9.51	13.97	59.12	2.91	9.4	14.23	1.7
[Cu(5-nitro-phen)(dopamine)] acetate	49.41	3.79	10.99	12.3	51.1	3.87	10.86	12.31	1.65
[Cu(5-nitro-phen)(phenylala)] Bph_4	69.68	4.63	7.14	7.98	69.97	4.73	7.16	8.12	1.75
[Cu(5-nitro-phen)(tyrosine)] Bph_4	68.46	4.82	7.1	8.05	67.92	4.63	7.09	7.9	1.7
[Cu(5-nitro-phen)(L-dopa)] Bph_4	66.44	4.43	6.89	7.82	66.12	4.19	6.89	7.74	1.65

Table VI 2

Magnetic susceptibility measurements and analytical data of Copper(II) ternary complexes

Name of complex	Experimental				Theoretical				μ_{eff}
	% C	% H	% N	% Cu	% C	% H	% N	% Cu	
[Cu(phen)(en)] $(Bph_4)_2$	79.00	5.35	6.20	6.46	77.4	5.7	5.83	6.6	1.95
[Cu(phen)(gly)] Bph_4	70.13	5.06	6.86	9.8	70.61	4.8	6.5	9.84	2.02
[Cu(phen)(cat)]	61.56	3.40	8.21	18.33	61.44	3.41	7.96	18.07	1.75
[Cu(phen)(2,3-dihydroxy-naphthalene)]	64.96	3.01	6.82	15.75	65.91	2.99	6.99	15.86	1.7
[Cu(phen)(dopamine)] acetate	56.12	4.3	8.83	13.14	56.34	4.27	8.96	13.56	1.8
[Cu(phen)(phenylala)] Bph_4	73.9	5.97	5.55	8.43	73.4	6.38	5.7	8.63	1.75
[Cu(phen)(tyrosine)] Bph_4	72.12	4.53	5.63	8.82	71.83	4.92	5.58	8.45	1.75
[Cu(phen)(L-dopa)] Bph_4	70.02	4.58	5.18	8.03	70.33	4.81	5.47	8.27	1.7

Table VI 3

Electronic spectral band of ternary complexes

Name of complexes	λ max
[Cu(phen)(en)] $(Bph_4)_2$	590
[Cu(phen)(gly)] Bph_4	606
[Cu(phen)(cat)]	685
[Cu(phen)(2,3-dihydroxynaphthalene)]	710
[Cu(phen)(dopamine)] acetate	625
[Cu(phen)(phenylalal)] Bph_4	606
[Cu(phen)(tyrosine)] Bph_4	606
[Cu(phen)(L-dopa)] Bph_4	606
[Cu(5-nitro-phen)(en)] $(Bph_4)_2$	591.8
[Cu(5-nitro-phen)(gly)] Bph_4	610
[Cu(5-nitro-phen)(cat)]	530
[Cu(5-nitro-phen)(2,3-dihydroxy-naphthalene)]	540
[Cu(5-nitro-phen)(dopamine)] acetate	520
[Cu(5-nitro-phen)(phenylala)] Bph_4	598.2
[Cu(5-nitro-phen)(tyrosine)] Bph_4	598.2
[Cu(5-nitro-phen)(L-dopa)] Bph_4	598.2

Table VI 4

IR absorptions and probable assignments

	Cu(phen) (gly)	Cu(5Nphen) (gly)	Cu(phen) (phenylala)	Cu(5Nphen) (phenylala)	Cu(phen) (tyro)	Cu(5Nphen) (tyro)	Cu(phen) (L-dopa)	Cu(5Nphen) (L-dopa)
$\nu as - \nu s$	230	340	220	250	220	230	230	250
ν(Cu-O)	335 W	338 W	320 s	330 s	330s	332 m	332 W	350 W
ν_{Cu-N}	468 W	470 W	408 W	410m	412m	415 W	412 W	418 W

Results & Discussions

TLC of all the complexes, using ethanol as solvent, show a single spot confirming their purity. The elemental analysis of the ternary complexes isolated in the present study are given in Table 1, alongwith the values of their magnetic moment. The analysis is consistent with the structure suggested. In case of the ternary complexes involving dopamine, co-ordinating from two phenolic groups and the amino group being protonated, one negative ion was found to be present. L-dopa is co-ordinating from aminocarboxylate end. Thus [CuAL-dopa] has one positive charge and one BPh_4 was found to be present.

All Cu(II) complexes are paramagnetic showing the presence of one unpaired electron as expected in square planar Cu(II) complexes. This also shows that there is no polymerization leading to Cu(II)-Cu(II) antiferromagnetic interaction.

IR Spectral Studies

The ternary complexes exhibit IR absorptions typical of co-ordinated ligands,[61-63] (Phen : 1625, 1515, 1420, 840, 700 cm^{-1} and 5-nitro-1,10-phenanthroline 1625, 1515, 1420, 840, 720 cm^{-1}). Furthermore in the case of amino acid complexes remarkable similarities are observed among these ternary complexes in the absorption regions due to the amino and carboxyl groups which are found to occur respectively in a) 3450 -

3200 cm^{-1}, 1600 - 1570 cm^{-1} and 600 - 610 cm^{-1} and b) 1640 - 1600 cm^{-1}, 1420 - 1380 cm^{-1}, 810 - 720 cm^{-1} and 490 - 460 cm^{-1}. These are, moreover comparable to those observed in the bis complexes of different amino acids,[64-67] where x-ray structural and related studies[68-71] have shown the Cu(II) ion to be chelated through the carboxyl oxygen and amino nitrogen.

