Studies of Some Ternary Complexes of Copper(II) involving π-Bonding Ligands

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The formation constants of complexes of the type $[CuAL]^+$, where A = 1,10-phenanthroline, 2-(2′-pyridyl)benzimidazole, or 2-(2′-pyridyl)imidazoline and = $MeCOCH_2CONPh^-(L^1)$, $MeCOCH_2CONC_6H_4OMe\text{-}o^-(L^2)$, $MeCOCH_2CONC_6H_4Me\text{-}o^-(L^3)$, or $PhCOCH_2CONPh^-(L^4)$, have been determined in dioxan–water (1 : 1 v/v) solutions and 0.1 mol dm^{-3} $Na[ClO_4]$ at 30 °C. The value of $\Delta \log K = \log K_{MAL}' - \log K_{ML}$ is positive (K_{MAL}' is for MA + L $\rightleftharpoons$ MAL) except when A is 2-(2′-pyridyl)imidazoline. Ultraviolet spectral studies of these complexes have also been carried out and show that there is no significant interaction between the two ligands through the metal d_π orbitals in the mixed-ligand complexes. Positive Δ log *K* values may be due to a lowering in repulsion between metal d_π electrons and ligand π electrons in the mixed-ligand complex.

WHEN a metal ion, M, is mixed with two ligands, A and L, the reaction can take place in three different ways, equations (1)—(3) (charges omitted for clarity). In the case of mixed-ligand complexes where A is 2,2′-bipyridyl (A^1), the reaction follows equation (2). The observed formation constant, K_{MAL}', is higher than expected from statistical considerations.[1] This has been explained [2,3] as being due to a M→bipyridyl π interaction which retains the same concentration of electrons around the metal ion in $[MA^1]^{2+}$ as in M^{2+}. Thus, the tendency of $[MA^1]^{2+}$ to bind with another ligand is not significantly lower than that of M^{2+} and hence when A = bipyridyl Δ log *K* [log K_{MAL}' − log K_{ML}] has a small negative value.

$$M + A + L \overset{K_{MAL}}{\rightleftharpoons} MAL \qquad (1)$$

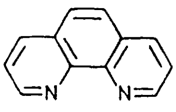
$$M + A \overset{K_{MA}}{\rightleftharpoons} MA; \quad MA + L \overset{K_{MAL}'}{\rightleftharpoons} MAL \qquad (2)$$

$$M + L \overset{K_{ML}}{\rightleftharpoons} ML; \quad ML + A \overset{K_{MAL}''}{\rightleftharpoons} MAL \qquad (3)$$

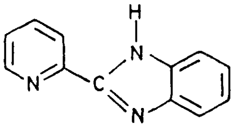
In the case of $[CuA^1L]^+$ complexes, where L is an anion of catechol (H_2cat),[2] β-diketone,[4] *o*-hydroxy-aromatic aldehyde or ketone,[5] or β-ketoanilide,[6] co-ordinating through two oxygen atoms, Δ log *K* is found to be positive. It has also been shown [5] that even when L is an anion of salicylaldimine, co-ordinating through one oxygen and one nitrogen, log K_{CuAL}' is equal to log K_{CuL}.

Sigel and co-workers [7] explained the greater stability of the $[CuA^1(cat)]$ complex by considering the existence of a co-operative effect due to interaction of the π systems of the two ligands, A^1 and cat, through the *d* orbitals of the metal ion. This mutually stabilizing effect of two ligands makes the ternary complex more stable. The existence of such interligand π interaction in the $[CuA^1(cat)]$ complex has been shown,[7] although not conclusively, by e.s.r. spectral studies. Similar explanations can be extended to the other $[CuA^1L]^+$ complexes, where L is an anion of β-diketone, aromatic *o*-hydroxy-aldehydes or -ketones, or salicylaldimine.

