or dichloromethane solution with an aqueous sodium dithionite solution in a Kewannee controlled-atmosphere box under purified nitrogen. Typically 1 mg of iron(III) porphyrin and 5 mg of sodium dithionite were dissolved in a mixture of 0.5 mL of toluene and several drops of water. The solutions were shaken to mix the two layers. After reduction was complete, as noted by a color change from green-brown to red, the two layers were allowed to separate. The aqueous layer was removed by a pipet. The toluene solution was then washed with a fresh sample of deoxygenated water to remove any remaining inorganic salts. The solvent was evaporated from the sample under vacuum, and the sample was dried for 12 h under continuous vacuum. The iron porphyrin was then dissolved in deoxygenated, deuterated toluene and transferred into an NMR tube in the controlled-atmosphere box. The NMR tube was sealed with a septum cap, and dry dioxygen was admitted to the sample. This solution could be used directly for spectroscopic examination. The iron porphyrin could be precipitated by the addition of heptane and collected by filtration.

Instrumentation. ^{1}H NMR spectra at 200 and 360 MHz were recorded on Nicolet NT-200 and NT-360 FT NMR spectrometers. Between 300 and 2000 transients were accumulated with use of a 90° pulse. Electronic spectra were measured with a Hewlett-Packard 8450A spectrophotometer. Infrared spectra were obtained from Nujol mulls of the solid complexes. A Perkin-Elmer 180 spectrometer was used to record the spectra. ESR spectra were recorded at the X band with a Bruker spectrometer. Samples were dissolved in toluene, and spectra were obtained from samples cooled to −150 °C. Magnetic susceptibilities of toluene solutions were measured with use of the Evans technique.[41]

Acknowledgment. We thank the National Institutes of Health (Grant No. GM26226) for support and Professor G. N. La Mar for discussions and a sample of $(T(F_5)PP)H_2$. L.L.-G. was on leave from the Institute of Chemistry, University of Wrocław, Wrocław, Poland.

Registry No. (TMP)FeOH, 81245-23-0; $(T(2,4,6\text{-}MeO)_3PP)$-FeOH, 81245-22-9; (TPP)FeCl, 16456-81-8; (TMP)FeCl, 77439-21-5; $(T(2,4,6\text{-}MeO)_3PP)FeCl$, 53470-05-6; $(T(3,4,5\text{-}MeO)_3PP)FeCl$, 81245-21-8; $(T(F_5)PP)FeCl$, 36965-71-6; $(T(3,4,5\text{-}MeO)_3PP)FeOH$, 81278-78-6; $(T(F_5)PP)FeOH$, 81278-77-5; $[(TPP)Fe]_2O$, 12582-61-5; $[(T(3,4,5\text{-}MeO)_3PP)Fe]_2O$, 81245-19-4; $[(T(F_5)PP)Fe]_2O$, 81245-20-7.

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Ternary Coordination Complexes of Copper(II) Containing Histamine and Some Amino Acids

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Received June 16, 1981

Equilibrium constants have been measured by pH titrimetry at 37 °C and I = 0.15 mol dm^{-3} ($NaClO_4$) for some ternary systems, $Cu^{II}AB$ [A = histamine; B = DL-2-aminobutyric acid (2-aba), DL-3-aminobutyric acid (3-aba), 4-aminobutyric acid (4-aba), DL-4-amino-3-hydroxybutyric acid (ahba), DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba), and DL-ornithine (Orn)], in aqueous perchlorate media. Very high stabilities were observed for all types of the ternary complex species CuAB, Cu((AB)H), or Cu($(AB)H_2$) detected. Copper(II) ternary complexes having six- and five-membered chelate rings are found to be more stable than those having six- and six- or six- and seven-membered chelate rings. It appears from the results that in the presence of histamine (A) dapa, daba, and Orn (B) bind copper(II) in a tridentate manner, while the other potentially tridentate ligand, ahba (B), coordinates in a bidentate manner. The trends in the $pK^H_{Cu((AB)H)}$ values suggest that the extra proton in the Cu((AB)H) complexes is attached to the ligand B. However, in the systems where Cu($(AB)H_2$) complexes were detected, the possibility for the attachment of one proton to the histamine (A) and the other to the ligand B was predicted.

