CHAPTER IV

Mixed-Ligand Complexes of Copper(II) : Isolation of Solid Complexes

The complexes studied in solution may not always be isolable. But if they can be isolated under the same conditions as studied in solution, the structure suggested through solution studies can be confirmed by various spectral studies. In the complexes of the type studied in the present thesis, the extent of Cu → L π interaction and also the extent of inter-ligand π interaction in mixed-ligand complexes are in question and hence the study of the complexes in solid state will be of interest. The complexes have, therefore, been isolated in the solid state and characterized.

Different types of mixed-ligand complexes have been prepared in solid state and characterized by various workers.[103-108] Herzog and coworkers[109] reported the formation of [(diacetato)(2,2'-dipyridyl)Cu(II)] complexes. Sarkar and Dutta[110] have observed that [cis diamine Co(II)] sulphate reacts readily with ethylenediamine, 2,2'-dipyridyl or 1,10-phenanthroline, liberating ammonia, resulting in the formation of mixed-ligand complex. The complexes of 2,3-dihydroxynaphthalene and 2,2'-dipyridyl or 1,10-phenanthroline have been studied with a series of oxycations.[111] Yamamoto and coworkers[112] 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.[113] Dutta and coworkers[114-117] 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[118,119] 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-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.[120] Ripan and Saceban reported[121] the synthesis of ternary complexes of UO(II) with 2,2'-dipyridyl or 1,10-phenanthroline and o-, m- or p-aminobenzoic acids.

Detailed studies were carried out by various workers[49,122-133] on the mixed-ligand complexes of different metal ions containing β-diketones and another ligand, from the point of view of elucidation of structure, kinetics of formation and reactions over the coordinated 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, poly phenols or o-hydroxy aromatic aldehydes and ketones have been reported from our laboratory.[35,134-136]

Bis complexes of β-ketoanilides and salicylamide derivatives with different metal ions have been isolated by various workers[137-148] to ascertain the structure, and coordination sites. The adduct compounds of composition

$[ZnL_2X]$, where L = acetoacetanilide and X = pyridine, 2-, 3- or 4-picoline, or quinoline were reported by Syamal.[149] Syamal and Ghanekar[150-152] have synthesized and characterized complexes of the formula $[Co(III)(BBBB)(A-A)]$, where BBBB are different tetradentate schiff bases and A-A = acetoacetanilide or other bidentate ligands. Mixed-ligand complexes of the composition $[B.L(OAC)_2]$, where L = acetoacetanilide or other bidentate ligands have also been prepared.[153]

This chapter deals with the preparation of the mixed-ligand complexes of the type $[CuAL]ClO_4$, where A = 2,2'-dipyridyl (A^1), 1,10-phenanthroline (A^2) or 2-(2'-pyridyl)benzimidazole (A^3) and L = an anion of acetoacetanilide (L^1), acetoacet-o-toluidide (L^2), acetoacet-o-anisidide (L^3), benzoatoacetanilide (L^4), salicylamide (L^5), salicylanilide (L^6) or 5-bromosalicylamide (L^7).

EXPERIMENTAL

Copper acetate of A.R. quality was obtained from BDH. All the other reagents used were the same as described in Chapters II and III.

Isolation of mixed-ligand complex :

The mixed-ligand complexes of the type $[CuAL]ClO_4$, where A = A^1 to A^3 and L = L^1 to L^7 were prepared as follows :

To 0.002M copper acetate in water-alcohol (1 : 1) mixture (25 ml) was added a mixture of equimolar quantities of A and L together in an alcohol-water (1 : 1) mixture (25 ml). The solution was refluxed for 15-20 minutes and then a 0.1M solution of sodium perchlorate in water was added till the precipitation was complete. The solid was filtered off and washed with warm alcohol. It was dried and analysed for all elements.

Cu(II) was estimated iodometrically. 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.

Conductivity measurements were carried out in methanol solutions (10^{-3}M) of the compounds using Toshniwal Conductivity Bridge Type CL01/01A.

