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Ternary Coordination Complexes of Copper(II) with Imidazole and Bidentate or Potentially Tridentate Ligands

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The formation equilibria involved in some new ternary systems of Cu(II) containing imidazole (A) and 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) (B) have been investigated in aqueous perchlorate medium at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4) by pH titrimetry. Enhanced stabilities were observed for all types of ternary complex species (CuABH , CuAB , CuA_2BH , or CuA_2B) detected in the systems studied. The results suggest that in the ternary systems where the ligand B forms a five-membered chelate ring, the CuA_2B complexes are more stable than CuAB , while in the systems where B forms a six-membered chelate ring, the CuA_2B complexes are less stable than CuAB . It appears that though ahba (B) is potentially tridentate, in the ternary systems containing imidazole (A) it binds in a bidentate manner. However, dapa, daba, and Orn (B) ligands coordinate in a tridentate manner with Cu(II) in presence of imidazole (A). The probable site of protonation in the CuABH and CuA_2BH types of complex species is discussed in terms of their stability constant data.

Introduction

Many biological processes where the activity depends on enzymes possessing metal ion centers owe their specific function to the formation of binary and ternary complexes.^{1,2} Considerable attention has been paid in recent years to the studies of Cu(II) complexes containing the imidazole group as a ligand since this group is one of the important binding sites for Cu(II) in many biological systems such as human albumin, sperm whale myoglobin, hemocyanin, bovine serum albumin, ceruloplasmin, and ribonuclease.¹ Thus, the Cu(II) complexes of several histidine-containing peptides have been studied¹⁻⁷ as models for copper interaction with this type of biomolecule. It was shown^{1,2} that histidyl residues in proteins are typically nonchelating. Hence, ternary complexes containing imidazole as a ligand seem to be of considerable interest. The effectiveness of the imidazole group to act as a metal binding site has been attributed to its great flexibility, its availability at physiological pH, and its capacity to form both σ and π bonds with metal ions.² By taking into account these aspects, we have been investigating the ternary complexes of Cu(II) containing imidazoles, peptides, or amino acids.⁸⁻¹⁷ The present paper deals with the study of the formation equilibria of seven new ternary systems of Cu(II) containing imidazole (A) and some bidentate amino acids [DL-2-aminobutyric acid (2-aba), DL-3-aminobutyric acid (3-aba), and 4-aminobutyric acid (4-aba)] or some potentially tridentate ligands [DL-4-amino-3-hydroxybutyric acid (ahba), DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba), and DL-ornithine (Orn)] by use of pH titrimetry at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4). The ahba ligand contains the aminoethanol moiety, $\text{NH}_2\text{CH}_2\text{CHOH}$, which is common to several compounds of pharmaceutical and biological importance. The compounds dapa, daba, and Orn are diaminocarboxylic acids of general formula: $\text{NH}_2\text{-(CH}_2)_n\text{CH(NH}_2\text{)COOH}$, where $n = 1$ (dapa), $n = 2$ (daba) and $n = 3$ (Orn). It may be mentioned that, prior to our work,⁹⁻¹² the stability constant data available^{18,19} on the ternary complexes containing imidazole were very few.

Experimental Section

All the ligands used were Fluka chemicals. The compounds dapa and Orn were used in the monoprotonated form, while daba was used in the diprotonated form. $\text{Cu}(\text{ClO}_4)_2$ and other reagents were prepared and estimated as described earlier.⁸⁻¹⁷

All the measurements were carried out at 37 °C at an ionic background of 0.15 mol dm^{-3} (NaClO_4). The accuracy in the experimental pH titration data, required for the computer-based analysis of the results, was achieved by using the apparatus and titration technique described elsewhere.^{15,17} Titrations were done on aliquots (50 cm^3) of solutions containing low concentrations of $\text{Cu}(\text{ClO}_4)_2$, imidazole (A), and the ligand (B) in 1:1:1 and 1:2:2 ratios with known volumes of standard CO_2 -free NaOH. The stability constants of the various ternary complex species were derived from the pH titration data by the MINQUAD-75 least-squares computer program²⁰ on an IBM 370 computer. The proton association constants for the free ligands A and B and the stability constant data for their binary complexes with Cu(II) estimated at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4) (Table I) were kept constant in the calculations. The calculations were restricted to systems below pH 8 in order to avoid the complications due to the hydrolysis of various complex species at higher pH ranges. The results obtained are reported in Table II. The charges of all the complex species reported in this paper are neglected for clarity.