Introduction

Considerable attention has been paid in recent years to the studies of complex-forming properties of histamine, which is of importance from the biological point of view.[1,2] Several workers[3-6] investigated the equilibrium chemistry of copper(II) ternary complexes containing histamine as a ligand. Gergely and Sovago[5] described studies relating to the copper(II)–histamine–amino acid ternary complexes, where the increased stability was explained by a large entropy effect. We have been investigating[7a-c] the stability and structure of ternary complex species of the type Cu($(AB)H_2$), Cu((AB)H), CuAB, Cu($(AB)H_{-1}$), or $CuAB_2$ in some copper(II)–histamine (A)–secondary ligand (B) systems toward a better understanding of the nature of metal ion complexation in biological processes. In the present paper, we report the equilibrium data for some new copper(II)–histamine (A)–amino acid (B) ternary systems obtained by pH titrimetry at 37 °C and I = 0.15 mol dm^{-3} ($NaClO_4$). The amino acids (B) chosen are DL-2-aminobutyric acid (2-aba), DL-3-aminobutyric acid (3-aba), 4-aminobutyric acid (4-aba), DL-4-amino-3-hydroxybutyric acid (ahba), DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba), and DL-ornithine (Orn). The amino acids 2-aba, 3-aba, and 4-aba are capable respectively of forming five-, six-, and seven-membered chelate rings with copper(II). The ahba ligand is potentially tridentate having amino-, hydroxy-, and carboxylate-donor groups. The compounds dapa, daba, and Orn are diaminocarboxylic acids of general formula $NH_2(CH_2)_nCH(NH_2)COOH$, where n = 1 (dapa), 2 (daba), and 3 (Orn).

Experimental Section

All the ligands used were obtained from Fluka. The compounds dapa and Orn were used in the monoprotonated form, while daba was

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Table I. Overall Formation Constants for the Copper(II)–Histamine (A) –2-aba, –3-aba, –4-aba, –ahba, –dapa, –daba, and –Orn (B) Binary Systems at 37 °C and I = 0.15 mol dm^{-3} ($NaClO_4$)[7b,8] [a]

	ligands							
	2-aba	3-aba	4-aba	ahba	dapa	daba	Orn	histamine
$\log \beta_{HB}$	9.43 (1)	9.95 (1)	10.15 (1)	12.88 (11)	9.37 (2)	9.93 (2)	10.22 (1)	9.39 (8)
$\log \beta_{H_2B}$	11.54 (1)	13.30 (1)	14.24 (1)	21.91 (2)	15.98 (3)	18.02 (4)	18.85 (2)	15.34 (1)
$\log \beta_{H_3B}$				25.78 (2)	17.37 (5)	19.88 (6)	20.99 (4)	
$\log \beta_{Cu((B)H)}$					15.37 (4)	16.99 (3)	17.67 (2)	13.46 (4)
$\log \beta_{CuB}$	8.10 (2)	7.16 (2)	6.07 (9)	13.02 (9)	10.61 (4)	10.94 (3)		9.24 (18)
$\log \beta_{Cu_2B_2}$				28.10 (30)				
$\log \beta_{Cu(B_2H_2)}$					30.16 (5)	32.92 (4)	34.32 (3)	
$\log \beta_{Cu(B_2H)}$					25.32 (6)	26.89 (4)	26.12 (6)	21.82 (6)
$\log \beta_{CuB_2}$	15.13 (4)	12.90 (5)		19.09 (24)	20.18 (5)	19.15 (6)		16.16 (4)

[a] Standard deviations are given in parentheses.

