Studies of Some Ternary Complexes of Copper(II) involving π-Bonding Ligands. Part 2 †

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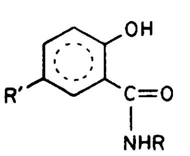
The proton–ligand formation constants of HL, formation constants of the binary complexes $[CuL]^+$ and $[CuL_2]$, and formation constants of the ternary complexes $[CuAL]^+$, where A = 2,2′-bipyridyl, 1,10-phenanthroline, 2-(2′-pyridyl)benzimidazole, or 2-(2′-pyridyl)imidazoline, and L = salicylamide ion, salicylanilide ion, 5-bromosalicylamide ion, or 5-bromosalicylanilide ion have been determined in dioxan–water (1 : 1, v/v) solutions, and 0.2 mol dm^{-3} $Na[ClO_4]$, at 30 °C. The mixed-ligand stability constants $K_{CuAL'}$, for the reaction $[CuA]^{2+} + L^- \rightleftharpoons [CuAL]^+$, have been calculated by three methods, namely, graphical linear plot, computer calculations considering complete formation of $[CuA]^{2+}$ prior to the formation of $[CuAL]^+$, and also considering all possible species to be present in solution. The values so obtained are very similar and the concentration plot confirms that the major species present in the solution are only $[CuA]^{2+}$ and $[CuAL]^+$. The value of $\Delta \log K = \log K_{CuAL'} - \log K_{CuL}$ is positive, except when A is 2-(2′-pyridyl)imidazoline. The majority of the mixed-ligand complexes have been synthesized and characterized. Electronic spectra confirm that there is no signifcant interaction between the two ligands through the metal $d\pi$ orbitals in the mixed-ligand complexes. The greater stability of the ternary complexes may be due to a lowering of repulsion between metal $d\pi$ electrons and the ligand electrons in these compounds.

In the case of mixed-ligand complexes of the type [MAL], where A is a tertiary amine, it has been observed that the mixed-ligand formation constant K^{MA}_{MAL} is much greater [1] than expected from statistical considerations. This has been proposed to be due to a M $\longrightarrow$ bipyridyl π interaction.[1-3] For the complexes [CuAL], where L is a bidentate ligand co-ordinating through two oxygens, $\Delta \log K = \log K_{CuAL'} - \log K_{CuL}$ ($\log K_{CuAL'}$ is constant for the reaction $[CuA]^{2+} + L^- \rightleftharpoons [CuAL]^+$) is found to be positive.[2,4] Sigel and co-workers [5] indicated an inter-ligand π interaction in mixed-ligand complexes on the basis of e.s.r. and electronic spectral studies and attributed the additional stability increase of the mixed-ligand complex (benzene-1,2-diolato)(2,2′-bipyridyl)-copper(II) to the co-operative effect due to interaction of the π systems of the two ligands. Existence of π back-bonding in mixed-ligand complexes was also shown by Martin and Prados [6] by a circular dichroism study. The greater stability of the mixed-ligand complexes of copper(II) was explained by Griesser and Sigel [2] in terms of a Jahn–Teller effect.

However, it has been observed that an additional stabilization with consequent positive Δ log *K* occurs in ternary complexes [CuAL] even in cases where the second ligand (L) is only σ bonding, like malonate.[2,7]

In a previous study [8] of ternary complexes $[CuAL]^+$, where A = 2,2′-bipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2′-pyridyl)benzimidazole (A^3), or 2-(2′-pyridyl)imidazoline (A^4), and L = acetoacetanilide ion (L^1), acetoacet-*o*-anisidide ion (L^2), acetoacet-*o*-toluidide ion (L^3), or benzoylacetanilide ion (L^4), it has been shown that in the mixed-ligand complex, π interaction between ligands A and L through metal $d\pi$ orbitals is not significant even though both $[CuA_2]^{2+}$ and $[CuL_2]$ have a π interaction. It has been suggested that the positive value of Δ log *K* may be due to a lowering in repulsion between metal $d\pi$ electrons and ligand (L) electrons in the mixed-ligand complex. The stability constant $\log K_{CuAL'}$ was calculated by considering complete formation of $[CuA]^{2+}$ and assuming a single-step reaction for the mixed-ligand complex formation. Therefore, a modified Irving–Rossotti titration technique [3] was used which is essentially a graphical linear plot method as used in the determination of formation constants of binary complexes.