Results and Discussion

Since the ternary systems in the present investigation contain a monodentate primary ligand (A), viz., imidazole, and a bidentate or potentially tridentate secondary ligand (B), one may expect the ternary complex species of stoichiometry CuA_2B in addition to the CuAB complex, because Cu(II) usually prefers to be four-coordinated. It is interesting that in all the copper(II)-imidazole (A)-secondary ligand (B)

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Table I. Stability Constants for the Proton and Copper(II) Complexes of 2-aba, 3-aba, 4-aba, ahba, dapa, daba, Orn, and Imidazole at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4) (Standard Deviations in Parentheses)

parameters	ligands							
	2-aba ^a	3-aba ^a	4-aba ^a	ahba ^b	dapa ^b	daba ^b	Orn ^b	imidazole ^c
$\log \beta_{\text{HB}}$	9.43 (1)	9.95 (1)	10.15 (1)	12.88 (11)	9.37 (2)	9.93 (2)	10.22 (1)	6.95 (2)
$\log \beta_{\text{H}_2\text{B}}$	11.54 (1)	13.30 (1)	14.24 (1)	21.91 (2)	15.98 (3)	18.02 (4)	18.85 (2)	
$\log \beta_{\text{H}_3\text{B}}$				25.78 (2)	17.37 (5)	19.88 (6)	20.99 (4)	
$\log \beta_{\text{CuBH}}$					15.37 (4)	16.99 (3)	17.67 (2)	
$\log \beta_{\text{CuB}}$	8.10 (2)	7.16 (2)	6.07 (9)	13.02 (9)	10.61 (4)	10.94 (3)		4.21 (9)
$\log \beta_{\text{Cu}_2\text{B}_2}$				28.10 (30)				
$\log \beta_{\text{CuB}_2\text{H}_2}$					30.16 (5)	32.92 (4)	34.32 (3)	
$\log \beta_{\text{CuB}_2\text{H}}$					25.32 (6)	26.89 (4)	26.12 (6)	
$\log \beta_{\text{CuB}_2}$	15.13 (4)	12.90 (5)		19.09 (24)	20.18 (5)	19.15 (6)		7.55 (14)
$\log \beta_{\text{CuB}_3}$								10.73 (16)
$\log \beta_{\text{CuB}_4}$								12.91 (24)

^a References 12 and 16. ^b Reference 13. ^c References 11 and 12.

systems except the one with B = 4-aba in this study, the CuA_2B ternary complex species was detected (Table II). The absence of CuA_2B species in the copper(II)–imidazole (A)–4-aba (B) system may be attributed to the steric factors associated with two imidazole rings and one seven-membered chelate ring in the square plane of Cu(II) in its CuA_2B complex. In the ternary systems with B = daba and Orn, the protonated ternary complex species of the type CuABH or CuA_2BH was also detected as reported in Table II.

The parameters generally used for indicating the stabilization of the ternary complex with respect to the binary ones,^{1,21} viz., (i) the difference in stability of the binary complex with that of the ternary complex, $\Delta \log K$, and (ii) the disproportionation constant, $\log X$, were calculated for all types of ternary complexes, viz., CuAB , CuABH , CuA_2BH , and CuA_2B , detected in the systems under study (eq 1–16). The



$$\Delta \log K_{\text{CuAB}} = \log \beta_{\text{CuAB}} - (\log \beta_{\text{CuA}} + \log \beta_{\text{CuB}}) \quad (2)$$



$$\Delta \log K_{\text{CuABH}} = \log \beta_{\text{CuABH}} - (\log \beta_{\text{CuA}} + \log \beta_{\text{CuBH}}) \quad (4)$$



$$\Delta \log K_{\text{CuA}_2\text{BH}} = \log \beta_{\text{CuA}_2\text{BH}} - (\log \beta_{\text{CuA}_2} + \log \beta_{\text{CuBH}}) \quad (6)$$



$$\Delta \log K_{\text{CuA}_2\text{B}} = \log \beta_{\text{CuA}_2\text{B}} - (\log \beta_{\text{CuA}_2} + \log \beta_{\text{CuB}}) \quad (8)$$



