Binary and Ternary Complexes of Copper(II) containing some Potentially Tridentate Ligands

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The multiple equilibria involved in some new ternary systems of general formula Cu^{II}–A–B [A = DL-2,3-diaminopropionic acid (dapa) or DL-2,4-diaminobutyric acid (daba); B = daba, DL-ornithine (Orn), DL-3-aminobutyric acid (3-aba), or DL-4-amino-3-hydroxybutyric acid (ahba) for the systems with A = dapa, and B = Orn, DL-2-aminobutyric acid (2-aba), 3-aba, or ahba for the systems with A = daba] have been studied pH-metrically at 37 °C and I = 0.15 mol dm^{-3} (Na[ClO$_4$]). Auxiliary data, such as the acid dissociation constants of dapa, daba, Orn, and ahba and their binary stability constants with Cu^{II}, have also been obtained under identical conditions. The results suggest that dapa, daba, and ahba bind in a tridentate manner in their 1 : 1 binary complexes. However, Orn appears to co-ordinate in a glycine-like mode both in the binary and ternary systems. The probable structures for the various binary and ternary complexes in this study are discussed in terms of their stability-constant data. In general, the results suggest that Cu^{II} prefers to have one five- and one six-membered chelate ring rather than two rings of the same size in its co-ordination sphere.

MUCH attention has been paid by several workers to the study of model mixed-ligand complexes in an effort to understand the nature of metal-ion complexation in biological processes.[1-3] Investigations on the co-ordination chemistry of potentially tridentate ligands are of considerable interest to many researchers because such studies are closely connected with peptide and protein complex chemistry. The co-ordination behaviour of the potentially tridentate ligands histidine, serine, arginine, threonine, tryptophan, tyrosine, *etc.* with transition-metal ions was studied in detail with regard to the biological applications.[1-3] These results were recently reviewed by Chow and McAuliffe.[4] Studies on the metal complexes of the diaminocarboxylic acids of general formula $NH_2(CH_2)_nCH(NH_2)COOH$, where $n = 1$ (2,3-diaminopropionic acid), $n = 2$ (2,4-diaminobutyric acid), $n = 3$ (ornithine), and $n = 4$ (lysine), were carried out by many workers.[1-10] The third donor group in these ligands is the nitrogen atom which is able to co-ordinate with hydrogen ions at intermediate pH values. Hence there is often significant competition between hydrogen and metal ions for co-ordinating with the third donor group, resulting in a number of complex equilibria. The first systematic study on the complex chemistry of diaminocarboxylic acids was carried out by Albert.[5] Subsequently, a number of reports [6-10] appeared on the diaminocarboxylic acid complexes of transition-metal ions. It is generally accepted that 2,3-diaminopropionic acid and 2,4-diaminobutyric acid co-ordinate in a tridentate manner, while orthinine and lysine bind in a glycine-like mode with Cu^{II}. However, recently Gergely *et al.*[10] suggested that ornithine can also bind in a tridentate manner with Cu^{II}.

Thus, although the binary copper(II) complexes of diaminocarboxylic acids were investigated by many workers, studies of the mixed-ligand complexes containing diaminocarboxylic acids are limited. Prior to this work, the only paper dealing with copper(II) ternary complex equilibria of this type was that by Brookes and Pettit.[11] We have already reported the multiple equilibria involved in the binary and ternary complexes of Cu^{II} with imidazoles, dipeptides, and some bidentate amino-acids.[12-17] The present paper deals with the stability and structure of some copper(II) ternary chelate systems of diaminocarboxylic acids. The diaminocarboxylic acids chosen were DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba), and DL-ornithine (Orn); some other ligands used were DL-2-aminobutyric acid (2-aba), DL-3-aminobutyric acid (3-aba), and DL-4-amino-3-hydroxybutyric acid (ahba). The compound ahba contains the aminoethanol moiety, NH_2CH_2CHOH, which is common to several compounds of pharmaceutical and biological importance. This moiety is capable of forming a five-membered chelate ring, with or without ionization of the hydroxy-group. All the experiments were carried out at 37 °C and with I = 0.15 mol dm^{-3} (Na[ClO$_4$]). As the acid dissociation constants of dapa, daba, Orn, and ahba and their binary stability constants with Cu^{II} were not available under these experimental conditions, they were re-estimated.