In order to see the effect of the presence of an aromatic ring in the secondary ligand (L) and the substitution over the aromatic ring on the mixed-ligand complex formation constant values, the present study of mixed-ligand complexes $[CuAL]^+$, where A = A^1, A^2, A^3, or A^4, and L = salicylamide (L^5), salicylanilide (L^6), 5-bromosalicylamide (L^7), or 5-bromosalicylanilide (L^8) anions, has been carried out. Formation constants have been determined in solution by graphical methods [3] and SCOGS (stability constants of generalized species) computer program,[9] and the solid complexes have also been isolated. The values of stability constants of β-ketoanilide (L^1—L^4) complexes studied earlier [8] have also been refined by computer technique. The secondary ligands selected in the present work have the structures shown below.



	L^5	L^6	L^7	L^8
R =	H	C_6H_5	H	C_6H_5
R′ =	H	H	Br	Br

EXPERIMENTAL

All the reagents used were of A.R. grade. The ligands A^3 and A^4 were prepared by a known method.[10] Bromination was carried out on L^5 and L^6 to obtain L^7 and L^8, respectively, using a mild brominating agent, *N*-bromosuccinimide. To a solution of L^5 or L^6 in dimethylformamide (dmf) (20 cm^3) was added a solution of *N*-bromosuccinimide in dmf

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† Part 1 is ref. 8.

($15\ cm^3$) in equimolar ratio. The mixture was stirred for an hour at room temperature and the clear solution was poured into ice-cold water ($300\ cm^3$). The resulting solid was filtered off, washed with water several times, and finally with alcohol. The compounds were recrystallized from light petroleum (b.p. 40—60 °C).

The proton–ligand formation constants of ligands L^5—L^8 and the formation constants of the binary complexes $[CuL]^+$ and $[CuL_2]$ were obtained in dioxan-water (1 : 1, v/v) solution and 0.2 mol dm^{-3} $Na[ClO_4]$ at 30 °C, using the Irving–Rossotti titration technique.[11,12] The formation constants of the ternary complexes $[CuAL]^+$ were determined by an extension [3] of the same technique (method 1 = m_1). An Elico pH 821 expanded-scale pH meter with an accuracy of ±0.01 pH units was used and pure nitrogen gas was bubbled through the solution during titration.

TABLE 1

Stability constants of β-ketoanilide derivatives (L^1—L^4) in dioxan–water (1:1, v/v) medium, I = 0.1 mol dm^{-3} ($Na[ClO_4]$) at 30 °C

				log $K_{CuAL'}$					
				A^1		A^2		A^3	A^4
L	K_1^H	log β_{CuL}	log β_{CuL_2}	m_2	m_3	m_2	m_3	m_2	m_2
L^1	11.60	8.86	16.56	9.62	9.66	9.23	9.31	9.26	8.71
L^2	11.40	9.10	16.09	9.88	9.91	9.16	9.26	9.13	8.49
L^3	11.30	8.57	15.74	9.34	9.37	8.90	8.96	9.02	8.43
L^4	10.40	8.15	15.24	9.30	9.33	8.60	8.67	8.65	8.27