Table II. Stability Constants for the Copper(II)–Histamine (A)–Secondary Ligand (B) Systems at 37 °C and I = 0.15 mol dm^{-3} ($NaClO_4$)[a]

	secondary ligands, B						
	2-aba	3-aba	4-aba	ahba	dapa	daba	Orn
$\log \beta_{Cu((AB)H_2)}$					29.37 (11)	28.79 (1.50)	31.46 (11)
$\log \beta_{Cu((AB)H)}$	21.68 (13)	21.48 (12)	21.64 (10)	27.14 (12)	24.75 (9)	25.72 (2)	26.87 (6)
$\log \beta_{CuAB}$	17.21 (6)	15.92 (8)	15.28 (11)	19.70 (7)	19.19 (10)	18.40 (5)	18.91 (14)
$pK^{H}_{Cu((AB)H_2)}$					4.62		4.59
$pK^{H}_{Cu((AB)H)}$	4.47	5.56	6.36	7.44	5.56	7.32	7.96
$\log K^{CuA}_{CuAB}$	7.97	6.68	6.04	10.46	9.95	9.16	9.67
$\log K^{CuB}_{CuAB}$	9.11	8.76	9.21	6.68	8.58	7.46	
$\Delta \log K_{Cu((AB)H_2)}$					0.54		0.33
$\Delta \log K_{Cu((AB)H)}$					0.14	−0.51	−0.04
$\Delta \log K_{CuAB}$	−0.13	−0.48	−0.03	−2.56	−0.66	−1.78	
$\log X_{Cu((AB)H)}$					3.18	2.36	3.26
$\log X_{CuAB}$	3.13	2.78		4.15	2.04	1.49	
$\log \beta_{Cu((AB)H_2)}$(calcd)					28.84	30.22	30.92
$\log \beta_{Cu((AB)H)}$(calcd)					23.46	24.84	25.54
$\log \beta_{CuAB}$(calcd)	15.94	14.83	14.45	17.92	18.47	17.95	
$\Delta \log \beta_{Cu((AB)H_2)}$					0.53		0.54
$\Delta \log \beta_{Cu((AB)H)}$					1.29	0.88	1.33
$\Delta \log \beta_{CuAB}$	1.27	1.09	0.83	1.78	0.72	0.45	

[a] Standard deviations are given in parentheses.

used in the diprotonated form. $Cu(ClO_4)_2$ and all other reagents were prepared and estimated as described previously.[7–12] Examinations by pH titrimetry were made at 37 °C under nitrogen with an ionic background of 0.15 mol dm^{-3} ($NaClO_4$). The equipment and the electrode standardization procedures were described elsewhere.[8–12] All the calculations were done with the aid of the MINIQUAD-75 computer program[13] on an IBM 370 computer, with the acid dissociation constants of the ligands and their parent binary stability constants with copper(II) fixed, estimated at identical conditions (Table I). The pK_w value of 13.62 was used in the calculations. The results obtained are recorded in Table II. The charges of all the complex species reported in this paper are neglected for clarity.

Results and Discussion

The ternary systems of copper(II) with a histamine primary ligand (A) and 2-aba, 3-aba, 4-aba, and ahba secondary ligands (B) gave rise to the formation of the two ternary species CuAB and Cu((AB)H), while in the systems with B = dapa, daba, and Orn the three ternary species CuAB, Cu((AB)H), and Cu((AB)H_2) were detected. All these complexes would be favored due to the stability-increasing effect of the imidazole group in histamine (A), since the secondary ligand (B) in all these systems contains an O-donor group.[2]

1. Stability and Structure of CuAB Complexes. The log K^{CuB}_{CuAB} values in Table II for most of the ternary systems are close to the stability constant value for the CuA (A = histamine) complex, suggesting that histamine (A) binds the metal in both the ternary and the binary systems in the same mode, i.e., via its primary amino and imidazole nitrogens forming a six-membered chelate ring. Again, the log K^{CuA}_{CuAB} values in Table II for the copper(II)–histamine (A)–2-aba, –3-aba, –4-aba, –dapa, –daba, and –Orn (B) ternary systems compare favorably to the corresponding values of log β_{CuB} values in Table I, indicating that the same type of bonding of these secondary ligands (B) as in their binary systems also occurs in the ternary systems. Thus, the copper(II)–histamine (A)–2-aba, –3-aba, and –4-aba (B) systems would contain respectively six- and five-, six- and six-, and six- and seven-membered chelate rings. The log β_{CuAB} values for these three systems (Table II) decrease in the order 2-aba > 3-aba > 4-aba, though their log β_{H_2B} values increase from 2-aba to 4-aba (Table I). It clearly demonstrates that the ternary chelate systems decrease in the ring size order: 6 and 5 > 6 and 6 > 6 and 7. The same trends are also reflected in the concentration distribution plots; i.e, in the copper(II)–histamine (A)–2-aba (B) system, about 91% of the total copper(II) was found to be present in the form of CuAB in a 1:1:1 solution; this species is even more favored in a 1:2:2 solution, its formation being to the extent of 99%. In the systems with B =