EXPERIMENTAL

All the ligands used were Fluka products of Puriss quality. The compounds dapa and Orn were used in the monoprotonated form while daba was used in the diprotonated form; Cu[ClO$_4$]$_2$ and the other reagents were prepared and estimated as described earlier.[12-17] Doubly distilled water was used for the preparation of all the solutions.

The pH titrations were carried out at 37 °C under nitrogen with a digital pH meter (Electronic Corporation of India Ltd., serial 053, pH 5651) with glass and calomel electrode assembly with an accuracy of ± 0.01 pH units. The electrode system was calibrated in terms of hydrogen-ion concentrations. Acid dissociation constants for the free ligands were determined by pH-metric titrations of the ligands with standard carbonate-free sodium hydroxide. The formation constants for the binary complexes were computed from titrations in which metal to ligand ratios were 1 : 1 and 1 : 2, while the constants for the ternary complexes were determined from titrations in which the metal and the ligands were in equimolar ratios. In all the titrations, a constant ionic strength of 0.15 mol dm^{-3} was maintained by the addition of sodium perchlorate.

Calculations have been restricted to systems below pH 8 since above this region there are complications due to the hydrolysis of the complex. All the calculations were done with the aid of the computer program [18] MINIQUAD-75 on an IBM-370 computer. The results are reported in Tables 1—3. The charges of the complex species reported in this paper are omitted for clarity.

TABLE 1

Stability constants for the proton and copper(II) complexes of dapa, daba, Orn, ahba, 2-aba, 3-aba, and glycine at 37 °C and I = 0.15 mol dm^{-3} (Na[ClO$_4$]). Standard deviations are given in parentheses

	Ligands A						
Parameter	dapa	daba	Orn	ahba	2-aba [a]	3-aba [a]	glycine [b]
$\log \beta_{\mathrm{HA}}$	9.37(2)	9.93(2)	10.22(1)	12.88(11)	9.43(1)	9.95(1)	9.45(2)
$\log \beta_{\mathrm{H_2A}}$	15.98(3)	18.02(4)	18.85(2)	21.91(2)	11.54(1)	13.30(1)	12.10(4)
$\log \beta_{\mathrm{H_3A}}$	17.37(5)	19.88(6)	20.99(4)	25.78(3)			
$\log \beta_{\mathrm{CuAH}}$	15.37(4)	16.99(3)	17.67(2)				
$\log \beta_{\mathrm{CuA}}$	10.61(4)	10.94(3)		13.02(9)	8.10(2)	7.16(2)	8.45(2)
$\log \beta_{\mathrm{Cu_2A_2}}$				28.10(30)			
$\log \beta_{\mathrm{CuA_2H_2}}$	30.16(5)	32.92(4)	34.32(3)				
$\log \beta_{\mathrm{CuA_2H}}$	25.32(6)	26.89(4)	26.12(6)				
$\log \beta_{\mathrm{CuA_2}}$	20.18(5)	19.15(6)		19.09(24)	15.13(4)	12.90(5)	15.54(5)
$\mathrm{p}K_{\mathrm{CuAH}}$	4.76	6.05					
$\mathrm{p}K_{\mathrm{CuA_2H}}$	5.14	7.74					
$\mathrm{p}K_{\mathrm{CuA_2H_2}}$	4.84	6.03	8.20				
$\log K_{\mathrm{CuA_2H}}$	9.95	9.90	8.45				
$\log K_{\mathrm{CuA_2}}$	9.57	8.21		6.07	7.03	5.74	7.09
$\log P$	6.00	7.06	7.45				
$\log P'$	11.42	13.06	13.88				

[a] Refs. 17 and 20. [b] Refs. 16 and 20.

RESULTS AND DISCUSSION

Binary Complexes of Copper(II) *with dapa, daba, and Orn.*—Our results from the detailed titration studies below pH 8 show that the 1 : 1 and 1 : 2 solutions of Cu^{II} and A = dapa or daba contain CuAH, CuA, CuA$_2$H$_2$, CuA$_2$H, and CuA$_2$ as the major species, while such solutions in the Cu^{II}–Orn system showed the presence of CuAH, CuA$_2$H$_2$, and CuA$_2$H. The stability-constant data obtained (Table 1) for these complex species are in good agreement with those reported in the literature [3-10] after making allowances for the changes in experimental conditions.