The formation constants of all the above complexes were subjected to refinement using the computer program SCOGS. This is a powerful physical technique, capable of calculating simultaneously or individually, association constants for any of the species formed in systems containing up to two metals and two ligands, provided that the degree of formation is pH-dependent. The sub-routine COGSNR (concentration of generalized species by the Newton–Raphson method) was used repeatedly to determine the concentrations of all the species in the solution. The computer output provides a list of concentration of each species selected up to a total number of twenty species. The method was used in two ways: (i) by considering the species present in the solution to be LH, L^-, $[CuA]^{2+}$, and $[CuAL]^+$ (method 2 = m_2) and (ii) taking into account all possible species to be present in the solution, *i.e.* HL, L^-, H_2A^{2+}, HA^+, A, $[CuL]^+$, $[CuL_2]$, $[CuA]^{2+}$, $[CuA_2]^{2+}$, and $[CuAL]^+$ (method 3 = m_3).

The stability constants of proton–ligands, and binary metal–ligand and mixed-ligand complexes were refined in steps. The K_1^H and K_2^H values were refined first and these values were treated as fixed parameters while refining the binary complex formation constants, log β_{CuL} and log β_{CuL_2}. Finally, only the mixed-ligand formation constants were subjected to refinement, while the refined values of all other constants were maintained as fixed parameters. The stepwise refinement gives proper convergency for all the formation constant values.

The calculations of mixed-ligand formation constants were performed in the pH range 4—6 and hence hydroxo-complex formation was not considered.

The refined values of the proton–ligand and binary metal–ligand formation constants obtained by computer technique and mixed-ligand complex stability constants of L^1—L^4 obtained by m_2 and m_3 are presented in Table 1. Refined proton–ligand, binary metal–ligand complex, and ternary complex stability constants of L^5—L^8 with A = A^1 and A^2 by all the three methods (m_1, m_2, and m_3) are presented in Table 2. However, in the cases of $[CuA^3L]^+$ and $[CuA^4L]^+$ calculation of mixed-ligand stability constants considering all possible species (m_3) could not be done. This is because the formation of $[CuA^3]^{2+}$ and $[CuA^4]^{2+}$ is complete at very low pH, and hence log β_{CuA^3} and log β_{CuA^4} values could not be determined by the pH-metric method. The formation constants were, therefore, determined only by presuming complete formation of $[CuA]^{2+}$ by m_1 and m_2, and the values are presented in Table 3.

Isolation of Mixed-ligand Complexes.—The mixed-ligand complexes $[CuAL][ClO_4]$ (A = A^1, A^2, or A^3; L = L^5, L^6, or L^7) were prepared as follows. To 0.002 mol dm^{-3} copper acetate in a water–ethanol mixture ($25\ cm^3$) were added equimolar quantities of A and L together in a water-ethanol mixture ($25\ cm^3$). The solution was refluxed for 10 min, and then 0.1 mol dm^{-3} aqueous sodium perchlorate was added until the precipitation was complete. The solid was filtered off and washed with warm ethanol. It was dried and analysed for all elements, and characterised by thin-layer chromatography (t.l.c.), conductance, and spectral studies (Table 4).

Spectral Measurements.—Electronic spectra of the compounds in dioxan–water (1 : 1, v/v) solution were obtained using a recording spectrophotometer SPECORD UV-VIS of Carl Zeiss Jena and 1-cm quartz cells. Solutions of 10^{-4} and 10^{-2} mol dm^{-3} were used for u.v. and visible regions respectively. Spectra of free ligands, of synthesized mixed-ligand complexes, of Cu^{II} + A + L mixed in a 1 : 1 : 1 mol ratio

TABLE 2

Stability constants of salicylamide derivatives (L^5—L^8) in dioxan–water (1:1, v/v) medium, I = 0.2 mol dm^{-3} ($Na[ClO_4]$) at 30 °C

				log $K_{CuAL'}$							
				A^1				A^2			
L	K_1^H	log β_{CuL}	log β_{CuL_2}	m_1	m_2	m_3	Δ log K	m_1	m_2	m_3	Δ log K
L^5	9.23	5.79	9.90	6.58	6.59	6.61	+0.82	6.61	6.59	6.67	+0.88
L^6	8.56	4.95	8.88	5.58	5.59	5.62	+0.67	5.64	5.66	5.73	+0.78
L^7	7.86	4.87	8.17	5.47	5.08	5.10	+0.23	5.46	5.34	5.40	+0.53
L^8	7.59	4.48	8.45	4.97	4.95	4.97	+0.49	4.87	4.79	4.84	+0.36

and binary complexes $[CuA_2]^{2+}$ and $[CuL_2]$ prepared by direct mixing of $CuCl_2$ and the ligands in the required proportion are presented in Tables 5 and 6.