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3-aba and 4-aba, the respective amounts of the total metal found in the form of CuAB ternary complex were 88 and 26% in their 1:1:1 solutions. The appreciable amount of the total metal in the form of CuAB complex with six- and seven-membered chelate rings in the copper(II)–histamine (A)–4-aba (B) system is quite interesting, because it was previously reported[8b] that six- and seven-membered chelate rings in the copper(II)– β-alanine (A)–4-aba (B) system are not favored due to steric factors. This may probably be accounted for by considering the stability-enhancing effect of the histamine (A) ligand in the copper(II)–histamine (A)–4-aba (B) system, siince 4-aba (B) ligand contains an O-donor group.

As pointed out above, the log $K^{CuA}{}_{CuAB}$ values in Table II for the copper(II)–histamine (A)–dapa, –daba, and –Orn (B) systems clearly suggest the tridentate binding of these secondary ligands (B) in their respective CuAB complexes. However, the bonding of this third donor group would be very weak due to the well-known Jahn–Teller distortions. Thus, it seems more reasonable to suggest a structure for the CuAB complexes in these three ternary systems with a glycine-like mode of binding of dapa, daba, or Orn (B) ligands, their terminal amino groups being weakly coordinated in the apical positions with histamine (A) completing the other two equatorial positions with imidazole and primary amino nitrogens. The respective amounts of the total metal found to be present in the form of CuAB complex species in these systems are 82, 59, and 48% at pH 8 in their equimolar solutions.

The log $K^{CuA}{}_{CuAB}$ value of 10.46 in the copper(II)–histamine (A)–ahba (B) system is ~2.6 log units lower than the log β_{CuB} value in the copper(II)–ahba (B) binary system (Table I), where ahba binds the metal with amino-, hydroxy-, and carboxylate-donor groups. This may probably be due to the fact that in the CuAB ternary complex, ahba (B) binds only with amino and hydroxy groups. This mode of binding of ahba (B) in CuAB would ultimately result in five- and six-membered chelate rings, which is the preferred arrangement for Cu(II). The same conclusion may be further confirmed by noting that the log $K^{CuB}{}_{CuAB}$ value for this ternary complex system is lower compared to those of all other systems in Table II; i.e., for the computation of this parameter (eq 1), the value of log β_{CuB}

$$\log K^{CuB}{}_{CuAB} = \log \beta_{CuAB} - \log \beta_{CuB} \quad (1)$$

used was that for the tridentate binding of ahba (B) in its CuB binary complex though it is bidentate in the CuAB ternary complex. In the copper(II)–imidazole (A)–ahba (B) system also, the bidentate binding of ahba (B) was reported.[9] About 52% of the total Cu(II) was found to be present in the form of CuAB complex in a 1:1:1 solution in the copper(II)–histamine(A)–ahba (B) system.

For the characterization of the stability of the ternary complex species CuAB in relation to that of the parent binary complexes, the values of Δ log K_{CuAB} (eq 2 and 3) and log X_{CuAB} (eq 4 and 5) were determined. The stabilization con-

$$CuA + CuB \rightleftharpoons CuAB + Cu \quad (2)$$

$$\Delta \log K_{CuAB} = \log \beta_{CuAB} - (\log \beta_{CuA} + \log \beta_{CuB}) \quad (3)$$

$$CuA_2 + CuB_2 \rightleftharpoons 2CuAB$$
$$X_{CuAB} = [CuAB]^2/([CuA_2][CuB_2]) \quad (4)$$

$$\log X_{CuAB} = 2 \log \beta_{CuAB} - (\log \beta_{CuA_2} + \log \beta_{CuB_2}) \quad (5)$$