TABLE 2

Stability constants for the ternary systems of copper(II) with primary ligand A = dapa at 37 °C and I = 0.15 mol dm^{-3} (Na[ClO$_4$]). Standard deviations are given in parentheses

	Secondary ligands, B			
Parameter	daba	Orn	3-aba	ahba
$\log \beta_{\mathrm{CuABH_2}}$	31.66(9)	32.54(14)		
$\log \beta_{\mathrm{CuABH}}$	26.23(15)	27.54(7)		
$\log \beta_{\mathrm{CuAB}}$	19.45(11)	19.65(9)	16.15(16)	19.82(22)
$\mathrm{p}K_{\mathrm{CuABH_2}}$	5.43	5.00		
$\mathrm{p}K_{\mathrm{CuABH}}$	6.78	7.89		
$\log K_{\mathrm{CuAB}}$	8.84	9.04	5.54	9.21
$\log K_{\mathrm{CuAB'}}$	8.51		8.99	6.80
$\Delta \log K_{\mathrm{CuABH_2}}$	−0.70	−0.50		
$\Delta \log K_{\mathrm{CuABH}}$	−1.37	−0.74		
$\Delta \log K_{\mathrm{CuAB}}$	−2.10		−1.62	−3.81
$\log X_{\mathrm{CuABH_2}}$	0.24	0.60		
$\log X_{\mathrm{CuABH}}$	−0.64	0.58		
$\log X_{\mathrm{CuAB}}$	−0.43		−0.78	0.37
$\log \beta_{\mathrm{CuABH_2}}$ (calc.)	31.84	32.54		
$\log \beta_{\mathrm{CuABH}}$ (calc.)	26.85	27.55		
$\log \beta_{\mathrm{CuAB}}$ (calc.)	19.96		16.84	19.93
$\Delta \log \beta_{\mathrm{CuABH_2}}$	−0.18	0.00		
$\Delta \log \beta_{\mathrm{CuABH}}$	−0.62	−0.01		
$\Delta \log \beta_{\mathrm{CuAB}}$	−0.51		−0.69	−0.11

The exceptionally high log β values of 10.61 and 10.94 respectively for the CuA dapa and daba complexes suggest a possible diamine-like bonding with some participation from the carboxyl oxygen atom. This tridentate nature of dapa in its CuA complex may be confirmed by noting that although the $\log \beta_{\mathrm{H_2A}}$ value of 15.98 for dapa (Table 1) is lower than that for diaminoethane (17.15) [9] by about a log unit, both dapa and diaminoethane CuA complexes do have comparable $\log \beta_{\mathrm{CuA}}$ values (10.61 and 10.52), suggesting the carboxyl co-ordination in the dapa complex. The same trends, but to a larger extent were also seen in the daba and 1,3-diaminopropane [9] $\log \beta_{\mathrm{H_2A}}$ and $\log \beta_{\mathrm{CuA}}$ values (respective values being 18.02 and 19.70 for $\log \beta_{\mathrm{H_2A}}$, and 10.94 and 9.77 for $\log \beta_{\mathrm{CuA}}$) confirming the carboxyl

TABLE 3

Stability constants for the ternary systems of copper(II) with primary ligand A = daba at 37 °C and I = 0.15 mol dm^{-3} (Na[ClO$_4$]). Standard deviations are given in parentheses