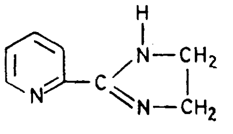
In the present work a study of complexes of the type $[CuAL]^+$, where A = 1,10-phenanthroline (A^2), 2-(2′-pyridyl)imidazoline (A^4), 2-(2′-pyridyl)benzimidazole (A^3), and L = acetoacetanilide ion (L^1), acetoacet-*o*-anisidide ion (L^2), acetoacet-*o*-toluidide ion (L^3), or benzoylacetanilide ion (L^4), has been carried out to determine the value of Δ log *K* and to see if there is any interligand π interaction through metal d_π orbitals. The primary ligands (A) used are similar to bipyridyl in co-ordinating through two N atoms and having delocalized π electrons.



A^2



A^3



A^4

EXPERIMENTAL

All the reagents used were of A.R. grade, except for 2-(2′-pyridyl)imidazoline and 2-(2′-pyridyl)benzimidazole which were prepared by a known method.[8] The proton–ligand and metal–ligand formation constants were determined in dioxan-water (1 : 1 v/v) solutions and 0.1 mol dm^{-3} $Na[ClO_4]$ at 30 °C.

The values of $\bar{n}_H$, pK_1^H, $\bar{n}$, pL, log K_1, and log K_2 were calculated by carrying out normal Irving–Rossotti titrations.[9,10] The formation constants of ternary complexes were determined by using an extension of the Irving–Rossotti titration technique.[3] The values of $\bar{n}$ and pL were calculated in the pH range 4—6.5 using the same equations as for binary systems.[10]

At $\bar{n} = 0.5$ in the formation curve, pL = log K_{MAL}'. More precise values were obtained by plotting pL at each point against log $[(1 - \bar{n})/\bar{n}]$ and obtaining a straight line.

At each point on the straight line, $\log K_{\mathrm{MAL}}' = \mathrm{pL} - \log[(1 - \bar{n})/\bar{n}]$. The average values have been recorded (Table 1). In each individual measurement, pH values were corrected for the dioxan medium, using the method adopted by Van Uitert and Haas.[11]

Isolation of Mixed-ligand Complexes.—The mixed-ligand complexes $[\mathrm{CuAL}][\mathrm{ClO_4}]$, where A = $\mathrm{A^1}$ or $\mathrm{A^2}$ and L = $\mathrm{L^1}$, $\mathrm{L^2}$, $\mathrm{L^3}$, or $\mathrm{L^4}$, were prepared as reported[12] earlier. The compound $[\mathrm{CuA^3L}][\mathrm{ClO_4}]$ was prepared as follows. To 0.002 mol $\mathrm{dm^{-3}}$ copper acetate in alcohol (25 $\mathrm{cm^3}$) was added a mixture of equimolar quantities of tertiary amine and β-ketoanilide in an alcohol–water (25 $\mathrm{cm^3}$) mixture. The solution was refluxed for 15—20 min, and then a 0.1 mol $\mathrm{dm^{-3}}$ solution of sodium perchlorate in water was added till the precipitation was complete. The solid was filtered off, washed with water, and finally with 50% ethanol–water mixture. It was dried, analysed for elements, and characterized by conductance, thin-layer chromatography, and spectral studies (Table 2).

Table 1

Ternary system stability constants of $\mathrm{Cu^{II}}$ in $\mathrm{Na[ClO_4]}$ (I = 0.1 mol $\mathrm{dm^{-3}}$)

		$\log K_{\mathrm{MAL}}'$ ($\Delta \log K$)		
L	$\log K_{\mathrm{ML}}$ *	$\mathrm{A^2}$	$\mathrm{A^3}$	$\mathrm{A^4}$
$\mathrm{L^1}$	8.86	9.23 (0.37)	9.20 (0.34)	8.68 (−0.18)
$\mathrm{L^2}$	8.84	9.26 (0.42)	9.10 (0.26)	8.46 (−0.38)
$\mathrm{L^3}$	8.30	8.91 (0.61)	8.99 (0.69)	8.33 (0.03)
$\mathrm{L^4}$	8.32	8.56 (0.24)	8.65 (0.33)	8.22 (−0.10)

* Values taken from ref. 6.