The interesting observation about the mode of co-ordination of L-dopa, tyrosine and dopamine can be inferred from the IR spectral data. For these metal complexes, which are ambidentate, it is possible to identify the unco-ordinated unionised phenolic oxygen or amino stretching frequencies. Busch et al[72-75] showed that it is possible to identify the unco-ordinated unionised carboxyl stretching frequencies. In the ternary complexes containing either tyrosine or L-dopa, the free unionised carboxyl stretching frequencies in the region 1700 - 1750 cm^{-1} and amino stretching frequencies in the region 3500 - 3400 cm^{-1} could not be detected, indicating that both the carboxyl group and amino group of tyrosine and L-dopa get deprotonated on complex formation. As similar pattern is observed for the amino and carboxyl IR absorptions in all these ternary complexes containing amino acids, it would appear that tyrosine and L-dopa are co-ordinating from amino carboxylate end in the ternary systems. There is also unco-ordinated unionised phenolic OH stretching frequency in the range 3600 - 3500 cm^{-1} present, indicating that

co-ordination is not from phenolic group. In case of dopamine ternary complexes there is no ionised phenolic stretching frequencies of phenolic groups and moreover there is unco-ordinated unionised $\overset{\text{amino}}{\wedge}$ stretching frequencies present indicating that the co-ordination is from phenolic groups and amino group is remaining unco-ordinated. This is consistent with the results from microanalysis and magnetic measurements.

The magnitude of symmetric and antisymmetric carboxylate stretching vibration i.e. ν_s and ν_{as} in the series of co-ordinated amino acids have been demonstrated by Nakamoto and Martell et al[76] to give a measure of the carboxylate - metal interactions. They further showed that for given ligand the difference ($\nu_{as} - \nu_s$) would increase as the M-O bond becomes more covalent, since the carboxylate stretching becomes correspondingly more asymmetrical. In the present series of amino acid complexes, this difference ($\nu_{as} - \nu_s$) for a given amino acid in the 5-nitro-1,10-phenanthroline series, is found to be greater by 10 - 50 cm^{-1} than that in the corresponding 1,10-phenanthroline series. A similar trend is also detected in the far IR absorption frequencies for the Cu-O and Cu-N stretching modes.[77-79] Thus the absorption frequency at $\sim$ 335 cm^{-1} due to Cu-O stretching is seen in each case to be of higher energy for the ternary system of the 5-nitro-1,10-phenanthroline series, the difference being in the range 10 - 15 cm^{-1}. The order for Cu-N stretching frequencies at $\sim$ 410 cm^{-1} in these complexes is the same as that far $\nu_{as} - \nu_s$ and ν_{COO^-}

though the differences here are smaller. These observations seem to imply that an amino acid is bonded more covalently to Cu(II) in the 5-nitro-1,10-phenanthroline series than in the 1,10-phenanthroline, which confers on the Cu(II) in $\left[Cu(5\text{-nitro-}1,10\text{-phen})\right]^{2+}$ a greater affinity for the electron pairs of oxygen and nitrogen donor atom of the amino acids.

Electronic Spectral Studies

The electronic spectra of these ternary Cu(II) complexes in solution and in solid state exhibit broad absorption bands in the visible region, and for each complex the absorption maxima are observed at approximately the same wavelength for both the solid and the solution. It would appear that these ternary complexes probably retain the structures in both states.

In view of the relatively low intensities of the band and their occurrence in the range 650 - 720 nm in case of amino acids and diamine containing ternary complexes, we tentatively conclude that these observed bands are very likely to be due to $dx^2 - y^2$ ----→ dxy transition. The second and third band due to dxz --→ dxy, dyz ----→ dxy transition is too near to the first band to be resolved.

The ternary complexes of $\left[CuAL\right]$ where L = catechol, 2,3-dihydroxynaphthalene or dopamine exhibit intense charge transfer band in the visible region i.e. 450 - 500 nm. There is no distinct absorption band

observed in the range 600 - 750 nm. This is because the d-d transition bands are of very low intensities compared to charge transfer band and are marked by the latter.

However, in the dianion complexes $[CuA\ O^{-}\text{-}O^{-}]$, the d-d transition band is at higher energy than in $[Cu(O^{-}\text{-}O^{-})_2]$ or $[CuA_2]$. In cases of amino acid, co-ordinating through $N\text{-}O^{-}$ also, d-d band of $[CuAL]$ is at higher energy, though not to the same extent as in case of $O^{-}\text{-}O^{-}$ co-ordinating ligand. In case of diamine complexes with N-N co-ordination, the d-d transition band is observed slightly higher than the intermediate between d-d transition bands of $[CuA_2]$ and $[CuL_2]$, as normally expected. Such observation have been made earlier and this is attributed to release in the repulsion in ternary complexes of repulsion between metal d electrons and lone pairs of electron over $O^{-}\text{-}O^{-}$. The two ligands can come closer in the ternary complex resulting in a stronger ligand field and hence the CFS in the ternary complex $[CuAL]$ is more than the average of $[CuA_2]$ or $[CuL_2]$. The effect is less in ternary complex containing amino acid with only one O^{-} and is absent in ternary complexes containing N-N co-ordinating diamines.