Magnetic studies :

The magnetic susceptibilities of the isolated complexes were determined by Guoy's method using Mettler balance and electromagnet of constant current strength (3 amps) in all cases. The procedure followed, for the measurements of magnetic susceptibilities is as follows :

The compound was dried, finely powdered and was filled up in the calibrated tube (with predetermined β values) upto the calibration mark with equal number of tappings. The temperature ($\sim 30\ ^{o}C$) was noted and the current of 3 amps was fixed in the electromagnet with the help of a rheostat connected in series. The tube was suspended with the help of a wire connected to the pan of the balance such that the portion of the tube filled with the compound remained in between the two magnetic poles. The weight of the (tube + compound) was noted in the absence of magnetic field. The weight was determined again in the presence of magnetic field. From the difference in weight (dw), molar susceptibilities of the complexes were determined,[154] using the following equation :

$$\chi_g = \frac{\alpha + 3\ dw}{m}$$

where $\alpha = \chi_2 \rho_2 V = 0.029\ V \,.\, 10^{-6}$

β = tube constant

dw = difference in the weight in the field and weight outside 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 calibrating 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,

$$\beta = \frac{(16.44\ m - 0.029\ V)\ .\ 10^{-6}}{dw}$$

The Pascal's diamagnetic correction[155] for the metal and other constituents of the complex was made, and from this χ_m (corrected), magnetic moment values were calculated.

The elemental analyses, molar conductance and the magnetic moment values (Bohr Magnetons) of all complexes have been presented in Table IV 1.

Spectral measurements :

The spectra were recorded on a Carl Zeiss SPECORD UV/VIS spectrophotometer with 1 cm matched quartz cells using ethanol as solvent. Solutions of concentrations 10^{-4} and 10^{-2} mol/lit were used for UV and visible regions, respectively. Spectra of free ligands, of synthesized mixed-ligand complexes, of Cu(II) + A + L mixed in 1 : 1 : 1 mole ratio of Cu(II) and ligands A and L, and binary complexes $[CuA_2]^{2+}$ and $[CuL_2]$ prepared by direct mixing of $CuCl_2$ and the ligands in the required proportions have been recorded in Tables IV 2 to IV 4.

Infrared spectra were recorded in Nujol or as KBr pellets on Beckman spectrometer 21.

Table IV 1 : Analytical data, magnetic moments and molar conductance of mixed-ligand complexes $[CuAL]ClO_4$

Name of the complex	Analyses % *				μ eff in B.M.	Λ/Ω^{-1} cm^{-2} mol^{-1} in methanol
	Cu	N	C	H		
[Acetoacetanilidato, 2,2'-dipyridyl Cu(II)] perchlorate	12.91 (12.83)	8.88 (8.48)	48.05 (48.46)	3.56 (3.63)	1.86	102.87
[Acetoacet-o-toluididato, 2,2'-dipyridyl Cu(II)] perchlorate	12.17 (12.47)	8.20 (8.25)	- -	- -	2.04	96.13
[Acetoacet-o-anisididato, 2,2'-dipyridyl Cu(II)] perchlorate	12.31 (12.10)	8.02 (8.00)	48.25 (47.98)	4.26 (3.81)	1.94	101.65
[Benzoatoacetanilidato, 2,2'-dipyridyl Cu(II)] perchlorate	11.30 (11.38)	7.51 (7.52)	54.75 (53.75)	4.23 (3.58)	1.96	105.25
[Salicylamidato, 2,2'-dipyridyl Cu(II)] perchlorate	13.80 (13.96)	8.92 (9.23)	44.50 (44.81)	3.00 (3.08)	1.95	98.00
[Salicylanilidato, 2,2'-dipyridyl Cu(II)] perchlorate	12.15 (11.96)	7.88 (7.90)	51.66 (51.93)	3.28 (3.39)	1.83	101.00
[5-Bromosalicylamidato, 2,2'-dipyridyl Cu(II)] perchlorate	11.95 (11.87)	8.28 (7.85)	- -	- -	2.00	111.25

cont...