Table 2

Analytical and conductance data

	Analyses (%) *				Λ/Ω^{-1} $\mathrm{cm^2\ mol^{-1}}$ in methanol
Compound	Cu	N	C	H	
$[\mathrm{CuA^3L^1}][\mathrm{ClO_4}]$	12.1 (11.9)	12.0 (10.5)	49.7 (49.4)	3.95 (3.55)	101.23
$[\mathrm{CuA^3L^3}][\mathrm{ClO_4}]$	11.5 (11.6)	10.5 (10.2)	50.8 (50.4)	4.05 (3.85)	98.18
$[\mathrm{CuA^3L^2}][\mathrm{ClO_4}]$	11.3 (11.3)	10.0 (9.9)			112.42
$[\mathrm{CuA^3L^4}][\mathrm{ClO_4}]$	10.5 (10.7)	9.9 (9.4)			105.15

* Calculated values are given in parentheses.

Spectral Measurements.—The spectra were recorded on a Carl Zeiss SPECORD u.v.–visible spectrometer with 1 cm quartz cells using ethanol as solvent. Solutions of concentration 10^{-4} and 10^{-2} mol $\mathrm{dm^{-3}}$ were used for u.v. and visible regions respectively.

Spectra of the synthesized mixed-ligand complexes, of $\mathrm{Cu^{II}}$ + A + L mixed in a 1 : 1 : 1 mol ratio of ligands A and L, and binary complexes $[\mathrm{CuA}]^{2+}$, $[\mathrm{CuA_2}]^{2+}$, $[\mathrm{CuL}]^+$, and $[\mathrm{CuL_2}]$, prepared by direct mixing of $\mathrm{CuCl_2}$ and the ligand in the required proportions, were all recorded in ethanol solutions (Tables 3 and 4).

RESULTS AND DISCUSSION

Stability Constants.—The modified Irving–Rossotti titration technique presumes the mixed-ligand complex formation reaction to take place according to equation (2). All the primary ligands (A) form 1 : 1 complexes with $\mathrm{Cu^{2+}}$ at low pH. These remain as stable species up to pH 6.5 where hydrolysis starts. All the secondary ligands (L) combine with $[\mathrm{CuA}]^{2+}$ in the pH range 4—6.5. Thus, it is presumed that all the $\mathrm{Cu^{2+}}$ ions are converted into $[\mathrm{CuA}]^{2+}$ which then combines with the secondary ligand in the same way as the free metal ion. The value of $\bar{n}$ corresponds to the average number of ligands (L) bound to $[\mathrm{CuA}]^{2+}$. As in the binary systems pL = −log[L], where [L] is the concentration of the free-ligand ion L^{n-}.

Table 3

Electronic spectra ($\mathrm{cm^{-1}}$) of free ligands and binary complexes in ethanol

