Equilibrium Studies on Copper(II) Mixed Ligand Complexes Containing L-Arginine & L-Histidine, Histamine or Imidazole

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Potentiometric studies have been carried out to determine the multiple equilibria involved in copper(II)-L-arginine (A)-L-histidine, histamine or imidazole (B) mixed systems at 37°C and $I = 0.15$ mol dm^{-3} (NaClO$_4$). The protonation constants for L-arginine and its binary stability constant with copper(II) have been also obtained under identical conditions. Data treatment indicates the presence of CuAH, CuA$_2$H and CuA$_2$H$_2$ binary complexes in the copper(II)-L-arginine (A) binary system and the mixed species of stoichiometry CuABH, CuABH, CuAB, CuAB H or CuAB, in the mixed ligand systems. The results suggest an increased stability for the mixed complexes compared to the statistical constant data. The nature of coordination sites of the various complex species detected is discussed in terms of their stability constant data.

MANY biological processes, where the activity depends on enzymes possessing metal ion centres, owe their specific function to the formation of binary and mixed ligand complexes[1,2]. The recent alleviation of the symptoms of (a) Wilson's disease[3,4], a genetic illness causing severe impairment of copper(II) metabolism, by the administration of D-penicillamine or triethylenetetramine and (b) Menke's disease[4], a disease characterised by rapidly progressive cerebral degeneration and the existence of abnormal spirally twisted hair, by administering copper(II)-(L-histidine)$_2$ complex are the best examples of the in vivo interaction of transition metal ions with amino acids. Thus, in order to relate the actual in vivo interaction between metal ions and body proteins, in recent years considerable attention has been paid[1-11] to the studies of binary and mixed ligand complexes. Investigations in this direction on the metal complexes of potentially terdentate ligands offer an excellent possibility of complex formation in vivo[7]. We have previously reported[8-11] some binary and mixed ligand complexes of this type. The present investigation is aimed at finding out the coordination behaviour of the potentially terdentate L-arginine (A) with copper(II) in the presence of another potentially terdentate L-histidine, or bidentate histamine or monodentate imidazole (B) under physiologically important conditions by potentiometry. In this paper L-arginine, L-histidine, histamine and imidazole ligands are respectively referred to as argn, hisd, hism and imiz. Metal complexes of argn and imiz are of special significance since both these form part of several proteins.

Materials and Methods

Copper(II) perchlorate solutions were prepared by neutralizing copper(II) carbonate with perchloric acid. The ligands argn, hisd, hism and imiz were obtained from Fluka Ag. Buchs, Switzerland. All the solutions were prepared in doubly distilled water. Acid-washed glassware and reagent grade chemicals were used throughout the work.

The pH measurements were carried out using the previously described equipment[10a]. The stability constants of the mixed-ligand systems were computed from the titrations in which the total concentrations of copper(II), ligand (A) and ligand (B) were in 1:1:1 and 1:2:2 molar ratios. All the titrations were done at 37°C and $I = 0.15$ mol dm^{-3} (NaClO$_4$). Calculations were made with the aid of the MINIQUAD-75 computer program[12] on an IBM 370 computer. The protonation constants of argn (A) and (B), the stability constants of their binary complexes with Cu(II), ionic product of water estimated at 37°C and $I = 0.15$ mol dm^{-3} (NaClO$_4$) were held constant during the calculation of the mixed ligand systems. Auxiliary data for hisd, hism and imiz have already been reported[8b] under these experimental conditions (Table 1). However, for argn data are not available and hence they have been estimated as per the experimental details described elsewhere[8b,10a]. All the calculations were restricted to pH below 8. However, in the copper(II)-argn binary system the calculations were restricted to pH 7.20 due to precipitation problem.

Results and Discussion

The results obtained are reported in Tables 1 and 2. Table 3 lists some other complex formation constants used for comparing the present results. The charges of the complexes species reported in this paper are omitted for clarity.