[Acetoacetanilidato, 1,10-phenanthroline Cu(II)] perchlorate	12.05 (12.23)	7.85 (8.09)	50.07 (50.84)	3.30 (3.47)	1.91	103.18
[Acetoacet-o-toluididato, 1,10-phenanthroline Cu(II)] perchlorate	11.23 (11.92)	8.00 (7.88)	- -	- -	1.92	108.61
[Acetoacet-o-anisididato, 1,10-phenanthroline Cu(II)] perchlorate	11.50 (11.57)	7.43 (7.65)	50.27 (50.25)	4.31 (3.64)	1.83	96.52
[Benzoatoacetanilidato, 1,10-phenanthroline Cu(II)] perchlorate	11.10 (10.91)	7.19 (7.21)	54.55 (55.64)	3.76 (3.43)	1.89	100.20
[Salicylamidato, 1,10-phenanthroline Cu(II)] perchlorate	13.11 (13.26)	8.53 (8.76)	47.29 (47.57)	2.94 (2.92)	1.85	109.23
[Salicylanilidato, 1,10-phenanthroline Cu(II)] perchlorate	11.07 (11.44)	7.98 (7.56)	54.49 (54.00)	3.51 (3.06)	2.01	99.50
[5-Bromosalicylamidato, 1,10-phenanthroline Cu(II)] perchlorate	11.16 (11.36)	7.93 (7.51)	40.32 (40.77)	2.62 (2.32)	1.88	101.50
[Acetoacetanilidato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	12.12 (11.90)	12.04 (10.48)	49.73 (49.43)	3.96 (3.56)	1.80	101.23
[Acetoacet-o-toluididato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	11.45 (11.59)	10.49 (10.22)	50.80 (50.36)	4.07 (3.83)	2.01	98.18

cont....

[Acetoacet-o-anisididato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	11.33 (11.37)	10.01 (9.93)	- -	- -	1.95	112.42
[Benzoatoacetanilidato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	10.45 (10.66)	9.87 (9.40)	54.90 (54.36)	3.69 (3.52)	1.75	105.15
[Salicylamidato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	12.51 (12.86)	11.39 (11.34)	- -	- -	1.98	106.25
[Salicylanilidato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	11.00 (11.14)	10.97 (9.82)	- -	- -	1.95	104.10
[5-Bromosalicylamidato, 2-(2'-pyridyl)-benzimidazole Cu(II)] perchlorate	11.12 (11.07)	9.74 (9.76)	- -	- -	1.95	98.75

* Calculated values are given in parentheses

Table IV 2

Electronic spectra (cm^{-1}) of free ligands in ethanol

Ligand	
A^1	49 500, 42 200, 35 200
A^2	49 200, 44 000, 37 800
A^3	49 000, 41 300, 32 200
L^1	49 000, 41 000
L^2	48 600, 41 600
L^3	48 000, 40 300, 35 000
L^4	48 800, 40 600, 32 000
L^5	48 000, 42 400, 33 000
L^6	47 000, 42 000 (sh), 31 500
L^7	48 000, 41 200, 33 000 (sh)
L^8	48 000, 43 000 (sh), 36 200, 32 500 (sh)

Table IV 3

Electronic spectra (cm^{-1}) of binary complexes in ethanol

Complex	
$[\mathrm{CuA^{1}}_{2}]^{2+}$	49 000, 41 000, 33 200, 32 000, 14 000
$[\mathrm{CuA^{2}}_{2}]^{2+}$	48 000, 44 000, 36 900, 34 000 (sh), 14 500
$[\mathrm{CuA^{3}}_{2}]^{2+}$	48 500, 41 300, 32 000, 30 800, 14 200
$[\mathrm{CuL^{1}}_{2}]$	49 000, 41 000, 33 000, 24 800,(sh), 13 500
$[\mathrm{CuL^{2}}_{2}]$	48 600, 41 600, 34 800, 24 000 (sh), 13 000
$[\mathrm{CuL^{3}}_{2}]$	48 000, 40 300, 34 800, 32 200, 23 500 (sh), 13 000
$[\mathrm{CuL^{4}}_{2}]$	48 800, 40 600, 30 200, 23 000 (sh), 12 500
$[\mathrm{CuL^{5}}_{2}]$	48 200, 42 000, 33 000, 24 000 (sh), 12 900
$[\mathrm{CuL^{6}}_{2}]$	47 000, 42 500 (sh), 31 500, 23 000 (sh), 12 800
$[\mathrm{CuL^{7}}_{2}]$	48 000, 41 200, 33 000 (sh), 23 000 (sh), 12 500
$[\mathrm{CuL^{8}}_{2}]$	48 000, 42 500 (sh), 36 500, 32 500 (sh), 22 500 (sh), 12 000

