

Computer based stability constants and absorption maximum values for the copper(II) ternary complexes containing L-cysteic acid and some selected ligands

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The present paper deals with the determination of stability constants for sixteen ternary systems viz. Cu(II)-L-cysteic acid (cya) (A)-L-phenylalanine (pha), dopamine (dopm), dopa, imidazole (Him), benzimidazole (Bimz), histamine (Hist), L-histidine (His), DL-2-aminobutyric acid (2aba), DL-3-aminobutyric acid (3aba), 4-aminobutyric acid (4aba), DL-4-amino-3-hydroxybutyric acid (ahba), 1,2-diaminopropane (dp), 1,3-diaminopropane (tp), DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba), and DL-ornithine (orn) (B). These systems have given rise to the formation of ternary complexes of the types CuAB, CuAB₂, CuABH or CuABH₂. Though dopa ligand binds Cu(II) in a mixed mode in its CuB complex, in the CuAB species, it binds in a pyrocatechol-like mode. In all other systems, the binding modes of the ligands A and B in the CuAB species are similar to their binding in their respective binary systems. In the CuABH₂ species in the Cu(II)-cya-dopm and dopa systems, the two protons reside with the ϕ -phenolato oxygen atoms of the respective secondary ligands. The possible protonation sites in the other CuABH and CuABH₂ ternary complexes in this study are discussed.

L-cysteine is not only an essential constituent of protein, but it also gets involved in a variety of biological metabolic processes. An important qualitative pathway of L-cysteine metabolism is its oxidation to L-cysteic acid. The pharmaceutical and biological applications of L-cysteic acid ligand have been studied in detail^{1,2}. However, the stability constant studies of Cu(II) ternary complex system containing L-cysteic acid ligand appear to be very little. This paper deals with the determination of the stability constants by pH-titrimetry at 37°C and $I=0.15$ (NaClO₄) on sixteen Cu(II) ternary complex systems involving L-cysteic acid (cya) as the primary ligand and five groups of secondary ligands viz. (i) phenylalanine (pha) and related ligands viz. dopamine (dopm) and dopa, (ii) imidazole (Him) and related ligands viz. benzimidazole (Bimz), histamine (Hist) and L-histidine (His), (iii) amino acids viz. DL-2-aminobutyric acid (2aba), DL-3-aminobutyric acid (3aba), DL-4-aminobutyric acid (4aba), and DL-4-amino-3-hydroxybutyric acid (ahba), (iv) diamines viz. 1,2-diaminopropane (dp), 1,3-diaminopropane (tp), and (v) diaminocarboxylic acids viz.

DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine (orn). The importance of these secondary ligands in the biological and chemical points of view has been well discussed³⁻⁷. The visible spectral measurements have also been done in some binary and ternary systems.

Materials and Methods

All the ligands used were Fluka products of Puriss quality. The method of preparation and determination of all the reagents and other experimental details were described earlier⁷. All the calculations have been made with the aid of the computer program⁸ MINIQUAD 75 on a Cyber 180/830A computer fixing the acid dissociation constants of the ligands and parent binary stability constants estimated under identical conditions.

The auxiliary data for the Cu(II)-cya, pha, dopm, dopa, Bimz, dp, and tp binary systems have been estimated under the present experimental conditions and for the remaining binary systems such data have been taken from the literature^{9,10} (Tables 1 and 2).

The absorption spectra in the visible region were recorded on a Perkin-Elmer UV-visible spectrophotometer model Lambda 3B interfaced with Nexus

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Table 1 — Stability constants for the proton and Cu(II) complexes of cya; pha, dopm, dopa, Bimz, Him, Hist and His at 37°C and $I=0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$. Standard deviations are given in parentheses.