stant Δ log β, included in Table II for various ternary complexes, results from the difference between the measured stability constant and that calculated on statistical grounds. It has been found from statistics that [2,14] the values of Δ log $K > -0.6$ (for tetracoordinated copper(II) complexes) or –0.9 (for tetragonal copper(II) complexes), log $X > 0.6$, and positive Δ log β demonstrate the marked stabilization of the ternary complexes. The values obtained for all these parameters in the case of CuAB complexes in Table II follow this trend. However, it may be noted that Δ log K_{CuAB} in the copper(II)–histamine (A)–ahba (B) system is very negative. This may easily be accounted for by considering the fact that for the computation of Δ log K_{CuAB} (eq 3), the log β_{CuB} value used was that for the tridentate binding of ahba, though it is bidentate in the CuAB ternary complex as described above.

2. Stability and Structure of Cu((AB)H) Complexes. The results in Table II for Cu((AB)H) complexes in the copper(II)–histamine (A)–2-aba, –3-aba, and –4-aba (B) systems are rather confusing. If we assume the likelihood of attachment of the extra proton in Cu((AB)H) to histamine (A) considering the fact that the protonated 1:1 and 1:2 binary complexes were detected[7b,15] only in the copper(II)–histamine (A) system and not in the copper(II) binary systems[8b,15] with 2-aba, 3-aba, or 4-aba (B) ligands, then the $pK^{H}{}_{Cu((AB)H)}$ values for all these three ternary systems should be comparable. However, this is not so. A careful analysis of these values shows that they follow the same trend as the protonation constant of the amino group of 2-aba, 3-aba, or 4-aba (B) (Table I), demonstrating that the site of protonation in the copper(II)–histamine (A)–2-aba, –3-aba, or –4-aba (B) ternary syystems is the amino group of the secondary ligand (B). The site of protonation in the Cu((AB)H) complex in the system with B = ahba would also be the amino group of this ligand; the high $pK^{H}{}_{Cu((AB)H)}$ value in this system may be attributed to the influence of the neighboring hydroxy group. In the case of copper(II)–histamine (A) –dapa, –daba, and –Orn (B) systems, the $pK^{H}{}_{Cu((AB)H)}$ values in Table II follow the same trend as the log β_{HB} and log $\beta_{Cu((B)H)}$ values in Table I. Hence it may be concluded beyond doubt that the extra proton in the Cu((AB)H) complexes in these three systems is attached to the secondary ligand (B), possibly to its terminal amino group as is the case with Cu((B)H), $Cu(B_2H)$, or $Cu(B_2H_2)$ dapa, daba, or Orn binary complexes.[8a] This mode of protonation in the Cu((AB)H) complexes in all these three systems would result in one six-membered chelate ring due to the coordination of histamine (A) and one five-membered chelate ring due to the coordination of the protonated secondary ligand (BH) in a glycine-like mode, which is the preferred arrangement for copper(II). The other possibility for the site of protonation in the Cu((AB)H) complex species in the copper(II)–histamine (A)–dapa (B) system of the α-amino group of dapa (B) as in its Cu((B)H) binary complex[8a] seems slight due to the preference for Cu(II) ternary chelates containing five- and six-membered rings rather than two six-membered rings as described in the beginning. More than the statistically expected 50% of the total metal was found to be present in the form of Cu((AB)H) complex species in the three systems with B = dapa, daba, or Orn.

Thus, since the extra proton in the Cu((AB)H) complexes in the copper(II)–histamine (A)–2-aba, –3-aba, –4-aba, –ahba, –dapa, –daba, and –Orn (B) systems is attached with the secondary ligands (B), the parameters Δ log $K_{Cu((AB)H)}$ and log $X_{Cu((AB)H)}$ must be defined by expressions 6–9. Since the

$$CuA + Cu((B)H) \rightleftharpoons Cu((AB)H) + Cu \quad (6)$$

$$\Delta \log K_{Cu((AB)H)} = \log \beta_{Cu((AB)H)} - (\log \beta_{CuA} + \log \beta_{Cu((B)H)}) \quad (7)$$

$$CuA_2 + Cu(B_2H_2) \rightleftharpoons 2Cu((AB)H)$$
$$X_{Cu((AB)H)} = [Cu((AB)H)]^2/([CuA_2][Cu(B_2H_2)]) \quad (8)$$

$$\log X_{Cu((AB)H)} = 2 \log \beta_{Cu((AB)H)} - (\log \beta_{CuA_2} + \log \beta_{Cl(B_2H_2)}) \quad (9)$$