Table IV 4
Electronic spectra (cm^{-1}) of ternary complexes in ethanol

Complex	
$[CuA^1L^1]^+$	48 800, 40 300, 33 200, 32 200, 24 000 (sh), 16 000
$[CuA^1L^2]^+$	48 800, 41 000, 34 000, 32 000, 24 000 (sh), 16 000
$[CuA^1L^3]^+$	48 800, 40 200, 33 400, 32 100, 23 500 (sh), 16 000
$[CuA^1L^4]^+$	48 800, 40 800, 33 200, 32 000, 30 000, 22 000 (sh), 16 000
$[CuA^1L^5]^+$	48 000, 42 000 (sh), 34 800 (sh), 33 200, 32 000, 23 500 (sh), 15 500
$[CuA^1L^6]^+$	47 000, 43 000 (sh), 33 200, 32 000, 22 800 (sh), 15 000
$[CuA^1L^7]^+$	48 000, 42 000 (sh), 35 000 (sh), 33 500, 32 000, 23 000 (sh), 15 800
$[CuA^1L^8]^+$	48 000, 42 000 (sh), 38 500 (sh), 35 000 (sh), 33 200, 32 000, 22 000 (sh), 15 000
$[CuA^2L^1]^+$	48 800, 44 000, 36 400, 34 000 (sh), 23 000 (sh), 15 500
$[CuA^2L^2]^+$	48 200, 44 200, 36 600, 34 000 (sh), 23 500 (sh), 15 500
$[CuA^2L^3]^+$	48 000, 44 400, 36 500, 34 000, 23 000 (sh), 15 500
$[CuA^2L^4]^+$	48 600, 44 000, 36 600, 33 800, 30 200, 22 000 (sh), 15 500

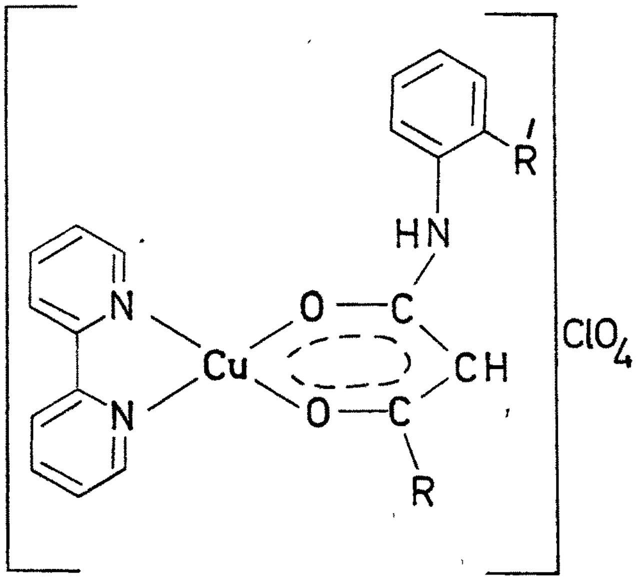
....cont.

$[CuA^2L^5]^+$	47 600, 44 000, 36 500, 33 800 (sh), 23 500 (sh), 15 000
$[CuA^2L^6]^+$	47 000, 44 000 (sh), 36 500, 34 000 (sh), 22 500 (sh), 15 000
$[CuA^2L^7]^+$	48 000, 44 200 (sh), 36 500, 34 000 (sh), 22 800 (sh), 15 000
$[CuA^2L^8]^+$	48 000, 44 000 (sh), 36 500, 34 000 (sh), 22 500 (sh), 15 000
$[CuA^3L^1]^+$	48 800, 41 000, 32 200, 29 800 (sh), 23 000 (sh), 15 500
$[CuA^3L^2]^+$	48 800, 41 000, 34 600, 30 400, 22 000 (sh), 15 500
$[CuA^3L^3]^+$	48 800, 41 200, 34 000 (sh), 32 000, 22 000 (sh), 15 000
$[CuA^3L^4]^+$	48 500, 41 300, 32 000, 30 800, 22 000 (sh), 15 000
$[CuA^3L^5]^+$	48 000, 41 800 (sh), 35 000 (sh), 30 800, 23 000 (sh), 15 000
$[CuA^3L^6]^+$	47 000, 42 000 (sh), 35 500 (sh), 30 500, 23 000 (sh), 15 000
$[CuA^3L^7]^+$	48 000, 41 500 (sh), 36 000 (sh), 31 000, 23 500 (sh), 15 000
$[CuA^3L^8]^+$	48 000, 41 200 (sh), 36 000, 31 000, 23 000 (sh), 15 000