Parameters	Ligands, B							
	cya	pha	dopm	dopa	Bimz	Him*	Hist*	His*
log β_{HB}	8.41 (1)	8.97 (4)	11.48 (4)	11.45 (5)	5.68 (9)	6.95 (2)	9.39 (8)	8.96 (3)
log $\beta_{\text{H}_2\text{B}}$	10.56 (4)	11.51 (8)	21.61 (3)	21.10 (4)	-	-	15.34 (1)	14.96 (5)
log $\beta_{\text{H}_3\text{B}}$	-	-	30.34 (4)	29.73 (6)	-	-	-	17.37 (9)
log $\beta_{\text{H}_4\text{B}}$	-	-	-	32.38 (8)	-	-	-	-
log β_{CuBH_2}	-	-	-	29.20 (6)	-	-	-	-
log β_{CuBH}	-	-	22.07 (6)	23.92 (8)	-	-	13.46 (4)	14.38 (4)
log β_{CuB}	8.60 (4)	8.12 (3)	15.44 (9)	18.08 (7)	3.44 (6)	4.21 (9)	9.24 (18)	10.27 (2)
log $\beta_{\text{CuB}_2\text{H}_2}$	-	-	-	-	-	-	-	27.41 (2)
log $\beta_{\text{CuB}_2\text{H}}$	-	-	-	-	-	-	21.82 (6)	23.96 (2)
log β_{CuB_2}	14.58 (6)	14.56 (6)	23.25 (9)	-	6.29 (8)	7.55 (14)	16.16 (4)	18.49 (4)
log β_{CuB_3}	-	-	-	-	8.70 (9)	10.73 (16)	-	-
log β_{CuB_4}	-	-	-	-	10.87 (9)	12.91 (24)	-	-
$\text{pK}_{\text{CuBH}_2}^{\text{H}}$	-	-	-	5.28	-	-	-	-
$\text{pK}_{\text{CuBH}}^{\text{H}}$	-	-	6.63	5.84	-	-	4.22	4.11
log $K_{\text{CuB}}^{\text{CuB}}$	5.98	6.44	7.81	-	2.85	3.34	6.92	8.22
log $K_{\text{CuB}_2}^{\text{CuB}_2}$	-	-	-	-	2.41	3.18	-	-
log $K_{\text{CuB}_3}^{\text{CuB}_3}$	-	-	-	-	2.17	2.18	-	-

-cya becomes primary ligand (A) in the ternary system

*Ref: 9

computer using Perkin-Elmer Computerised Spectroscopic Software. Matched quartz cells of path length 1.0 cm calibrated before use was employed. The 1:1 and 1:2 solutions in the case of binary systems, and 1:1:1 solutions in the ternary systems at the particular pH (where the respective complexes have been found using the species distribution plots to have maximum concentration have been used for measuring the spectra. All the results are recorded in Tables 1-5. The charges of all the complexes are omitted for clarity.

Results and Discussion

A. Binary complex equilibria

The present study on Cu(II)-cya(A) system shows that only CuA and CuA₂ type of binary complexes are important below pH 8. The log K_1 and log K_2 values in Table 1 in this system compare favourably to those values reported in the Cu(II) complexes of α -amino acids¹⁰. The earlier results on Cu(II)/Ni(II)/Pd(II)-cya systems¹¹⁻¹³ also demonstrate the glycine-like mode of binding of cya, while

Table 2 – Stability constants for the proton and Cu(II) complexes of 2aba, 3aba, 4aba, ahba, dp, tp, dapa, daba and orn at 37 °C and $I = 0.15 \text{ mol dm}^{-3} \text{ Na ClO}_4$. Standard deviations are given in parentheses.