TABLE 3

Ternary system stability constants of mixed-ligand complexes [CuAL] in dioxan–water (1 : 1, v/v) medium, $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$) at 30 °C

	$\log K_{CuAL'}$					
	A^3			A^4		
L	m_1	m_2	$\Delta \log K$	m_1	m_2	$\Delta \log K$
L^5	6.74	6.74	+0.95	5.98	5.95	+0.21
L^6	5.83	5.85	+0.90	5.14	5.00	+0.05
L^7	5.80	5.85	+0.98	4.91	4.83	−0.04
L^8	5.30	5.31	+0.83	4.12	3.95	−0.53

TABLE 4

Analytical and conductance data

	Analyses [a] (%)				Λ [b]/Ω^{-1} cm^{-2} mol^{-1}
Compound	Cu	N	C	H	
$[CuA^1L^5][ClO_4]$	13.8 (13.9)	8.9 (9.2)	44.5 (44.8)	3.00 (3.10)	98.00
$[CuA^1L^6][ClO_4]$	12.2 (12.0)	7.9 (7.9)	51.7 (51.9)	3.30 (3.40)	101.00
$[CuA^1L^7][ClO_4]$	12.0 (11.9)	8.3 (7.9)			111.25
$[CuA^2L^5][ClO_4]$	13.1 (13.3)	8.5 (8.8)	47.3 (47.6)	2.95 (2.90)	109.23
$[CuA^2L^6][ClO_4]$	11.1 (11.4)	8.0 (8.6)	54.5 (54.0)	3.50 (3.05)	99.50
$[CuA^2L^7][ClO_4]$	11.2 (11.4)	7.9 (7.5)	40.3 (40.8)	2.60 (2.30)	101.50
$[CuA^3L^5][ClO_4]$	12.5 (12.9)	11.4 (11.3)			106.25
$[CuA^3L^6][ClO_4]$	11.1 (11.1)	9.7 (9.8)			98.75

[a] Calculated values are given in parentheses. [b] In methanol.

TABLE 5

Electronic spectral band energies (cm^{-1}) and absorption coefficients (log ε) * of free ligands and binary complexes in dioxan–water (1 : 1, v/v) medium

Compound	λ (log ε)
A^1	47 500, 42 400 (4.15), 35 200 (4.18)
A^2	48 300, 43 800 (4.05), 37 600 (4.19)
A^3	48 700, 45 000 (4.27), 41 500 (4.20), 32 300 (4.43)
$[CuA^1{}_2]^{2+}$	48 000, 42 000 (4.60), 33 500 (4.56), 32 300 (4.51), 13 500 (2.79)
$[CuA^2{}_2]^{2+}$	48 000, 44 200 (5.09), 36 800 (4.81), 34 000 (sh) (4.28), 13 500 (2.75)
$[CuA^3{}_2]^{2+}$	48 500, 45 000 (4.28), 41 000 (4.31), 32 000 (sh) (4.00), 31 000 (4.32), 13 200 (2.53)
L^5	47 100, 42 300 (4.05), 33 000 (3.70)
L^6	48 200, 36 800 (4.09), 32 500 (sh) (3.96)
L^7	48 000, 41 000 (sh) (4.00), 31 800 (3.69)
L^8	48 000, 36 200 (4.00), 32 000 (sh) (3.90)
$[CuL^5{}_2]$	47 200, 42 000 (4.32), 33 000 (4.02), 23 800 (sh) (2.07), 12 900 (1.89)
$[CuL^6{}_2]$	48 000, 37 000 (4.39), 32 000 (sh) (4.29), 23 000 (sh) (2.10), 12 800 (1.90)
$[CuL^7{}_2]$	48 000, 41 200 (sh) (4.38), 31 800 (3.90), 23 000 (sh) (2.01), 12 500 (1.80)
$[CuL^8{}_2]$	47 500, 36 000 (4.40), 31 500 (sh) (4.10), 22 500 (sh) (2.04), 12 000 (1.83)