RESULTS AND DISCUSSION

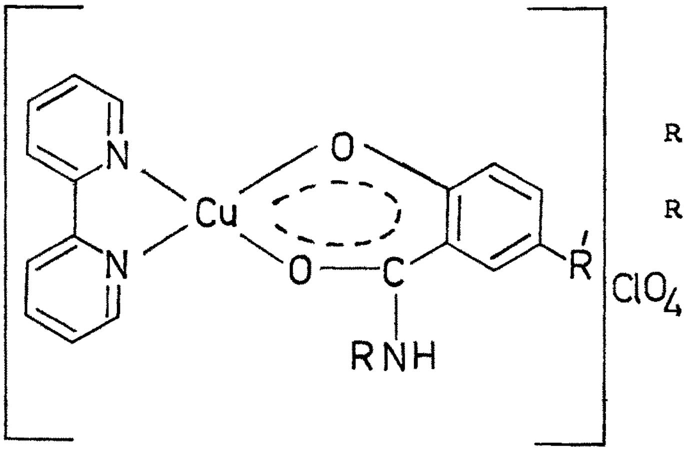
TLC of all the complexes using ethanol as solvent show a single dot confirming their purity. The elemental analyses of the isolated mixed-ligand complexes correspond to the general composition $[CuAL]ClO_4$. Molar conductance of the complexes in methanol correspond to 1 : 1 electrolytes, showing the presence of ionic ClO_4^-.

The mixed-ligand complexes $[CuA^1L]ClO_4$, where $L = L^1$ to L^7 can be represented as follows :



R = H or C_6H_5

R' = H, CH_3 or OCH_3



R = H or C_6H_5

R' = H or Br

Similar structures can be shown in cases where A = A^2 or A^3.

All Cu(II) complexes are paramagnetic showing the presence of one unpaired electron, which means that dimerization does not take place in these complexes. Otherwise a lowering in the magnetic moment values would have been observed due to Cu(II) — Cu(II) interactions. However, the magnetic moment values are slightly more than the spin only value. This may be because of orbital moment contribution to the magnetic moment value.

Infrared spectra :

Infrared spectra confirm the presence of perchlorate ion outside the coordination sphere. The free ClO_4^- ion gives rise to two IR bands : a weak band at ~920 cm^{-1} due to the symmetrical stretching mode ν_1, which is strictly IR forbidden and ν_3 the asymmetrical stretching mode at ~1100 cm^{-1} which is IR allowed. When perchlorate is coordinated[155] to a metal ion its symmetry is lowered from Td to C_{3v} and thus ν_1 becomes IR allowed and triple degeneracy of ν_3 is partly removed. Consequently, the IR spectral band at ~920 cm^{-1} becomes more intense and ~1100 cm^{-1} band is resolved into two. All the present complexes studied show a strong band at ~1100 cm^{-1} corresponding to ν_3 and the band at ~920 cm^{-1} corresponding to ν_1 is absent. This shows that ClO_4^- has T_d symmetry in the complex and is ionic in nature.

Band in the range ~3400 cm^{-1} are absent indicating the absence of water molecules in these complexes and dissociation of hydrogen from -OH after complexation. There is also a band observed at ~3300 cm^{-1} corresponding to ν_{N-H} stretching of the amide/anilide group. The fact that there is no significant change in the ν_{N-H} of the free ligands and their mixed-ligand complexes, is an adequate confirmation that the coordination is not from nitrogen of the amide/anilide. The band in the region ~1580 cm^{-1} corresponds to $\nu_{C=O}$ stretch of the coordinated carbonyl group.

The bands at ~3040 cm^{-1} and ~2900 cm^{-1} correspond to aromatic and aliphatic ν_{C-H} stretching frequencies, respectively. $\nu_{C=C}$ and $\nu_{C=N}$ stretching vibrations of the dipyridyl ring also occur in the range ~1600 cm^{-1}. The bands ~1450 cm^{-1} and ~1250 cm^{-1} correspond to wagging and deformation of $-CH_2$ group. The bands ~1520 cm^{-1}, ~1490 cm^{-1}, ~1450 cm^{-1} and ~1310 cm^{-1} may correspond to ring stretching modes. The ν_{C-C} stretching bands also occur in the region ~1200 cm^{-1}. The band at ~770 cm^{-1} corresponds to C—H out of plane deformation. The band ~1150 cm^{-1} is due to C—N stretching. The band ~740 cm^{-1} corresponds to the coupled Cu—N vibrations.