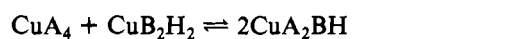
$$X_{\text{CuAB}} = [\text{CuAB}]^2 / ([\text{CuA}_2][\text{CuB}_2]) \quad (10)$$

$$\log X_{\text{CuAB}} = 2 \log \beta_{\text{CuAB}} - (\log \beta_{\text{CuA}_2} + \log \beta_{\text{CuB}_2}) \quad (10)$$



$$X_{\text{CuABH}} = [\text{CuABH}]^2 / ([\text{CuA}_2][\text{CuB}_2\text{H}_2]) \quad (11)$$

$$\log X_{\text{CuABH}} = 2 \log \beta_{\text{CuABH}} - (\log \beta_{\text{CuA}_2} + \log \beta_{\text{CuB}_2\text{H}_2}) \quad (12)$$



$$X_{\text{CuA}_2\text{BH}} = [\text{CuA}_2\text{BH}]^2 / ([\text{CuA}_4][\text{CuB}_2\text{H}_2]) \quad (13)$$

$$\log X_{\text{CuA}_2\text{BH}} = 2 \log \beta_{\text{CuA}_2\text{BH}} - (\log \beta_{\text{CuA}_4} + \log \beta_{\text{CuB}_2\text{H}_2}) \quad (14)$$



$$X_{\text{CuA}_2\text{B}} = [\text{CuA}_2\text{B}]^2 / ([\text{CuA}_4][\text{CuB}_2]) \quad (15)$$

$$\log X_{\text{CuA}_2\text{B}} = 2 \log \beta_{\text{CuA}_2\text{B}} - (\log \beta_{\text{CuA}_4} + \log \beta_{\text{CuB}_2}) \quad (16)$$

stabilization constant, $\Delta \log \beta$, included in Table II for the various ternary complex species results from the difference between their stabilities measured and those calculated on statistical grounds.²² Since more coordination sites are available for bonding the first ligand to a metal ion than for bonding the second ligand, negative values for $\Delta \log K$ are expected.^{1,21} Depending on the geometry of the complex and the denticity of the ligands, the statistically expected value for $\Delta \log K$ will vary. In general, it may be stated that considerably less negative $\Delta \log K$ indicates marked stabilities of the ternary complexes. The $\Delta \log K$ values for the various ternary complex species in Table II follow this trend. Again, the value of $\Delta \log K$ characterizes the coordination tendency of, e.g., the ligand B toward CuA or CuA_2 relative to aquated metal ion. Thus, the negative $\Delta \log K$ values in all the ternary systems except the one with B = 4-aba in Table II indicate that the secondary ligands (B) prefer to add onto the aquated Cu(II) ion rather than to the corresponding CuA or CuA_2 (A = imidazole) complexes. The positive $\Delta \log K_{\text{CuAB}}$ value in the system with B = 4-aba shows that the 4-aba ligand (B) prefers to add onto the imidazole binary complex CuA rather than to the aquated Cu(II). As one expects from statistical considerations,^{1,21} the $\log X$ values are higher than 0.6, and $\Delta \log \beta$ are positive for all the ternary complex species in Table II, suggesting their enhanced stabilities, which is in agreement with the conclusions derived from the $\Delta \log K$ values described above.