Compound	
$\mathrm{A^1}$	49 500, 42 200, 35 200
$\mathrm{A^2}$	49 200, 44 000, 37 800
$\mathrm{A^3}$	49 000, 41 300, 32 200
$[\mathrm{CuA^1}]^{2+}$	49 000, 41 000, 33 200, 32 000
$[\mathrm{CuA^1_2}]^{2+}$	49 000, 41 800, 34 000, 32 200
$[\mathrm{CuA^2}]^{2+}$	48 000, 44 200, 36 400, 34 000 (sh)
$[\mathrm{CuA^2_2}]^{2+}$	48 000, 44 000, 36 900, 34 000 (sh)
$[\mathrm{CuA^3}]^{2+}$	48 500, 41 300, 35 000, 31 000
$[\mathrm{CuA^3_2}]^{2+}$	48 500, 41 300, 32 000, 30 800
$\mathrm{L^1}$	49 000, 41 000
$\mathrm{L^2}$	48 000, 40 300, 35 000
$\mathrm{L^3}$	48 600, 41 600
$\mathrm{L^4}$	48 800, 40 600, 32 000
$[\mathrm{CuL^1}]^+$	49 000, 41 000, 33 000, 24 800 (sh), 12 500
$[\mathrm{CuL^1_2}]$	49 000, 41 000, 33 000, 24 800 (sh), 15 500
$[\mathrm{CuL^2}]^+$	48 000, 40 300, 34 800, 32 200, 23 500 (sh), 12 000
$[\mathrm{CuL^2_2}]$	48 000, 40 300, 34 800, 32 200, 24 000 (sh), 15 000
$[\mathrm{CuL^3}]^+$	48 600, 41 600, 34 800, 24 000 (sh), 12 000
$[\mathrm{CuL^3_2}]$	48 600, 41 600, 34 800, 24 000 (sh), 15 500
$[\mathrm{CuL^4}]^+$	48 800, 40 600, 30 200, 23 000 (sh), 12 500
$[\mathrm{CuL^4_2}]$	48 800, 40 600, 30 200, 23 000 (sh), 15 000

It has been shown[13] that for $[\mathrm{CuA^1L}]^+$ systems the values of stability constants obtained by the present method are in agreement with the values obtained by more precise methods which take account of all possible species at equilibrium and where calculations are per-

Table 4

Electronic spectra ($\mathrm{cm^{-1}}$) of mixed-ligand complexes in ethanol

Compound	
$[\mathrm{CuA^1L^1}]^+$	48 800, 40 300, 33 200, 32 200, 24 000 (sh), 16 000
$[\mathrm{CuA^1L^2}]^+$	48 800, 40 200, 33 400, 32 100, 23 500 (sh), 16 000
$[\mathrm{CuA^1L^3}]^+$	48 800, 41 000, 34 000, 32 000, 24 000 (sh), 16 000
$[\mathrm{CuA^1L^4}]^+$	48 800, 40 800, 33 200, 32 000, 30 000, 22 000 (sh), 16 000
$[\mathrm{CuA^2L^1}]^+$	48 800, 44 000, 36 400, 34 000 (sh), 23 000 (sh), 15 500
$[\mathrm{CuA^2L^2}]^+$	48 000, 44 400, 36 500, 34 000, 23 000 (sh), 15 500
$[\mathrm{CuA^2L^3}]^+$	48 200, 44 200, 36 600, 34 000 (sh), 23 500 (sh), 15 500
$[\mathrm{CuA^2L^4}]^+$	48 600, 44 000, 36 600, 33 800, 30 200, 22 000 (sh), 15 500
$[\mathrm{CuA^3L^1}]^+$	48 800, 41 000, 32 200, 29 800 (sh), 23 000 (sh), 15 500
$[\mathrm{CuA^3L^2}]^+$	48 800, 41 200, 34 000 (sh), 32 000, 22 000 (sh), 15 000
$[\mathrm{CuA^3L^3}]^+$	48 800, 41 000, 34 600, 30 400, 22 000 (sh), 15 500
$[\mathrm{CuA^3L^4}]^+$	48 500, 41 300, 32 000, 30 800, 22 000, 15 500

formed by computer programming. This confirms that the reaction is of type (2).

The proton–ligand stability-constant values show that β-ketoanilides are more basic, but form less stable complexes, than β-diketones. This may be due to there being less M→L π interaction in β-ketoanilide complexes. However, the values of the formation constants of the ternary complexes of β-ketoanilides are greater than those of the corresponding binary complexes except when A = 2-(2′-pyridyl)imidazoline. Thus, the value of Δ log *K* = log $K_{\mathrm{CuAL}}{}'$ − log K_{CuL} is positive when L = β-ketoanilide, whereas for L = β-diketone Δ log *K* is zero.[4] There is, therefore, greater stabilization of a ternary complex of the type $[\mathrm{CuAL}]^+$, where L = β-ketoanilide.