Copper(II)-argn (A) binary system: A detailed study was recently carried out by Brookes and Pettit[13] on this system where the binary species CuAH and CuA$_2$H$_2$ were found to be present. However, the present investigation indicates the presence of three binary species CuAH, CuA$_2$H,

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TABLE 1.— PROTON LIGAND STABILITY CONSTANTS AND STABILITY CONSTANTS OF COPPER(II) COMPLEXES OF ARGN, HISD, HISM AND IMIZ (A); TEMP — 37°, I — 0.15 mol dm^{-3} (NaClO$_4$); STD. DEV. ARE GIVEN IN PARENTHESES

Parameter	argn	hisd	hism	imiz
$\log \beta_{HA}$	11.43(5)	8.96(3)	9.39(8)	6.95(2)
$\log \beta_{H_2A}$	20.22(7)	14.69(5)	15.34(1)	—
$\log \beta_{H_3A}$	22.30(10)	17.37(9)	...	....
$\log \beta_{CuAH}$	19.14(17)	14.39(4)	13.46(4)	....
$\log \beta_{CuA}$	—	10.27(2)	9.24(18)	4.21(9)
$\log \beta_{CuA_2H_2}$	38.11(13)	27.41(21)	...	...
$\log \beta_{CuA_2H}$	26.85(15)	23.96(2)	21.82(6)	...
$\log \beta_{CuA_2}$	...	18.49(4)	16.16(4)	7.55(14)
$\log \beta_{CuA_3}$	..	...	..	10.73(16)
$\log \beta_{CuA_4}$	....	...	..	12.91(24)

(a) Refs 8b and 11 ; number of data points in the copper (II)—argn (A) system is 96.

TABLE 2 — STABILITY CONSTANTS OF MIXED COPPER(II)-ARGN (A)-HISD, HISM OR IMIZ (B) SYSTEMS [TEMP — 37°; I — 0.15 mol dm^{-3} (NaClO$_4$) STD. DEV. ARE GIVEN IN PARENTHESES]

Parameter	hisd	hism	imiz
		Ligands B	
$\log \beta_{CuABH_2}$	33.26(39)	—	...
$\log \beta_{CuABH}$	29.71(7)	28.80(4)	23.67(14)
$\log \beta_{CuAB}$	22.48(13)	21.16(8)	16.53(23)
$\log \beta_{CuAB_2H}$	—	..	27.57(11)
$\log \beta_{CuAB_2}$	—	..	20.76(24)
pK^H_{CuABH}	7.23	7.64	7.14
$\log Q$	18.28	17.37	12.24
$\Delta \log K_{CuABH}$	-0.30	0.42	0.32
$\log X_{CuABH}$	2.82	3.33	1.68
$\log \beta_{CuABH}(Calc.)$	28.60	27.43	22.58
$\Delta \log \beta_{CuABH}$	1.11	1.37	1.09
$\log K^{CuAH}_{CuABH}$	10.57	9.56	4.53
$pK^H_{CuABH_2}$	3.55	...	...
$\Delta \log K_{CuABH_2}$	-0.26	...	...
$\log X_{CuABH_2}$	1.00	....	...
$\log \beta_{CuABH_2}(Calc.)$	33.06	...	...
$\Delta \log \beta_{CuABH_2}$	0.20	...	...
$\log K^{Cu B}_{CuAB}$	12.21	11.92	12.32
$\log Q'$	—	—	16.14
$\Delta \log K_{CuAB_2H}$	....	...	0.88
$\log X_{CuAB_2H}$	....	....	4.12
$\log \beta_{CuAB_2H}(Calc.)$	...	....	25.81
$\Delta \log \beta_{CuAB_2H}$	—	....	1.76
$\log K^{CuABH}_{CuAB_2H}$	....	...	3.90
$\log K^{CuAB}_{CuAB_2}$	—	....	4.23
No. of data points	92	93	100