It may be noted that the $\Delta \log K_{\text{CuA}_2\text{B}}$ value of -3.98 in the copper(II)–imidazole (A)–ahba (B) system is negative with high magnitude compared to other systems in Table II. Again, the $\log K_{\text{CuB}}^{\text{CuA}_2\text{B}}$ value in this system is less than that value in other systems by ~ 3.5 log units (Table II). This discrepancy may probably be accounted for by considering the bidentate mode of binding of ahba secondary ligand (B) via amino N and hydroxy O donor groups in this CuA_2B ternary species: though it is tridentate in its CuB binary complex,¹³ i.e., for computing the parameters, $\Delta \log K_{\text{CuA}_2\text{B}}$ (eq 8) and $\log K_{\text{CuB}}^{\text{CuA}_2\text{B}}$ (eq 17), the $\log \beta_{\text{CuB}}$ used was that for the

$$\log K_{\text{CuB}}^{\text{CuA}_2\text{B}} = \log \beta_{\text{Cu}_2\text{B}} - \log \beta_{\text{CuB}} \quad (17)$$

tridentate binding of ahba (B) in its CuB binary complex, though it is bidentate in the CuA_2B ternary species. The basis for this bidentate binding of ahba (B) ligand in the CuA_2B ternary species is that Cu(II) usually prefers to have tetra-coordination and, of the four positions in the square plane of Cu(II) in this complex, two positions would be occupied by the imidazole nitrogens in the two imidazole ligands (A) and the remaining two sites may be filled up by the amino N and

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Table II. Stability Constants for the Copper(II)-Imidazole (A)-Secondary Ligand (B) Systems at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4) (Standard Deviations in Parentheses)

results	secondary ligands, B						
	2-aba	3-aba	4-aba	ahba	dapa	daba	Orn
$\log \beta_{\text{CuABH}}$						21.23 (19)	21.43 (5)
$\log \beta_{\text{CuAB}}$	11.67 (18)	10.62 (10)	10.44 (6)			14.89 (24)	14.37 (2)
$\log \beta_{\text{CuA}_2\text{BH}}$							24.98 (4)
$\log \beta_{\text{CuA}_2\text{B}}$	15.30 (12)	13.68 (11)		16.59 (7)	17.61 (14)	18.07 (42)	
$\text{pK}_{\text{CuABH}}^{\text{H}}$						6.34	7.06
$\log \beta_{\text{CuABH}}^{\text{CuA}_2\text{BH}}$							3.55
$\log K^{\text{CuAB}}_{\text{CuA}_2\text{B}}$	3.63	3.06				3.18	
$\log K^{\text{CuA}}_{\text{CuAB}}$	7.46	6.41	6.23			10.68	10.16
$\log K^{\text{CuA}_2}_{\text{CuA}_2\text{B}}$	7.75	6.13		9.04	10.06	10.52	
$\log K^{\text{CuB}}_{\text{CuAB}}$	3.57	3.46	4.37			3.95	
$\log K^{\text{CuB}}_{\text{CuA}_2\text{B}}$	7.20	6.52		3.57	7.00	7.13	
$\log K^{\text{CuBH}}_{\text{CuA}_2\text{BH}}$							7.31
$\Delta \log K_{\text{CuABH}}$						0.03	-0.45
$\Delta \log K_{\text{CuAB}}$	-0.64	-0.75	0.16			-0.26	
$\Delta \log K_{\text{CuA}_2\text{BH}}$							-0.24
$\Delta \log K_{\text{CuA}_2\text{B}}$	-0.35	-1.03		-3.98	-0.55	-0.42	
$\log X_{\text{CuABH}}$						1.99	0.99
$\log X_{\text{CuAB}}$	0.66	0.79				3.08	
$\log X_{\text{CuA}_2\text{BH}}$							2.73
$\log X_{\text{CuA}_2\text{B}}$	2.56	1.55		1.18	2.13	4.08	
$\log \beta_{\text{CuABH}}(\text{calcd})$						19.99	20.69
$\log \beta_{\text{CuAB}}(\text{calcd})$	11.09	9.98	9.60			13.10	
$\log \beta_{\text{CuA}_2\text{BH}}(\text{calcd})$							24.09
$\log \beta_{\text{CuA}_2\text{B}}(\text{calcd})$	14.50	13.38		16.48	17.02	16.51	
$\Delta \log \beta_{\text{CuABH}}$						1.24	0.74
$\Delta \log \beta_{\text{CuAB}}$	0.58	0.64	0.84			1.79	
$\Delta \log \beta_{\text{CuA}_2\text{BH}}$							0.89
$\Delta \log \beta_{\text{CuA}_2\text{B}}$	0.80	0.30		0.11	0.59	1.56	

hydroxy O atoms of ahba (B). However, the results in Table II for the CuA_2B complexes with B = dapa, daba, and Orn suggest a possible tridentate binding of these secondary ligands (B) in their corresponding CuA_2B complexes.