Parameters	Ligands, B								
	2aba ^a	3aba ^a	4aba ^a	ahba ^a	dp	tp	dapa ^a	daba ^a	orn ^a
log β_{HB}	9.43 (1)	9.95 (1)	10.15 (1)	12.88 (9)	9.87 (9)	9.99 (8)	9.37 (2)	9.93 (2)	10.22 (1)
log $\beta_{\text{H}_2\text{B}}$	11.54 (1)	13.30 (1)	14.24 (1)	21.91 (2)	17.01 (9)	18.31 (9)	15.97 (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 β_{CuBH}	-	-	-	-	-	-	15.37 (4)	16.99 (3)	17.67 (2)
log $\beta_{\text{Cu}_2\text{B}_2}$	-	-	-	28.10 (30)	-	-	-	-	-
log β_{CuB}	8.10 (2)	7.16 (2)	6.07 (9)	13.02 (9)	10.45 (3)	9.47 (8)	10.61 (4)	10.94 (3)	-
log $\beta_{\text{CuB}_2\text{H}_2}$	-	-	-	-	-	-	30.16 (5)	32.92 (4)	34.32 (3)
log $\beta_{\text{CuB}_2\text{H}}$	-	-	-	-	-	22.12 (9)	25.32 (6)	26.89 (4)	26.12 (6)
log β_{CuB_2}	15.13	12.90 (4)	- (5)	19.09 (24)	19.33 (5)	16.92 (9)	20.18 (5)	19.15 (9)	-
$pK_{\text{CuB}_2\text{H}}^{\text{H}}$	-	-	-	-	-	5.20	5.14	7.74	-
log $K_{\text{CuB}_2}^{\text{CuB}}$	7.03	5.74	-	6.07	8.88	7.45	9.57	8.21	-

^a ref.10

in the Zn(II)-cya(A) system, cya binds the metal through its amino group¹⁴.

The log β values in Table 1 for the CuB and CuB₂ species in the Cu(II)-dopm(B) system bear favourable comparison respectively with those values of 13.66 and 24.96 in the Cu(II)-pyrocatechol system¹⁵. This demonstrates the formation of chelate using the phenolic hydroxyl group of the dopm ligand. The CuBH species in this system has been found to be favoured in the lower pH ranges indicating the site of protonation to be with the terminal amino group of the ligand and the protonated ligand binds the metal in a pyrocatechol mode. Gergely and Kiss¹⁶ demonstrated the ambidentate binding of dopa in its Cu(II) binary complexes. It coordinates via the amino acid chain (N,O) at lower pH, while in the intermediate pH interval there is mixed mode of binding. The complexes CuBH₂, CuBH and CuB have been detected in the present experimental conditions in the Cu(II)-dopa (B) system. The log K_1 values obtained in this system is higher than those values of 7.0 and 14.0 respectively expected for the (N,O) and (O,O) mode of binding of the dopa ligand. This higher value

can be accounted by considering the mixed mode of binding of this ligand, in which oxygen atoms of the phenolic hydroxy and carboxylic groups are linked to the metal ion. This appears to be reasonable, because CuB dopa species has been found to have maximum preference in the pH range of 4.7 to 7.5. Earlier ESR studies¹⁷ on Cu(II)-dopa system also indicated this type of binding in the CuB dopa species. As in the case of CuBH dopm complex, in the CuBH dopa complex also it can be expected from the stability constant data in Table 1 that the extra proton is attached to the primary amino group of the ligand. The CuBH₂ dopa species has been found to be favoured at lower and intermediate pH ranges. This demonstrates that the dopa ligand, with its phenolate oxygen atoms protonated, binds the metal in a glycine-like manner in its CuBH₂ species.

The present results on the Cu(II)-phy, Bim, dp, and tp(B) binary systems in Table 1 bear favourable comparison with the literature values¹⁸ after giving allowance for the change in the experimental conditions.

Spectral measurements

λ_{\max} values for the mono and bis complexes in the Cu(II)-cya, 2aba, dp, tp, dapa and daba binary systems are reported in Table 3. The comparable λ_{\max} values in the mono and bis complexes in the Cu(II)-cya and 2aba systems demonstrate glycine-like mode of binding of cya in its 1:1 and 1:2 complexes similar to the binding of 2aba ligand.

The absorption maximum values in Table 3 for the CuB and CuB₂ dp and tp complexes corresponds to diamine-like mode of binding of these ligands^{19,20}. The λ_{\max} value of 613 nm obtained for the CuB dapa complex is lesser compared to those values of 659 and 694 nm respectively for the CuB dp and 2aba complexes. Similarly the λ_{\max} value of 605 nm for the CuB daba species is lesser than those values of 635 and 694 nm respectively for the CuB tp and 2aba complexes. These trends demonstrate higher ligand field strength for dapa and daba ligands in their CuB complexes indicating the tridentate mode of binding. The λ_{\max} value of 600 nm for the CuB₂ dapa species is higher than that value of 545 for the CuB₂ dp species. Again the value of 600 nm for the CuB₂ species is higher than that value of 573 for the CuB₂ tp species. These trends suggest that binding of the carboxylato group of dapa and daba in their CuB₂ complexes do not give rise to high ligand field strength.