CuA$_2$H$_2$ in addition to the species HA, H$_2$A and H$_3$A. The mode of metal-ligand bonding in the CuAH argn complex is certainly glycine-like with the proton residing on the guanido group of argn. This is supported by the fact that the log P values of 7.71 (Eq. 1) for the CuAH argn complex compares

$$\log P = \log \beta_{CuAH} - \log \beta_{HA} \qquad ...(1)$$

TABLE 3.—STABILITY CONSTANTS OF COPPER(II)-GLYCINE (A) HISD, HISM OR IMIZ (B) MIXED SYSTEMS AND COPPER (II) GLYCINE (A) BINARY SYSTEM
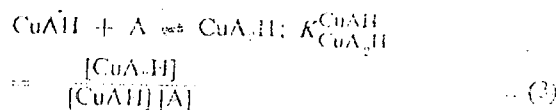
[Temp. 37°; I 0.15 mol dm^{-3} (NaClO$_4$)]

Parameter	hisd	hism	imiz
		Ligands B	
$\log \beta_{CuABH}$	22.23	21.45	
$\log \beta_{CuAB}$	18.02	17.27	11.92
$\log \beta_{CuAB_2}$			15.54

$\log \beta_{HA}$ — 9.45		$\log \beta_{H_2A}$ 12.10	
$\log \beta_{CuA}$ 8.45		$\log \beta_{CuA_2}$ 15.54	

Refs. 8c and 11

favourably with the log β_{CuA} value of 8.45 (Table 3) for the copper(II)-glycine (A) binary system. Similarly the comparable log P' (Eq. 2) value of 15.42 for the CuA$_2$H argn complex with the log β_{CuA_2} value of

$$\log P' \quad \log \beta_{CuA_2H} - \log \beta_{HA} \qquad ...(2)$$

15.54 in the copper (II)-glycine (A) (Table 3) suggests that the CuA$_2$H argn complex is presumed to contain two glycine-like ligands with one of the two guanido groups being protonated. The possibility of binding of the other guanido group with the metal in the CuA$_2$H argn complex may be ruled out, because the log $K^{CuAH}_{CuA_2H}$ (Eqs 3 and 4) value of 7.71 is of the order expected for the glycine-like bonding.

$$CuAH + A \rightleftharpoons CuA_2H; \quad K^{CuAH}_{CuA_2H}$$

$$= \frac{[CuA_2H]}{[CuAH][A]} \qquad ...(3)$$

$$\log K^{CuAH}_{CuA_2H} = \log \beta_{CuA_2H} - \log \beta_{CuA} \qquad ...(4)$$

In the CuA$_2$H$_2$ argn complex, the binding of each argn ligands is certainly in glycine-like mode, resulting in two five-membered chelate rings and the sites of protonation are the guanido groups of two argn ligands. This is because the log P'' (Eq. 5) value of 15.25 is close to log β_{CuA_2} in the copper(II)-glycine (A) system (Table 3).

$$\log P'' = \log \beta_{CuA_2H_2} - 2 \log \beta_{HA} \qquad ...(5)$$

The concentration species distribution diagrams obtained for the copper(II)-argn (A) system do not have the same qualitative features reported[10a] earlier for the copper(II)-diaminocarboxylic acid binary systems. In a 1 : 2 solution of copper(II) and argn (A), the maximum amounts of the total metal found to be present in the form of CuAH, CuA$_2$H and CuA$_2$H$_2$ are respectively 77.7, 43.9 and 78.5 per cent.
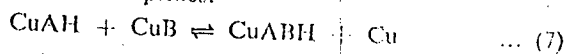
(ii) Copper(II)-argn (A)-hisd, hism or imiz (B) mixed ligand systems — In the mixed ligand system