The $\log \beta_{\text{CuAB}}$ and $\log K^{\text{CuA}}_{\text{CuAB}}$ values in Table II for the copper(II)-imidazole (A)-2-aba (B), -3-aba (B), and -4-aba (B) systems decrease in the order B = 2-aba > 3-aba > 4-aba. This indicates that the ring size order $5 > 6 > 7$ found¹⁶ in the Cu(II) binary chelate systems of 2-aba, 3-aba, and 4-aba is also true in the case of Cu(II) ternary chelate systems with the imidazole primary ligand (A). It may be noted that the respective $\log \beta_{\text{CuAB}}$ and $\log \beta_{\text{CuA}_2\text{B}}$ values of 11.67 and 15.30 in the copper(II)-imidazole (A)-2-aba (B) system (Table II) are in good agreement with those values of 11.97 and 15.91 reported¹⁰ in the copper(II)-imidazole (A)-glycine (B) system at 37 °C and $I = 0.15 \text{ mol dm}^{-3}$ (NaClO_4). The slightly lower stabilities of CuAB and CuA_2B complexes in the system with B = 2-aba compared to those in the system with B = glycine may be attributed to the steric factors associated with the alkyl substituent of 2-aba in the former system. The $\log K^{\text{CuA}}_{\text{CuAB}}$ values in Table II for the copper(II)-imidazole (A)-daba (B) and -Orn (B) systems are close to comparable to their corresponding $\log \beta_{\text{CuB}}$ values (Table I), suggesting the tridentate binding of these secondary ligands (B) in their CuAB ternary complexes.

Previously, π -bonding effects have been invoked^{19,23} to explain the decrease in stability with an increase in the number of coordinated imidazole molecules in the Cu(II) complexes. Thus, by considering the factors (i) the loss of π bonding in going from an in-plane coordinated imidazole to two out-of-plane cis-coordinated imidazoles as observed^{24,25} in the *cis*-

bis(imidazole) complexes and (ii) the statistical effect resulting from the reduction in available binding sites for the coordination of the second imidazole molecule, one may expect high stabilities for the CuAB complexes compared to those for CuA_2B complexes, i.e., $\Delta \log K_{\text{CuA}_2\text{B}}$ values must be more negative compared to the $\Delta \log K_{\text{CuAB}}$ values. The results in Table II show that $\Delta \log K_{\text{CuA}_2\text{B}}$ values in the copper(II)-imidazole (A)-3-aba and daba (B) systems are more negative compared to their respective $\Delta \log K_{\text{CuAB}}$ values, suggesting less stability for the CuA_2B complexes than for their CuAB complexes. But, in the ternary systems with B = 2-aba or Orn, the $\Delta \log K_{\text{CuAB}}$ or $\Delta \log K_{\text{CuABH}}$ values are more negative than the corresponding $\Delta \log K_{\text{CuA}_2\text{B}}$ or $\Delta \log K_{\text{CuA}_2\text{BH}}$ values, suggesting more stability for the CuA_2B or CuA_2BH complexes compared to their corresponding CuAB or CuABH complexes. These results demonstrate that formation of CuA_2B from CuAB depends on the size of the chelate rings due to the ligand B. If B forms a six-membered chelate ring as in the case of the systems with B = 3-aba or daba, then CuA_2B would have less stability than CuAB. In the systems with B = 2-aba or Orn, B forms a five-membered chelate, and hence CuA_2B has a higher stability than their CuAB complexes. Thus, it may be concluded that the size of the chelate rings due to the ligand B in CuAB overpowers factors i and ii described above in the formation of CuA_2B from CuAB. The same results may be further confirmed from the higher $\log K^{\text{CuAB}}_{\text{CuA}_2\text{B}}$ values of 3.63 and 3.55 in the systems with B = 2-aba and Orn compared to the values of 3.06 and 3.18 (Table II) in the systems with B = 3-aba and daba. A comparison of the $\log K^{\text{CuAB}}_{\text{CuA}_2\text{B}}$ values in Table II with the \log