* Units of ε are dm^3 mol^{-1} cm^{-1}.

TABLE 6

Electronic spectral band energies (cm^{-1}) and log ε values of mixed-ligand complexes in dioxan–water (1 : 1, v/v) medium

Compound	λ (log ε)
$[CuA^1L^5]^+$	47 100, 42 000 (sh) (4.43), 34 500 (sh) (4.20), 33 300 (4.32), 32 300 (4.30), 24 000 (sh) (2.51), 16 000 (1.90)
$[CuA^1L^6]^+$	48 000, 42 000 (sh) (4.43), 33 500 (4.36), 32 300 (4.34), 23 300 (sh) (2.45), 15 900 (1.90)
$[CuA^1L^7]^+$	48 000, 43 000 (4.63), 40 000 (4.30), 33 500 (4.38), 32 300 (4.34), 23 500 (sh) (2.49), 16 000 (1.85)
$[CuA^1L^8]^+$	47 500, 42 000 (4.60), 35 000 (sh) (4.41), 33 200 (4.33), 32 000 (4.30), 23 000 (sh) (2.44), 15 500 (1.85)
$[CuA^2L^5]^+$	48 000, 43 800 (4.66), 36 600 (4.49), 34 000 (sh) (4.23), 23 800 (sh) (2.45), 15 800 (1.78)
$[CuA^2L^6]^+$	48 000, 45 000 (4.62), 36 600 (4.53), 34 000 (sh) (4.28), 23 300 (sh) (2.51), 15 800 (1.78)
$[CuA^2L^7]^+$	48 000, 45 000 (4.75), 36 700 (4.54), 34 000 (sh) (4.26), 23 300 (sh) (2.53), 15 300 (1.90)
$[CuA^2L^8]^+$	48 000, 44 000 (4.70), 36 000 (4.54), 34 000 (sh) (4.29), 23 300 (sh) (2.52), 15 500 (1.85)
$[CuA^3L^5]^+$	48 000, 45 300 (4.57), 41 300 (sh) (4.46), 34 000 (sh) (4.20), 30 000 (4.32), 23 300 (sh) (2.42), 15 500 (1.85)
$[CuA^3L^6]^+$	48 000, 45 000 (4.53), 41 000 (4.48), 36 000 (sh) (4.38), 31 000 (4.42), 23 400 (sh) (2.42), 15 500 (1.81)
$[CuA^3L^7]^+$	48 000, 41 000 (sh) (4.45), 35 000 (sh) (4.11), 29 800 (4.32), 23 000 (sh) (2.45), 15 300 (1.80)
$[CuA^3L^8]^+$	48 000, 45 000 (4.40), 41 000 (sh) (4.45), 36 000 (4.20), 31 300 (4.01), 23 000 (sh) (2.48), 15 500 (1.81)

RESULTS AND DISCUSSION

Stability Constants.—The proton–ligand formation constants $K_1{}^H$ and binary metal–ligand formation constants, log β_{CuL} and log β_{CuL}, refined by the computer program, for the β-ketoanilides (L^1—L^4) are nearly equal to the values reported earlier.[13]

In cases where L = salicylamide derivatives (L^5—L^8), the refined values of $K_1{}^H$, log β_{CuL}, log β_{CuL_2}, and log $K_{CuAL'}$ obtained by the computer technique are nearly equal to the values obtained graphically. The $K_1{}^H$ value of L^5 is lower than that of L^6. This is because the anilide ring in L^6 reduces the basicity due to electron withdrawal and resonance. As expected, the $K_1{}^H$ values of L^7 and L^8 are reduced due to substitution of a bromine atom. This substituent, being electron withdrawing in nature, facilitates the proton dissociation.