with B = hisd, the presence of three mixed species, CuABH₂, CuABH and CuAB was confirmed, while the system with B = hism the formation of only CuABH and CuAB complexes was indicated. It may be mentioned that Brookes and Pettit[11] also studied the copper(II)-argn (A)-hisd (B) system, however they found only one mixed-ligand species, CuABH. The mixed ligand complexes of stoichiometry CuABH, CuAB, CuAB₂H and CuAB₂ were found to be present in the copper(II)-argn(A)-imiz(B) system.
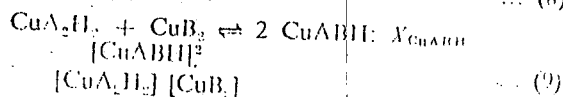
The pK^{H}_{CuABH} values in Table 2 for all the three mixed systems in this study are close and comparable suggesting the possibility for the extra proton in these CuABH complexes to be attached to argn (A) ligand, obviously to its guanido group as is the case with the CuAH or CuA₂H argn binary complexes. The same arguments become more clear, if it is noted that log Q (Eq. 6) values

$$\log Q = \log \beta_{CuABH} - \log \beta_{HA} \qquad \ldots (6)$$

in Table 2 for the systems with B = hisd, hism or imiz are close and comparable to the respective log β_{CuAB} values in Table 3 for the copper(II)-glycine (A)-hisd, hism or imiz (B) systems. The values obtained as per Eqs (7-10) for (a) Δlog K, the difference in stability of the binary complex with that of the mixed ligand complex and (b) log X, the disproportionation constant are included in Table 2 for the CuABH complexes.

$$CuAH + CuB \rightleftharpoons CuABH + Cu \qquad \ldots (7)$$

$$\Delta \log K_{CuABH} = \log \beta_{CuABH} - (\log \beta_{CuAH} + \log \beta_{CuB}) \qquad \ldots (8)$$

$$CuA_2H_2 + CuB_2 \rightleftharpoons 2 CuABH: X_{CuABH}$$

$$\frac{[CuABH]^2}{[CuA_2H_2][CuB_2]} \qquad \ldots (9)$$

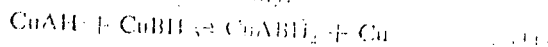$$\log X_{CuABH} = 2 \log \beta_{CuABH} - (\log \beta_{CuA_2H_2} + \log \beta_{CuB_2}) \qquad \ldots (10)$$

The stabilisation constant, log β_{CuABH} in Table 2 results from the difference in the stability constant measured for the mixed complex and that calculated on statistical grounds[16]. On statistical consideration[16], values of Δ log K > -0.6, log X > 0.6, and Δ log β to be positive demonstrate the marked stabilization of the mixed ligand complexes compared to the binary complexes. The same trends are seen in the values obtained (Table 2) for the CuABH complexes in all the three systems under study. The positive Δ log K_{CuABH} values in Table 2 for the systems with B = hism and imiz suggest that B prefers to bind to CuAH complex rather than to the solvated metal ion. It may be noted that the log β_{CuABH} value of 29.71 in the copper(II)-argn (A)—hisd (B) system in our study is in good agreement with the value of 29.25 reported by Brookes and Pettit[14], after making allowance for the changes in experimental conditions.
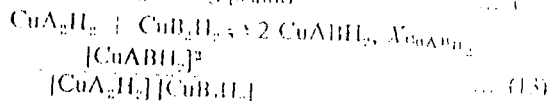
The log K^{CuAH}_{CuABH} values in Table 2 for all the three

systems with B = hisd, hism or imiz are close and comparable to the corresponding log β_{CuAB} values (Table 3), demonstrating the terdentate, bidentate and monodentate binding of hisd, hism and imiz (B) with copper(II) in the presence of argn (A). Thus the square plane of copper(II) in the CuABH species in the copper(II)-argn (A)-hism (B) system would contain one five-membered ring due to the coordination of argn (A) in a glycine-like mode, and one six-membered chelate ring due to the binding of hism (B) and the extra proton in it would be attached to the guanido group of argn (A). This structure would be more favoured due to (a) the stability-enhancing effect of the imidazole group on the formation of copper(II) mixed ligand complexes, provided an O-donor ligand is present[6b] and (b) the preference for copper(II) complexes containing five- and six-membered chelate rings[16b]. The CuABH species in the copper(II)-argn (A)- hisd (B) system would also have a similar structure except that the carboxylate oxygen of hisd (B) would coordinate occupying a very distorted axial position.