	Secondary ligands, B			
Parameter	Orn	2-aba	3-aba	ahba
$\log \beta_{\mathrm{CuABH}}$	27.26(12)			
$\log \beta_{\mathrm{CuAB}}$	19.66(26)	17.35(11)	16.30(12)	19.93(13)
$\mathrm{p}K_{\mathrm{CuABH}}$	7.60			
$\log K_{\mathrm{CuAB}}$	8.72	6.41	5.36	8.99
$\log K_{\mathrm{CuAB'}}$		9.25	9.14	6.91
$\Delta \log K_{\mathrm{CuABH}}$	−0.67			
$\Delta \log K_{\mathrm{CuAB}}$		−1.69	−1.80	−4.03
$\log X_{\mathrm{CuABH}}$	1.05			
$\log X_{\mathrm{CuAB}}$		0.42	0.55	1.62
$\log \beta_{\mathrm{CuABH}}$ (calc.)	27.03			
$\log \beta_{\mathrm{CuAB}}$ (calc.)		17.44	16.32	19.42
$\Delta \log \beta_{\mathrm{CuABH}}$	0.23			
$\Delta \log \beta_{\mathrm{CuAB}}$		−0.09	−0.02	0.51

co-ordination in the CuA daba complex. This stability enhancement in the CuA daba complex compared to that in the CuA dapa complex may be attributed to the involvement of one six- and one five-membered chelate ring in the daba complex which is the preferred arrangement for Cu^{II} compared to the two five-membered rings in the CuA dapa complex.

The log P values in Table 1 calculated from equation (1) for the CuAH dapa, daba, and Orn complexes are nearly as expected for the glycine-like mode of binding; *i.e.* in these CuAH complexes α-aminocarboxyl chelation

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

is involved with the proton residing on the ω-amino-group. However, a lower log P value for the CuAH dapa complex suggests the possibility of ω-aminocarboxyl chelation with the proton attaching to the α-amino-group. A comparison of the K' values for reaction (2) with those for the similar reaction (3) with glycine [log K' values being −0.61 (dapa), −1.03 (daba), −1.18 (Orn), and −1.00 (glycine)] also confirms a difference in bonding in the CuAH dapa complex. The

$$Cu + H_2A \overset{K'}{\rightleftharpoons} CuAH + H \qquad (2)$$

$$Cu + HA \rightleftharpoons CuA + H \qquad (3)$$

same arguments were also put forward by Brookes and Pettit.[9] Thus, for the CuAH dapa complex, one may suggest two equilibrium structures: one structure in which α-aminocarboxyl chelation is involved and the ω-amino-group is protonated and in the other ω-aminocarboxyl chelation with the proton attached to the α-amino-group.

Thus, since the site of protonation is the ω-amino-group in the CuAH daba and Orn complexes and to some extent in the CuAH dapa complex, it may be concluded that in their CuA_2H complexes also, the proton is attached to the ω-amino-group. The log K_{CuA_2H} ($CuAH + A \rightleftharpoons CuA_2H$) values of 9.95 and 9.90 respectively for the dapa and daba complexes are of the order expected for the tridentate bonding of A^- in the Cu(AH)A complex. However, for the Orn complex, this quantity is only 8.45 suggesting a glycine-like mode of binding of A^- in its Cu(AH)A complex.

With regard to the CuA_2H_2 dapa, daba, and Orn complexes, the log P' values in Table 1 derived from expression (4) are comparable to the overall formation constant values for the CuA_2 glycine complex. Hence it

$$\log P' = \log \beta_{CuA_2H_2} - 2 \log \beta_{HA} \qquad (4)$$

may be concluded that in the CuA_2H_2 dapa, daba, and Orn complexes, the two ligands bind in a glycine-like mode resulting in two five-membered chelate rings with the two protons residing on their ω-amino-groups. However, the lower log P' value for the CuA_2H_2 dapa complex (Table 1) suggests the possibility of one more equilibrium structure for it. Considering the preference for copper(II) complexes to contain one five- and one six-membered chelate ring, it appears more reasonable to suggest the other equilibrium structure for the CuA_2H_2 dapa complex, with the two ligands binding in two different ways, *i.e.* one ligand binds in a glycine-like mode with a protonated ω-amino-group while the co-ordination of the other involves ω-aminocarboxyl chelation and a protonated α-amino-group.