The binary system stability constants (log β_{CuL} and log β_{CuL_2}) are in agreement with the basicities of the ligands. However, the values are lower than log $K^{Cu}_{Cu(Hsal)}$ (Hsal = salicylaldehyde).[14] This probably means that in these complexes the co-ordination takes place from phenolic oxygen and amide/anilide nitrogen rather than phenolic oxygen and amide/anilide oxygen. The titration curves are, however, smooth indicating that the co-ordination sites remain the same over the whole pH range; but this may not be conclusive evidence. The i.r. spectral data of the solid complexes (discussed later) confirm that the co-ordination is from both the oxygen atoms. Thus the co-ordination sites in both Hsal and salicylamide (Hsalam) complexes being similar, the lower stability of [Cu(Hsalam)] than [Cu(Hsal)] shows that the Cu–L π interaction in this complex is less than in case of [Cu(Hsal)].

It is interesting to observe that in the ternary complexes $[CuAL]^+$, where L = L^1—L^8, the values of the formation constants obtained by the use of the extension of the Irving–Rossotti titration technique [3] presuming that the formation of the complex is in steps, $[CuA]^{2+} + L^- \rightleftharpoons [CuAL]^+$, and the values obtained by using the two computer methods are nearly equal for all the ligands L^1—L^8. This shows that the presumption that $[CuA]^{2+}$ formation is almost complete in the lower pH range and L^- combines with $[CuA]^{2+}$ forming $[CuAL]^+$ is valid. This is further confirmed by observing the plot of the concentration of various species (as percentage of total Cu^{2+} present) against pH as shown in the Figure. It is observed that in the lower pH range (1—3), Cu^{2+} and $[CuA]^{2+}$ are the major species and in the higher pH range (3—7) the major species are $[CuA]^{2+}$ and $[CuAL]^+$, totalling almost 100%. The concentrations of the other species $[CuA_2]^{2+}$, $[CuL]^+$, and $[CuL_2]$ are negligible. Such observation was also made by Griesser and Sigel [2] in the case of other [CuA(O–O)] complexes (O–O = *OO*-bonded ligand). Thus this study validates the use of the extension of the Irving–Rossotti titration technique for the determination of the formation constant values of the ternary complexes containing bipyridyl or similar diamines and secondary ligands co-ordinating through two oxygen atoms.

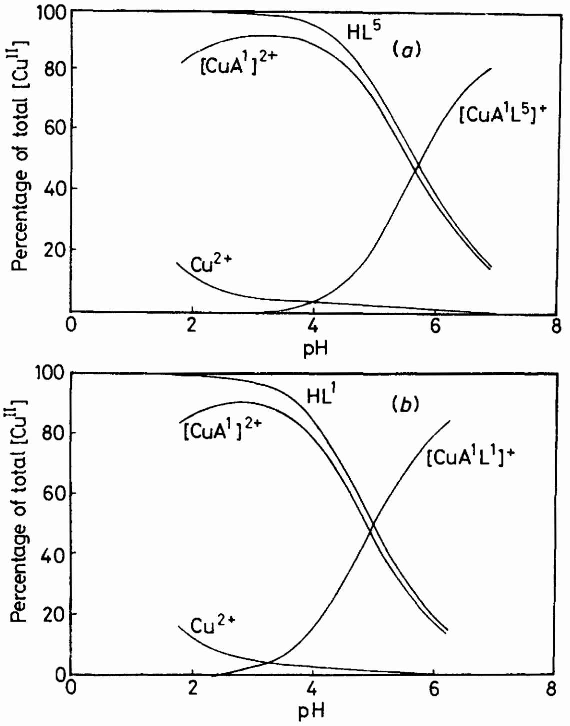

FIGURE Variation of concentration of different species with pH: (*a*) $Cu^{II} + A^1 + L^5$ system and (*b*) $Cu^{II} + A^1 + L^1$ system