The comparison of the log K and log β and also the stabilization constant β in Table 2 for the CuABH₂ mixed complex in the copper(II)-argn (A)- hisd (B) system with values calculated on statistical grounds[16b], indicate its marked stability.
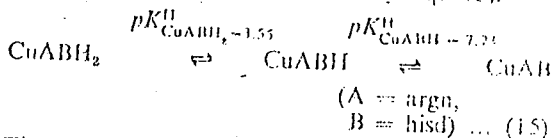
$$CuAH + CuBH_2 \rightleftharpoons CuABH_2 + Cu \qquad \ldots (11)$$

$$\Delta \log K_{CuABH_2} = \log \beta_{CuABH_2} - (\log \beta_{CuAH} + \log \beta_{CuBH_2})$$

$$CuA_2H_2 + CuB_2H_4 \rightleftharpoons 2 CuABH_2, X_{CuABH_2}$$

$$\frac{[CuABH_2]^2}{[CuA_2H_2][CuB_2H_4]} \qquad \ldots (13)$$

$$\log X_{CuABH_2} = 2 \log \beta_{CuABH_2} - (\log \beta_{CuA_2H_2} + \log \beta_{CuB_2H_4}) \qquad \ldots (14)$$

It may be predicted that of the two extra protons in CuABH₂ species, one would be attached to argn (A), possibly to its guanido group, and the other would reside upon hisd (B), probably attaching to its primary amino group as is the case with the CuBH, CuB₂H₂ or CuB₂H hisd binary complexes[8b]. The reactions may be represented by Eq. (15).
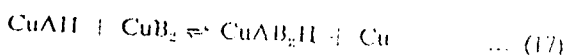
$$CuABH_2 \underset{pK^{H}_{CuABH_2} = 3.55}{\rightleftharpoons} CuABH \underset{pK^{H}_{CuABH} = 7.24}{\rightleftharpoons} CuAB$$

(A = argn, B = hisd) ... (15)

The log β_{CuAB} values in Table 2 decrease in the order of B as : hisd > hism > imiz, suggesting terdentate, bidentate and monodentate binding of these three ligands (B) in their respective CuAB complexes when A = argn. It is doubtful whether the unprotonated guanido group of argn (A) participates in the bonding, since this would require the formation of an eight-membered chelate ring which is less favoured for copper(II) due to the well-known steric reasons. The log K^{CuB}_{CuAB} values in Table 2 also support this argument. Thus the metal-ligand bind-

ing in the CuAB complexes in copper(II)-argn (A) hisd, hism or imiz (B) systems would be similar to those described earlier for the CuABH complexes in these systems. The parameters log K, log X and Δ log-β for CuAB complexes in this study could not be derived using the expressions described elsewhere[6b,8d,10a] because the stability constant data could not be obtained for the CuA or CuA$_2$ argn binary complexes (Table 1).

As in the other protonated mixed complexes, described in the beginning, it appears that in the CuAB$_2$H species in copper(II)-argn(A)-imiz (B) system also the extra proton is attached to the guanido group of argn (A). A comparable log Q' (Eq. 16) value of 16.14 with the log β_{CuAB_2} value of 15.91 in the copper(II)-glycine (A)—imiz (B) system confirms

$$\log Q' = \log \beta_{CuAB_2H} - \log \beta_{HA} \qquad ..(16)$$

this argument. The Δ log K, log X (Eqs 17-20) and the stabilization constant, Δ log β values included in Table 2 for the CuAB$_2$H species very well show its marked stability.