The log K_{CuA} − log K_{CuA_2} ($CuA + A \rightleftharpoons CuA_2$) value of 1.04 in the Cu^{II}–dapa system shows tridentate binding of both dapa ligands in its CuA_2 complex. But the above quantity in the Cu^{II}–daba system is 2.73, which suggests steric hindrance, provided both the ligands bind in a tridentate mode. Hence some other type of binding must be involved. Again, considering the preference for copper(II) chelates to contain both five- and six-membered rings, it seems more reasonable to suggest a structure for the CuA_2 daba complex with one daba binding in a glycine-like mode and other daba co-ordinating in a diamine-like manner. But, if this is the only structure, then one would have expected a higher log K_{CuA_2} for the CuA_2 daba complex. So, one may propose one more equilibrium structure for the CuA_2 daba complex with some tridentate behaviour of daba *i.e.* by having three nitrogens and one oxygen in the equatorial plane with the fourth nitrogen in an apical position, this arrangement being free from steric interference. The Cu^{II}–Orn system in our study below pH 8 did not show the presence of CuA_2.

The concentration distribution diagrams in terms of percentage bound Cu^{II} as a function of pH were obtained both for 1 : 1 and 1 : 2 solutions in the Cu^{II}–dapa,–daba, and –Orn systems. As expected, it was found that the CuAH and CuA complexes predominated in 1 : 1 solutions, while in the 1 : 2 solutions the bis complexes predominated. The diagrams for 1 : 2 solutions of Cu^{II} and dapa, daba, and Orn are given in Figure 1.

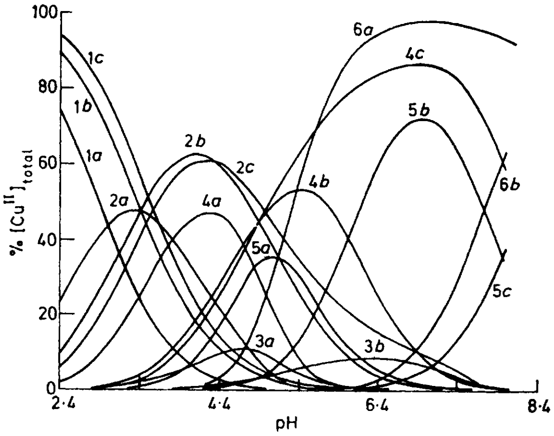

FIGURE 1 Species distribution for the Cu^{II}–dapa (*a*), daba (*b*), or Orn (*c*) (A) systems at a metal : ligand ratio of 1 : 2. Unbound Cu^{II} (1), CuAH (2), CuA (3), CuA_2H_2 (4), CuA_2H (5), and CuA_2 (6)

Binary Complexes of Copper(II) *with* DL-4-*Amino*-3-*hydroxybutyric Acid* (*ahba*).—Although many workers[3] reported the formation equilibria involved in the Cu^{II}–ahba system, a more detailed study was carried out recently by Braibanti and Mori[19] at 25 °C and $I = 0.1$ mol dm^{-3} (KCl). Our results at 37 °C and $I = 0.15$ mol dm^{-3} ($Na[ClO_4]$) likewise showed the presence of three binary complex species CuA, Cu_2A_2, and CuA_2 in addition to HA, H_2A, and H_3A and their formation constants (Table 1) are similar to the values reported by Braibanti and Mori.[19] The exceptionally high log β_{CuA} value indicates a possible tridentate binding of ahba *via* amine, hydroxy-, and carboxy-groups in its CuA complex. The Cu_2A_2 species would have a structure consisting of two CuA units held together by bridging alcohol oxygen atoms. The log K_{CuA} − log K_{CuA_2} value of 6.07 suggests bidentate binding of the ahba ligands through amine and hydroxy-groups in its CuA_2 complex.

The auxiliary data for 2-aba and 3-aba used in this work have been reported already.[17,20] However, these values are included in Table 1.

Ternary Systems of Copper(II).—Two groups of ternary systems were studied: (*i*) Cu^{II}–dapa (A)–daba, Orn, 3-aba, or ahba (B) and (*ii*) Cu^{II}–daba (A)–Orn, 2-aba, 3-aba, or ahba (B). The Cu^{II}–dapa–2-aba system was also studied, but no appreciable complexing was revealed. The Cu^{II}–dapa (A)–daba or Orn (B) ternary systems showed the presence of three ternary complexes, $CuABH_2$, CuABH, and CuAB, while in the Cu^{II}–daba–Orn system CuABH and CuAB mixed species were detected. In all other ternary systems only the CuAB type of ternary species was found to be present.