The extent of stabilization of the mixed-ligand complex should depend on the extent of π delocalization in $[\mathrm{CuA}]^{2+}$. The order of formation constants of the ternary complexes is $[\mathrm{CuA^1L}]^+ > [\mathrm{CuA^2L}]^+ \simeq [\mathrm{CuA^3L}]^+ > [\mathrm{CuA^4L}]^+$.

The stabilization of the above mixed-ligand complexes can be explained by considering the co-operative effect of π interaction of the two ligands through metal d_π orbitals as discussed [7] earlier.

Electronic Spectra.—In order to see the possibility of interligand π interaction through metal d_π orbitals, mixed-ligand complexes were isolated and studied. The analysis of compounds corresponds to the composition $[\mathrm{CuA^3L}][\mathrm{ClO_4}]$. Molar conductances of all the complexes correspond to 1 : 1 electrolytes, showing the presence of ionic $\mathrm{ClO_4}^-$. Infrared spectra confirm the 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 which supports the tetrahedral structure of $\mathrm{ClO_4}^-$. This indicates that the perchlorate is outside the co-ordination sphere.

The u.v. spectra of the synthesized ternary complexes are superimposable over the spectra of $\mathrm{Cu^{II}} + \mathrm{A} + \mathrm{L}$, a 1 : 1 : 1 mixture. This shows that the ternary complex is formed immediately in solution. The spectra are discussed for the representative case of the $[\mathrm{CuA^1L^1}]^+$ complex. Bipyridyl shows bands at 49 500, 42 200, and 35 200 cm^{-1}. The bands in the lower-energy region correspond to π→π* transitions. On co-ordination with metal ion, $[\mathrm{CuA^1}]^{2+}$ shows bands at 49 000, 41 000, 33 200, and 32 000 cm^{-1}. The appearance of a new band and the shift in the π→π* transition shows that there is interaction between the π orbitals of $\mathrm{Cu^{II}}$ and those of the bipyridyl 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 $[\mathrm{CuL^1}]^+$ the bands are observed 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 $\mathrm{Cu^{II}}$ and ligand π orbitals. The spectra of $[\mathrm{CuA^1}]^{2+}$ and $[\mathrm{CuL^1{}_2}]$ are similar to $[\mathrm{CuA^1}]^{2+}$ and $[\mathrm{CuL^1}]^+$ respectively.

The spectra of $[\mathrm{CuA^1L^1}]^+$ has bands at 48 800, 40 300, 33 200, 32 200, and 24 000(sh) cm^{-1}, showing all the transitions of $[\mathrm{CuA^1}]^{2+}$ and $[\mathrm{CuL^1}]^+$ without any significant shift. Thus, although there is metal–ligand interaction in $[\mathrm{CuA^1}]^{2+}$ and $[\mathrm{CuL^1}]^+$, there is no significant change in the π-orbital energies due to mixed-ligand complex formation. This raises doubt about the interligand π interaction.

An alternative explanation may be as follows. β-Diketones are known to form chelate rings with π delocalization and pseudo-aromatic character. This Cu–L π interaction results in greater stability of copper–β-diketone complexes. However, β-ketoanilides have an additional lone pair of electrons on the anilide nitrogen. Because of this increased π-electron density in the chelate ring, due to a nitrogen lone pair, there is repulsion between the metal and the ligand. The repulsion between the β-ketoanilide π electrons and the copper(II) d_π electrons is greater in the binary complex but is reduced in $[\mathrm{CuAL}]^+$ due to the delocalization of copper(II) d_π electrons over the tertiary amine π orbitals. This leads to a positive value of Δ log *K* in the $[\mathrm{CuAL}]^+$ complex, where L = β-ketoanilide.

Thus, the stabilization of the ternary complex $[\mathrm{CuAL}]^+$ is due to the reduction in the repulsion between the ligand π electrons and the metal d_π electrons, with no significant interligand π interaction.

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