$$CuAH + CuB_2 \rightleftharpoons CuAB_2H + Cu \qquad ..(17)$$

$$\Delta \log K_{CuAB_2H} = \log \beta_{CuAB_2H}$$
$$- (\log \beta_{CuAH} + \log \beta_{CuB_2}) \qquad ..(18)$$

$$CuA_2H_2 + CuB_4 \rightleftharpoons 2 CuAB_2H; X_{CuAB_2H}$$
$$= \frac{[CuAB_2H]^2}{[CuA_2H_2][CuB_4]} \qquad ..(19)$$

$$\log X_{CuAB_2H} = 2 \log \beta_{CuAB_2H}$$
$$- (\log \beta_{CuA_2H_2} + \log \beta_{CuB_4}) \qquad ..(20)$$

However, these parameters could not be computed for the CuAB$_2$ mixed species due to the same reasons mentioned in the case of CuAB complexes. The log $K_{CuAB_2H}^{CuABH}$ or log $K_{CuAB_2}^{CuAB}$ values in Table 2 are much higher than the log $K_{CuB_2}^{CuB_4}$ value[8a] of 2.19 demonstrating that the addition of one more imiz (B) to a mixed ligand system is more favoured compared to that in the copper(II)-imiz (B) binary system i.e. the π-acceptor property of imiz is manifest greater in the mixed ligand system compared to that in the binary system of imiz.

It seems to be interesting to find out the order of stability obtained for the unsaturated mixed complexes, CuABH or CuAB and compare it with those of the corresponding saturated complexes, CuAB$_2$H or CuAB$_2$ in the copper(II)-argn (A)-imiz (B) system. Considering the factors[9b,15-17] viz. (a) the loss of π-bonding in going from an in-plane coordinated imiz to two out-of-plane cis-coordinated imiz as observed in the cis-bis (imiz) complexes and (b) the statistical effect resulting from the reduction in available binding sites for the coordination of second imiz molecule, one would expect greater stability for the unsaturated mixed complex than that for the saturated complex. But the Δ log K values in Table 2 for
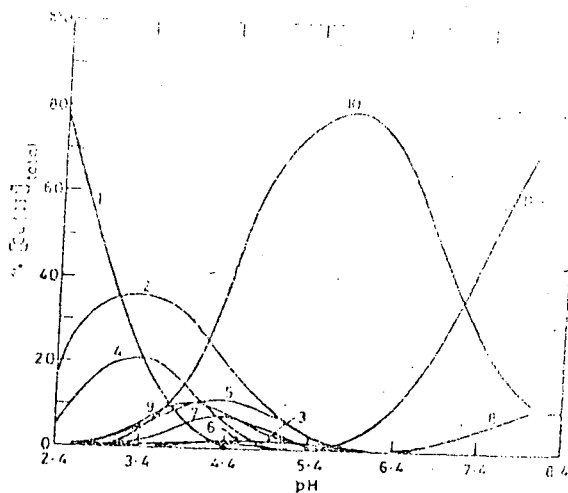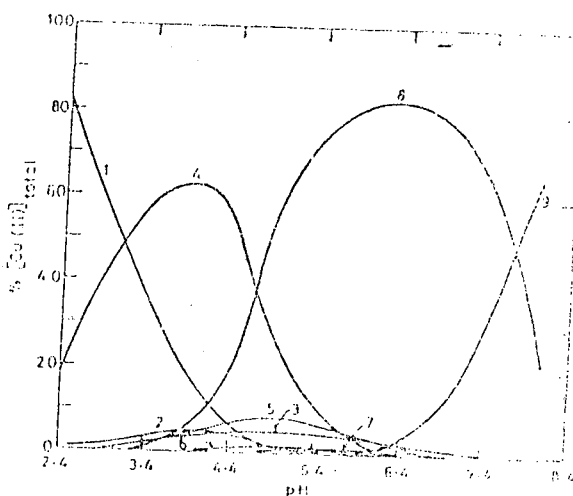

Fig. 1 — Species distribution for the copper(II)-argn (A) hisd (B) system at a Cu-A-B ratio of 1 : 1 : 1 [Unbound copper(II) (1), CuAH (2), CuA$_2$H$_2$ (3), CuBH (4), CuB(5), CuB$_2$H (6), CuB$_2$H (7), CuB$_3$ (8), CuAB$_2$H (9), CuABH (10) and CuAB (11). The species CuA$_2$H is not shown due to its very low concentration].