In the case of $[CuAL]^+$ complexes ($L = L^5$—L^8), it is observed that $\Delta \log K$ is positive except when $A = A^4$. The order of formation constants of the mixed-ligand complexes of different tertiary diamines with the series of secondary ligands (L^5—L^8) is $[CuA^3L]^+ > [CuA^1L]^+ \simeq [CuA^2L]^+ > [CuA^4L]^+$. The order is different from that for the β-ketoanilide (L^1—L^4) complexes. However, the order is the same as for the mixed-ligand complexes $[CuAL]^+$, where L is a σ-bonding ligand like malonic acid, amino-acid, or amine.[15] This is further support to the contention that Cu–L π interaction does not contribute much to the stability of these complexes, for $L = L^5$—L^8.

The extra stabilization of these mixed-ligand complexes cannot, therefore, be explained by considering a π interaction between the tertiary amines and the secondary ligand orbitals through metal *d*π orbitals. The alternative explanation, in terms of electron repulsion as extended by us,[8] is applicable in these cases. In the formation of the binary complexes, there is electron repulsion between metal-ion *d*π electrons and the electrons present in the ligand, L^-. However, in the ternary complexes, the repulsion is reduced due to the back donation of metal *d*π electrons to the tertiary amine molecules. Due to the increased electron density over the ligand L^-, co-ordinating through O^- and amide/anilide oxygen, with a lone pair of electrons on the N atoms, repulsion is greater in the binary complex and release of the repulsion in the ternary complex makes $\Delta \log K$ positive.

Salicylanilide complexes have less positive $\Delta \log K$ values than salicylamide complexes. This may be because of the delocalization of the anilide nitrogen lone pair over the aromatic ring to which it is attached. However, the difference of 0.1 log unit is too small to be interpreted in detail. In the case of bromo-derivatives the effect is greater. The $\Delta \log K$ values for the L^7 and L^8 complexes are less positive than those of the L^5 and L^6 complexes, respectively, due to the electron withdrawal from the phenyl ring by the substituent bromine atom. This is in keeping with the observation made by Sigel *et al.*[16] in mixed-ligand complexes of substituted benzene-1,2-diol with Cu^{II} and 2,2′-bipyridyl, that electron-withdrawing substituents lower the stability whereas the electron-donating substituents increase it. This observation is interesting because this shows the effect of groups not directly linked to the metal ion on the stability of the ternary complexes. This effect is similar to the role of substituent groups, not directly linked to the metal ion, in increasing the efficiency of metallo-enzymes.

The dependence of the $\Delta \log K$ values on the π-accepting properties of the tertiary base has been observed by Sigel.[17,18] In these complexes also, it is observed that as the $Cu \longrightarrow A$ π interaction goes on increasing, $\Delta \log K$ becomes more positive. The ligand A^4 co-ordinates *via* one pyridine nitrogen and one imidazoline nitrogen. In this case, π interaction is possible only with the pyridine ring as imidazoline is a saturated ring with no delocalized π-electron cloud. Therefore, it is less π-interacting than A^1, A^2, or A^3 and these ternary complexes are less stable than other ternary complexes, resulting in negative $\Delta \log K$ values. This fact is further confirmed by comparing the electronic spectra of the mixed-ligand complexes with the binary complexes.