The diprotonated $CuABH_2$ complexes in both the Cu^{II}–dapa (A)–daba or Orn (B) systems predominated below pH 4.5. The parameters Δ log K, log X, and Δ log β calculated from the expressions (5)—(9) for the $CuABH_2$ complexes in these systems (Table 2) do not deviate much from their corresponding statistically expected values.[21] This suggests that the complexes are not markedly stabilized. With regard to their solution structures, it may be suggested with certainty that of the two protons therein, one would be attached to the dapa primary ligand (A) and the other to the daba or Orn secondary ligand (B). The protons in the protonated 1 : 1 complexes in the Cu^{II}–daba, Orn systems are attached to their ω-amino-groups. In the CuAH dapa complex, the results suggest a possible attachment of the proton either to the ω-amino-group or to the α-amino-group, thus the CuAH dapa complex has two equilibrium structures as described earlier. The same types of bonding may be expected for the $CuABH_2$ complexes with A = dapa and B = daba or Orn, *i.e.* $CuABH_2$ may be assigned two equilibrium structures where in one structure the proton of the dapa (A) ligand resides on its ω-amino-group and in the other it is attached to its α-amino-group while the proton in the daba or Orn secondary ligand (B) would be attached to ω-amino-group in both structures. Thus, the first structure would involve two five-membered chelate rings, while the second one would have one six- and one five-membered ring which is the preferred arrangement for copper(II) complexes. In both Cu^{II}–dapa (A)–daba or Orn (B) systems, *ca.* 15% of the total metal was present in the form of $CuABH_2$.

$$CuAH + CuBH \rightleftharpoons CuABH_2 + Cu \qquad (5)$$

$$\Delta \log K_{CuABH_2} = \log \beta_{CuABH_2} - (\log \beta_{CuAH} + \log \beta_{CuBH}) \qquad (6)$$

$$CuA_2H_2 + CuB_2H_2 \rightleftharpoons 2\ CuABH_2,\ X_{CuABH_2} = [CuABH_2]^2/[CuA_2H_2][CuB_2H_2] \qquad (7)$$

$$\log X_{CuABH_2} = 2 \log \beta_{CuABH_2} - (\log \beta_{CuA_2H_2} + \log \beta_{CuB_2H_2}) \qquad (8)$$

$$\Delta \log \beta_{CuABH_2} = \log \beta_{CuABH_2} \text{(expt.)} - \log \beta_{CuABH_2} \text{(calc.)} \qquad (9)$$

With regard to the CuABH ternary complex species in the Cu^{II}–dapa (A)–daba or Orn (B) and Cu^{II}–daba (A)–Orn (B) systems, comparison of the calculated values of Δ log K, log X, and Δ log β [equations (10)—(14)] with the corresponding statistically expected values[21] suggests that their formation is less favourable. The pK_{CuABH} (CuAB + H $\rightleftharpoons$ CuABH) values of 6.78 and 7.89 respectively in the Cu^{II}–dapa (A)–daba or Orn (B) systems are close to the pK_a values for the protonated 1 : 1 or 1 : 2 Cu^{II}–daba or Orn complexes (Table 1) and hence it may be concluded that the protons in these CuABH complexes are also attached to the ω-amino-group of the daba or Orn secondary ligand (B). The possibility for the attachment of the proton to the dapa primary ligand (A) may be ruled out because of its lower pK_{CuAH} (CuA + H $\rightleftharpoons$ CuAH) value (Table 1) compared to the pK_{CuABH} values (Table 2). With regard to the site of protonation in the CuABH species in the Cu^{II}–daba (A)–Orn (B) system, it is not possible to determine unambiguously the site of the proton since its pK_{CuABH} value (Table 3) is similar to the pK_a values for the protonation of 1 : 1 and 1 : 2 daba or Orn complexes (Table 1). However, we favour the attachment of the proton to the ω-amino-group of the Orn secondary ligand (B). If this is the case, then Orn (B) would bind in a glycine-like mode and daba (A) would co-ordinate in a diamine-like manner, thus the CuABH species in the Cu^{II}–daba (A)–Orn (B) system would have a five- and a six-membered chelate ring which is the preferred arrangement for Cu^{II}.