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$K^{\text{CuA}_2\text{CuA}_4}$ value of 2.19 in the copper(II)-imidazole (A) binary system¹¹ suggests that addition of one more imidazole to a ternary complex system is more favored compared to that addition in the binary system because in all the systems in this study the former parameter is higher than the latter. The $\log K^{\text{CuB}}_{\text{CuA}_2\text{B}}$ values in Table II for all the ternary systems except the one with B = ahba are very near those values expected for the coordination of two imidazole molecules, i.e., ~ 7 log units, since¹¹ $\log \beta_{\text{CuA}_2} = 7.55$. The probable reason for obtaining smaller $\log K^{\text{CuB}}_{\text{CuA}_2\text{B}}$ values in the system with B = ahba compared to those of other systems in Table II was discussed in the beginning.

The protonated ternary complexes, CuABH in the copper(II)-imidazole (A)-daba (B) or -Orn (B) systems were found to be more favored near pH 6, while the CuA₂BH species in the system with B = Orn predominated above pH 6. With regard to the site of protonation in these complexes, its possibility with the imidazole primary ligand (A) may be ruled out because in the copper(II)-imidazole (A) binary system no protonated binary complex species were detected.¹¹ Hence, the extra protons in these CuABH and CuA₂BH complexes must be attached to the secondary ligands (B). From consideration of the earlier reports^{13,26,27} that the site of protonation in the CuBH, CuB₂H₂, and CuB₂H daba or Orn (B) complexes is their ω -amino groups, it may be concluded that the extra protons in these CuABH and CuA₂BH ternary complexes are also residing with the ω -amino groups of daba or Orn secondary ligands (B). The pK_a values (Table II) obtained for the protonation of these complexes also agree with this suggestion. For example, the $pK^{\text{H}}_{\text{CuABH}}$ value of 6.34 in the copper(II)-imidazole (A)-daba (B) system compares well with the $pK^{\text{H}}_{\text{CuBH}}$ value of 6.05 in Table I for the copper(II)-daba (B) binary system. Thus, with it in mind that the site of protonation in these CuABH or CuA₂BH ternary complexes is the ω -amino group of B, the constants $\log K'$ and $\log K''$ were calculated (eq 18 and 19). The values obtained

$$\log K' = \log \beta_{\text{CuABH}} - \log \beta_{\text{HB}} \quad (18)$$

$$\log K'' = \log \beta_{\text{CuA}_2\text{BH}} - \log \beta_{\text{HB}} \quad (19)$$

are (i) $\log K'$ for the CuABH complex with B = daba is 11.30 and for the complex with B = Orn it is 11.21 and (ii) the $\log K''$ value for the CuA₂BH complex with B = Orn is 14.76. The $\log K'$ values in both the systems are close to comparable to the $\log \beta_{\text{CuAB}}$ value of 11.67 in the copper(II)-imidazole (A)-2-aba (B) system (Table II), where one imidazole, and one amino N and one carboxyl O of 2-aba are involved in binding. This demonstrates well that the protons in the CuABH complexes are attached to the ω -amino groups of daba or Orn (B) and these secondary ligands (B) bind with the metal in a glycine-like mode as in the binding of 2-aba. The $\log K''$ value of 14.76 obtained for the CuA₂BH complex in the system with B = Orn compares favorably to the $\log \beta_{\text{CuA}_2\text{B}}$ value of 15.30 in the system with B = 2-aba (Table II), suggesting glycine-like binding of Orn with the proton residing in its ω -amino group in the CuA₂BH complex species.