Fig. 2 — Species distribution for the copper(II) argn (A)-hism (B) system at a Cu-A-B ratio of 1 : 1 : 1. [Unbound copper(II) (1), CuAH (2), CuA$_2$H (3), CuBH (4), CuB (5), CuB$_2$H (6), CuB$_2$ (7), CuABH (8) and CuAB (9). The species CuA$_2$H is not shown due to its very low concentration].

the CuAB$_2$H complex are more positive compared to that for the CuABH suggesting more stability for the former. The same observation, i.e. greater stabilities for the saturated complexes, CuAB$_2$H or CuAB$_2$ compared to unsaturated complexes CuABH or CuAB complexes were also noticed[9b,22] in the copper(II)-glycine, DL-2-aminobutyric acid or DL-ornithine (A)-imiz (B) mixed systems where the chelation of all these primary ligands (A) results in a five-membered ring. However, in the systems where the primary ligand (A) forms a six-membered chelate ring, higher stabilities for the CuAB compared to
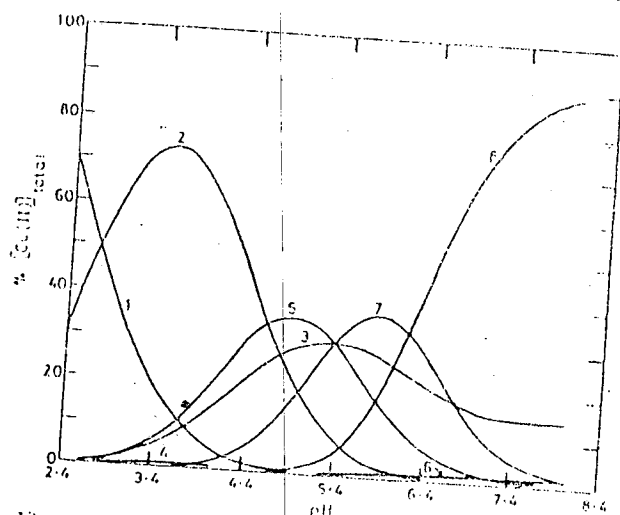
Fig. 3 — Species distribution for the copper(II) argn (A)-imiz (B) system at a Cu-A-B ratio of 1 : 2 : 2. [Unbound copper(II) (1), CuAH (2), CuAH₂ (3), CuB (4), CuABH (5), CuAB(6), CuAB₂H (7) and CuAB₂ (8). The species CuA₂H, CuB₂, CuB₃ and CuB₄ are not shown because of their very low concentrations].

CuAB₂ complexes were reported[10]. Thus, in general, it may be stated that in the copper(II)-A-imiz (B) mixed systems, the stability order between $CuAB_2$ and CuAB mixed complexes is primarily determined by the chelate ring size due to ligand (A), in addition to the factors (a) and (b) mentioned above, i.e. if A forms a five-membered chelate ring, the $CuAB_2$ complexes would be more stable than CuAB and the reverse would be true if the chelation of A results in a six-membered ring.

Figures 1–3 represent the distribution of various binary and mixed complex species in terms of per cent bound copper(II) as a function of pH in the copper (II)-argn (A)-hisd, hism or imiz (B) mixed systems. In the former two systems, the concentration of all the complex species were found to be in

appreciable amounts even in their 1 : 1 :1 solutions (Figs 1 and 2), while in the system with B = imiz, most of the complexes especially $CuAB_2H$ and $CuAB_2$ complexes attain their maximum concentrations in 1 : 2 : 2 solutions (Fig. 2). These diagrams depict the marked stabilities of the mixed ligand complex species where their concentrations reached over the statistically expected 50% of the total bound copper(II). The other qualitative features observed[11] for the concentration distribution diagrams of the mixed ligand systems are also seen in these diagrams.

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