$$CuA + CuBH \rightleftharpoons CuABH + Cu \qquad (10)$$

$$\Delta \log K_{CuABH} = \log \beta_{CuABH} - (\log \beta_{CuA} + \log \beta_{CuBH}) \qquad (11)$$

$$CuA_2 + CuB_2H_2 \rightleftharpoons 2\ CuABH,\ X_{CuABH} = [CuABH]^2/[CuA_2][CuB_2H_2] \qquad (12)$$

$$\log X_{CuABH} = 2 \log \beta_{CuABH} - (\log \beta_{CuA_2} + \log \beta_{CuB_2H_2}) \qquad (13)$$

$$\Delta \log \beta_{CuABH} = \log \beta_{CuABH} \text{(expt.)} - \log \beta_{CuABH} \text{(calc.)} \qquad (14)$$

The Δ log K, log X, and Δ log β values (calculated from the expressions described earlier[12-17]) in Tables 2 and 3 for the CuAB complexes in all eight ternary systems in this study suggest that there is no marked stabilization for ternary complex formation. The Δ log K values for the CuAB complexes in the Cu^{II}–dapa (A)–daba or Orn (B) and Cu^{II}–daba (A)–Orn (B) systems are more negative than those for the $CuABH_2$ and CuABH ternary complex species (Tables 2 and 3). This may be explained by the fact that Cu^{II} usually prefers to be four-co-ordinate. The primary ligands (A) used in the present work are tridentate ligands and hence the number of available co-ordination sites for the binding of the secondary ligand (B) is lower which could be the cause of the more negative Δ log K values. With regard to the solution structures of these CuAB complexes, the dapa or daba primary ligands (A) bind in a diamine-like manner, probably with a very weak axial carboxyl bond as in their 1 : 1 binary complexes. The ligands Orn, 2-aba, and 3-aba bind in a bidentate manner. Although ahba in its 1 : 1 copper(II) binary complex binds in a terdentate manner, in the ternary complexes involving this ligand it may co-ordinate in a bidentate manner through N-amino- and O-hydroxy-groups. These results are evident from the log β_{CuAB}, log K_{CuAB} ($CuA + B \rightleftharpoons CuAB$), and log $K_{CuAB'}$ ($CuB + A \rightleftharpoons CuAB$) values in Tables 2 and 3. Thus, the CuAB complex species in the Cu^{II}–dapa (A)–daba, Orn, 3-aba, or ahba (B) and Cu^{II}–daba (A)–Orn, 2-aba, 3-aba, or ahba (B) systems would have five- and six-, five- and five-, five- and six-, or five- and five- and six- and five-, six- and five-, six- and six-, and six- and five-membered chelate rings respectively. The concentration distribution diagram for the Cu^{II}–dapa (A)–daba (B) system is given in Figure 2. The diagrams for all other ternary systems in this study showed the same qualitative features as Figure 2.

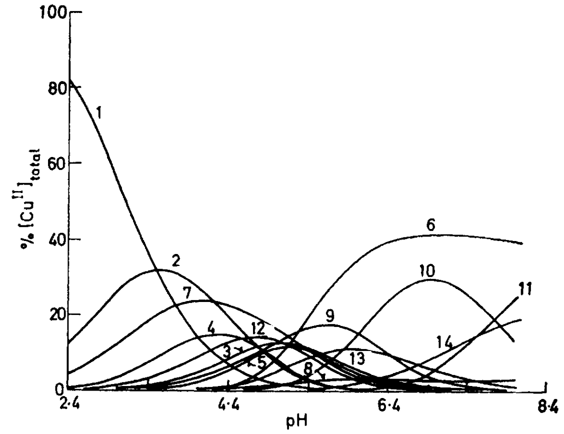

FIGURE 2 Species distribution for the Cu^{II}–dapa (A)–daba (B) system at a metal : A : B ratio of 1 : 1 : 1. Unbound Cu^{II} (1), CuAH (2), CuA (3), CuA_2H_2 (4), CuA_2H (5), CuA_2 (6), CuBH (7), CuB (8), CuB_2H_2 (9), CuB_2H (10), CuB_2 (11), $CuABH_2$ (12), CuABH (13), and CuAB (14)

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