The distribution of various species (as percentages of total metal) as a function of pH has been calculated for all the copper(II)-imidazole (A)-secondary ligand (B) systems in this study. In all these systems, the concentration of the binary species of copper(II)-imidazole (A) was found to be very low.

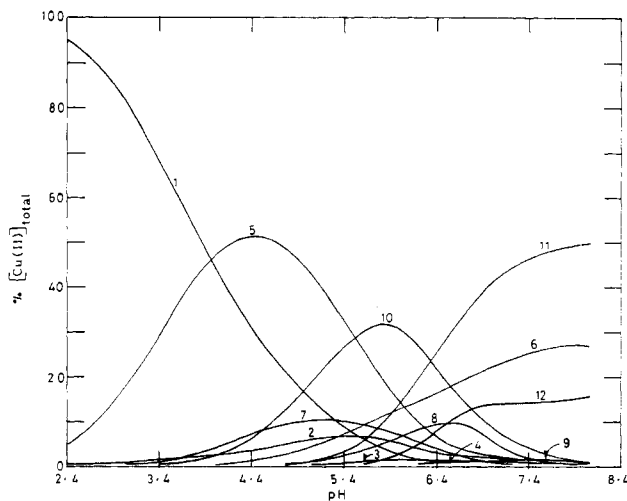


Figure 1. Distribution diagram for the copper(II)-imidazole (A)-daba (B) system at a Cu:A:B ratio of 1:1:1 for unbound Cu(II) (1), CuA(2), CuA₂ (3), CuA₃ (4), CuBH (5), CuB (6), CuB₂H₂ (7), CuB₂H (8), CuB₂ (9), CuABH (10), CuAB (11), and CuA₂B (12). The species CuA₄ could not be shown because of its very low concentration.

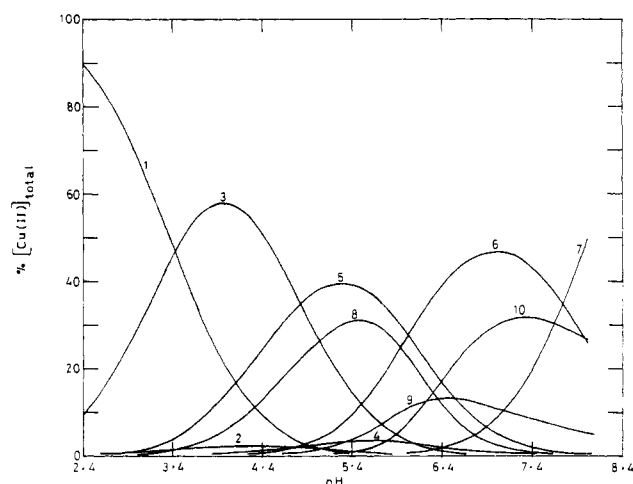


Figure 2. Distribution diagram for the copper(II)-imidazole (A)-daba (B) system at a Cu:A:B ratio of 1:2:2 for unbound Cu(II) (1), CuA (2), CuBH (3), CuB (4), CuB₂H₂ (5), CuB₂H (6), CuB₂ (7), CuABH (8), CuAB (9), and CuA₂B (10). The species CuA₂, CuA₃, and CuA₄ could not be shown because of their very low concentrations.

It is also observed that the CuABH and CuAB ternary complexes were found to be favored in 1:1:1 solutions, while the higher order ternary species of the type CuA₂BH and CuA₂B reached their maximum in 1:2:2 solutions. The predominance of the ternary complexes over corresponding binary species is observed in all the systems, which is in agreement with the stabilization of the ternary complexes over and above their statistical probability. Also, it was noted that the percentage of the free metal ion was almost negligible near pH 7 in 1:1:1 solutions and pH 6 in 1:2:2 solutions in all the systems justifying the assumption that hydrolyzed metal complexes are absent in the pH ranges employed in this investigation. As a demonstration of these trends, the typical distribution pattern of the species in the copper(II)-imidazole (A)-daba (B) system in both 1:1:1 and 1:2:2 solutions is given in Figures 1 and 2.

Registry No. Cu, 7440-50-8; imidazole, 288-32-4; 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.

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