T.l.c. of all the complexes using ethanol as solvent showed 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 data of the complexes correspond to 1 : 1 electrolytes, showing the presence of ionic ClO_4^-. Infrared spectra confirm their ionic nature; there is a band at *ca.* 1 100 cm^{-1} corresponding to the asymmetric stretch ν_{asym}(Cl–O). The band at *ca.* 920 cm^{-1} corresponding to ν_{sym}(Cl–O) is absent and this supports the tetrahedral structure of ClO_4^-. This indicates that the perchlorate is outside the co-ordination sphere. Bands at *ca.* 3 400 cm^{-1} are absent indicating the absence of water molecules in the compounds and dissociation of hydrogen from –OH after complexation. There is also a band observed at *ca.* 3 300 cm^{-1} correponding to ν(N–H) stretching of the amide/anilide group. The fact that there is no significant change in the ν(N–H) stretching frequency of the free ligands and in the mixed-ligand complexes is an adequate confirmation that the co-ordination is not from nitrogen of the amide/anilide. The band at *ca.* 1 600 cm^{-1} corresponds to the ν(C $\overset{...}{-}$ O) stretch of the co-ordinated carbonyl group.

Electronic Spectra.—The u.v. spectra of the synthesized ternary complexes are superimposable over the spectra of Cu^{II} + A + L (1 : 1 : 1 mixture). This shows that the ternary complex is formed immediately in solution.

The specific bands are discussed in the case of $[CuA^1L^5]^+$ complex. 2,2′-Bipyridyl shows bands at 47 500, 42 400, and 35 200 cm^{-1}. The high-intensity bands in the lower energy region correspond to a $\pi \longrightarrow \pi^*$ transition. $[CuA^1_2]^{2+}$ shows bands at 48 000, 42 000, 33 500, and 32 300 cm^{-1}. The appearance of a new band (with a high value of log ε) and the shift in the $\pi \longrightarrow \pi^*$ transition shows that there is interaction between the π orbitals of Cu^{II} and those of the 2,2′-bipyridyl molecule. The bands in salicylamide occur at 47 100, 42 300, and 33 000 cm^{-1}, having high intensity; the low-energy bands correspond to a $\pi \longrightarrow \pi^*$ transition. In $[CuL^5_2]$, besides bands at 47 200, 42 000, and 33 000 cm^{-1}, an additional band is observed at 23 800 (sh) cm^{-1} (log $\varepsilon = 2.07$). This indicates that there is π interaction between Cu^{II} and salicylamide π orbitals and the band at 23 800 (sh) cm^{-1} corresponds to a Cu $\longrightarrow$ L^5 $\pi \longrightarrow \pi^*$ transition.

The mixed-ligand complexes were studied in solution at pH *ca.* 6. It can be seen from the Figure that around this pH the concentration of $[CuAL]^+$ is *ca.* 90%. The concentration of other species is very low and they will have low absorptions. Hence the absorption spectral bands are due to the mixed-ligand species only. The spectrum of $[CuA^1L^5]^+$ shows high-intensity bands at 47 100, 42 000 (sh), 34 500 (sh), 33 300, 32 300, and 24 000 (sh) cm^{-1} and thus shows all the $\pi \longrightarrow \pi^*$ bands of $[CuA^1_2]^{2+}$ and $[CuL^5_2]$ without any significant shift in energy.

Thus, although there is a metal–ligand π interaction in the binary complexes, there is no significant change in the π-orbital energies due to mixed-ligand complex formation. Absence of inter-ligand π interaction in 8-quinolinolato(arylhydroxycarboxylato)copper(II) complexes was shown by Schulman *et al.*[19] through a similar electronic spectral study. This indicates that in these complexes also, there is no significant inter-ligand π interaction through metal $d\pi$ orbitals.

Further, a glance at the *d–d* transition bands of $[CuA^1_2]^{2+}$ (13 500 cm^{-1}), $[CuL^5_2]$ (12 900 cm^{-1}), and $[CuA^1L^5]^+$ (16 000 cm^{-1}) clearly shows that the crystal field in the mixed-ligand complex is greater than in the corresponding binary complex. 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 2,2′-bipyridyl 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 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 bands to higher energy in the mixed-ligand complex.

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