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stability constant data for the Cu((B)H) and $Cu(B_2H_2)$ complexes are not known for the copper(II)–2-aba, –3-aba, –4-aba, and –ahba (B) binary systems,[8] the above two parameters could not be determined for the copper(II)–histamine (A)–2-aba, –3-aba, –4-aba, and –ahba (B) ternary systems. Comparison of the values obtained for $\Delta \log K_{Cu((AB)H)}$, $\log X_{Cu((AB)H)}$, and $\Delta \log \beta_{Cu((AB)H)}$, the stabilization constant in Table II for the copper(II)–histamine (A)–dapa, –daba, and –Orn (B) systems, with those values expected on statistical grounds[2,14] clearly indicates the greater stabilities of Cu((AB)H) complexes in all these systems.

3. Stability and Structure of $Cu((AB)H_2)$ Complexes. The diprotonated complexes $Cu((AB)H_2)$ were detected in appreciable amounts in the copper(II)–histamine (A)–dapa and –Orn (B) systems below pH 6. The system with B = daba also showed the presence of $Cu((AB)H_2)$ complex; however, its concentration was not found to be in appreciable amounts. Due to the high standard deviation in the experimentally observed $\log \beta_{Cu((AB)H_2)}$ value in this system (Table II), the other derived constants were not computed. It is reasonable to suggest that, of the two protons in the $Cu((AB)H_2)$ in the copper(II)–histamine (A)–dapa or –Orn (B) systems, one would be attached to the histamine (A), i.e., to its primary amino group as in the Cu((A)H) or $Cu(A_2H)$ complexes,[7b] and the other would reside on the terminal amino group of dapa or Orn (B) ligands.[8a] The formation of CuAB from $Cu((AB)H_2)$ may be represented by eq 10–12. The trends

$$Cu((AB)H_2) \xrightleftharpoons{pK^H_{Cu((AB)H_2)} = 4.62} Cu((AB)H) \xrightleftharpoons{pK^H_{Cu((AB)H)} = 5.56} CuAB \quad (A = \text{histamine, B = dapa}) \quad (10)$$

$$Cu((AB)H_2) \rightleftharpoons Cu((AB)H) \xrightleftharpoons{pK^H_{Cu((AB)H)} = 7.32} CuAB \quad (A = \text{histamine, B = daba}) \quad (11)$$

$$Cu((AB)H_2) \xrightleftharpoons{pK^H_{Cu((AB)H_2)} = 4.59} Cu((AB)H) \xrightleftharpoons{pK^H_{Cu((AB)H)} = 7.96} CuAB \quad (A = \text{histamine, B = Orn}) \quad (12)$$

in the $pK^H_{Cu((AB)H_2)}$ and $pK^H_{Cu((AB)H)}$ values of these reactions demonstrate clearly that the former is for the protonation of histamine (A), while the latter denotes the protonation of dapa, daba, or Orn (B) ligands. $\Delta \log K$ (eq 13 and 14) and $\Delta \log$

$$Cu((A)H) + Cu((B)H) \rightleftharpoons Cu((AB)H_2) + Cu \quad (13)$$

$$\Delta \log K_{Cu((AB)H_2)} = \log \beta_{Cu((AB)H_2)} - (\log \beta_{Cu((A)H)} + \log \beta_{Cu((B)H)}) \quad (14)$$

$$Cu(A_2H_2) + Cu(B_2H_2) \rightleftharpoons 2Cu((AB)H_2)$$

$$X_{Cu((AB)H)} = [Cu((AB)H_2)]^2/([Cu(A_2H_2)][Cu(B_2H_2)]) \quad (15)$$

$$\log X_{Cu((AB)H_2)} = 2 \log \beta_{Cu((AB)H_2)} - (\log \beta_{Cu(A_2H_2)} + \log \beta_{Cu(B_2H_2)}) \quad (16)$$