Electronic spectra :

The UV spectra of the synthesized ternary complexes are superimposable over the spectra of Cu(II) + A + L, a 1 : 1 : 1 mixture. This shows that the ternary complex is formed immediately in solution.

The specific bands are discussed in cases of $[CuA^1L^1]^+$ and $[CuA^1L^5]^+$.

Dipyridyl shows bands at 49 500, 42 200 and 35 200 cm^{-1}. The bands in the lower energy region correspond to $\pi \longrightarrow \pi^*$ transition. $[CuA^1_2]^{2+}$ shows bands at 49 000, 41 000, 33 200 and 32 000 cm^{-1}. The appearance of a new band and the shift in $\pi \longrightarrow \pi^*$ transitions shows that there is interaction between the π orbitals of Cu(II) and those of the dipyridyl molecule. Acetoacetanilide shows bands at 49 000 and 41 000 cm^{-1}. The low energy band at 41 000 cm^{-1} corresponds to a transition involving π orbitals. In $[CuL^1_2]$ the bands are at 49 000, 41 000, 33 000 and 24 800(sh) cm^{-1}. The new bands at 33 000 and 24 800(sh) cm^{-1} show that there is interaction between Cu(II) and ligand π orbitals. The spectra of $[CuA^1L^1]^+$ has bands at 48 800, 40 300, 33 200, 32 200 and 24 000(sh) cm^{-1}, showing all the transitions of $[CuA^1_2]^{2+}$ and $[CuL^1_2]$ without any significant shift.

The bands in salicylamide(L^5) occur at 48 000, 42 400 and 33 000 cm^{-1}. In $[CuL^5_2]$, besides the bands at 48 200, 42 000 and 33 000 cm^{-1}, an additional band is observed at 24 000(sh) cm^{-1}. This indicates that there is π interaction between Cu(II) and salicylamide π orbitals resulting in $\pi \rightarrow \pi^*$ transition at 24 000(sh) cm^{-1}. The spectrum of $[CuA^1L^5]^+$ has bands at 48 000, 42 000(sh), 34 800(sh), 33 200, 32 000, 23 500(sh) cm^{-1} and shows all the $\pi \rightarrow \pi^*$ bands of $[CuA^1_2]^{2+}$ and $[CuL^5_2]$ without any significant shift.

Thus, although there is metal-ligand π interaction in the binary complexes, there is no significant change in the π orbital energies due to mixed-ligand complex formation. This indicates that in these complexes there is no significant inter-ligand π interaction through metal $d\pi$ orbitals.

The visible spectra of all these complexes show a broad band around 16 000 cm^{-1}. This broad band is a combination of $^2A_{1g} \leftarrow {}^2B_{1g}$, $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_{1g} \leftarrow {}^2B_{1g}$ transitions,[156] corresponding to D_{4h} symmetry, most probably square planar in these cases.

Further, a glance at the d-d transition bands of $[CuA^1_2]^{2+}$ 14 000 cm^{-1}, $[CuL^1_2]$ 13 500 cm^{-1}, $[CuL^5_2]$ 12 900 cm^{-1}, $[CuA^1L^1]^+$ 16 000 cm^{-1} and $[CuA^1L^5]^+$ 15 500 cm^{-1} clearly shows that the crystal field in the mixed-ligand complex is greater than in the binary complexes.

Normally in a mixed-ligand complex there should be creation of an average field compared to the fields in the binary complexes. The deviation from this expectation can be due to special behaviour of dipyridyl and similar tertiary diamines which accept the metal $d\pi$ electrons, thus reducing the electron density over the metal ion. The second ligand, therefore, is repelled to a lesser extent in the mixed-ligand complex as compared to the binary complexes. In other words, the second ligand can create a stronger field in the ternary complex and this is responsible for the shift of d-d transition to a higher energy region in the mixed-ligand complex.

Thus, the stabilization of the ternary complex $[CuAL]^+$ is due to the reduction in the repulsion between the ligand π electrons and the metal $d\pi$ electrons, with no significant inter-ligand π interaction.