β, the stabilization constant in Table II for the $Cu(AB)H_2$ complexes in these systems, clearly indicate their marked stabilities. However, $\log X_{Cu((AB)H_2)}$ (eq 15 and 16) could not be computed since the stability constant data for the $Cu(A_2H_2)$ complex with histamine are not available.[7b]

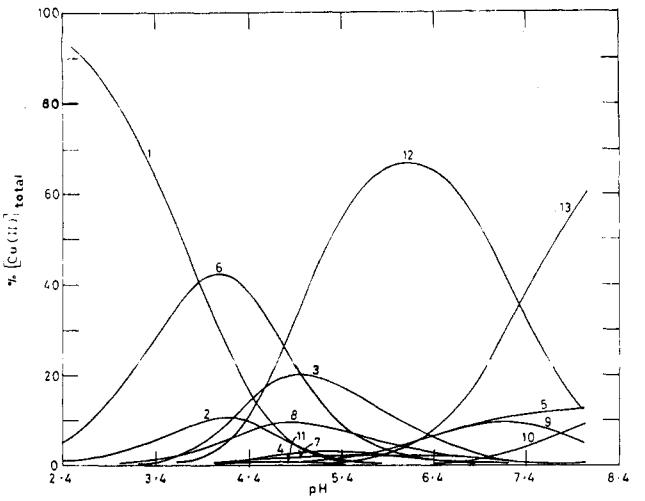

Figure 1. Distribution diagram for the copper(II)–histamine (A)–daba (B) system at a Cu:A:B ratio of 1:1:1: (1) unbound Cu(II), (2) Cu((A)H), (3) CuA, (4) $Cu(A_2H)$, (5) CuA_2, (6) Cu((B)H), (7) CuB, (8) $Cu(B_2H_2)$, (9) $Cu(B_2H)$, (10) CuB_2, (11) $Cu((AB)H_2)$, (12) Cu((AB)H), and (13) CuAB.

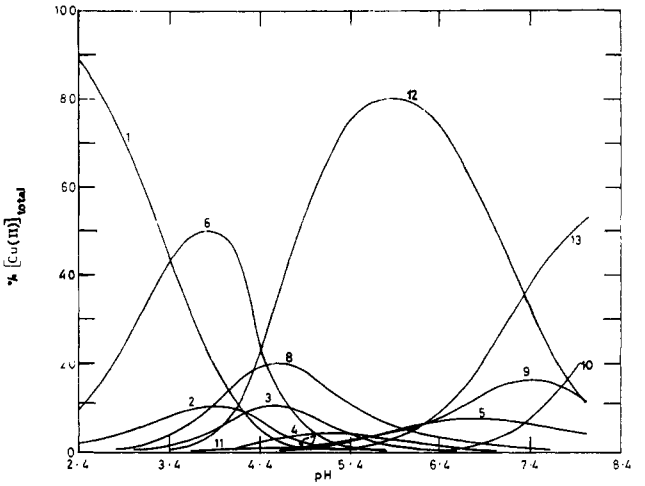

Figure 2. Distribution diagram for the copper(II)–histamine (A)–daba (B) system at a Cu:A:B ratio of 1:2:2, with species as in Figure 1.

4. Distribution of Various Complex Species as a Function of pH for the Various Ternary Systems. The distribution diagrams obtained in terms of percent bound Cu(II) as a function of pH in all the seven ternary systems in this study show the same qualitative features such as (i) the preferential formation of the ternary complex species over binary complexes and (ii) existence of a number of species in equilibrium at all pH values in the ternary systems compared to those in the binary systems where in certain pH regions the concentration of one complex strongly predominates. These results demonstrate well the discriminating quality of the histamine (A) ligand[2] in the formation of Cu(II) ternary complexes with amino acids (B). For the depiction of these aspects, the distribution diagrams obtained for the copper(II)–histamine (A)–daba (B) system in 1:1:1 and 1:2:2 solutions are given in Figures 1 and 2.

Registry No. Cu, 7440-50-8; histamine, 51-45-6; 2-aba, 2835-81-6; 3-aba, 2835-82-7; 4-aba, 56-12-2; ahba, 924-49-2; dapa, 6018-54-8; daba, 2577-63-1; Orn, 616-07-9.