B. Cu(II)-ternary complex equilibria (i) Cu(II)-Cya(A)-pha, dopm and dopa ternary systems — The Cu(II)-cya(A)-dopm and dopa (B) systems showed the ternary complexes CuABH₂, CuABH and CuAB, while in the pha secondary ligand system only CuAB type of species has been detected. The $\log K_{CuAB}^{CuB}$ values in Table 4 in all these three systems correspond to the glycine-like mode of binding of cya (A) primary ligand in its CuAB complexes. Since $\log K_{CuAB}^{CuB}$ value of 6.83 in the pha secondary ligand system bears favourable comparison with the \log

$K_{CuB_2}^{CuB}$ value of 6.44 in the Cu(II)-pha(B) system, it can be expected that pha coordinates the metal in a glycine-like mode in the CuAB species.

In the CuB dopm binary species, dopm binds through the phenolic hydroxo groups, while in the CuB dopa species dopa binds the metal through the oxygen atoms of phenolic hydroxo and carboxylato groups. The $\log \beta_{CuAB}$ values of 21.12 and 21.42 respectively in the Cu(II)-cya(A)-dopm and dopa (B) systems are comparable. This suggests that dopa ligand in the latter system binds the metal through the phenolic hydroxo groups only. The CuAB species in this system is more favoured above pH 7 (Fig. 1), and in this pH region as indicated earlier dopa binds Cu(II) only through the phenolic hydroxo groups. This different mode of binding of dopa in its CuB binary and CuAB ternary species has also been reflected in the $\log K_{CuAB}^{CuB}$ value of 12.82, which is lesser than the $\log K_1$ value of 18.08 for the CuB dopa species.

Since only in the Cu(II)-dopm(B) and not in the Cu(II)-cya(A) binary system, protonated species has been found to be present (Table 1) it can be inferred that in the CuABH species in the Cu(II)-cya(A)-dopm/dopa(B) systems, the extra proton resides with the dopm/dopa(B) secondary ligands. The comparable $\log \beta_{CuABH}$ value of 29.83 in Cu(II)-cya (A)-dopa(B) system with that value of 29.59 in the dopm(B) secondary ligand system indicates similar mode of binding in the CuABH species in both Cu(II)-cya(A)-dopm and dopa(B) systems.

Since in the CuBH₂ binary species in the Cu(II)-dopa(B) system the dopa ligand with its hydroxo groups protonated binds the metal in a glycine-like mode, it may be expected that in the CuABH₂ species in the Cu(II)-cya(A)-dopa(B) system, the extra two protons reside with the hydroxo groups of dopa(B) and this ligand binds the metal in a glycine-like mode. The same type of coordination can be expected for

Table 3 — Absorption maximum values in nm for the 1:1 and 1:2 binary complexes and CuAB ternary complexes

Species	Binary complexes						Ternary complexes						
	Ligands						Cu(II)-cya(A)-B systems			Cu(II)-2aba(A)-B systems			
	cya	2aba	dp	tp	dapa	daba	dp	tp	dapa	daba	daba	tp.	dp
1:1	695	694	635	613	605		585	593	587	604	621	594	584
1:2	628	628	545	573	559	600							

Table 4 — Stability constants in the Cu(II)-cya(A)-secondary ligand(B) ternary system at 37°C and $I=0.15 \text{ mol dm}^{-3}$ NaClO₄. Standard deviations are given in parentheses.

Parameters	Secondary ligand, B						
	pha	dopm	dopa	Bimz	Him	Hist	Hin
$\log \beta_{\text{CuABH}_2}$	-	35.09 (8)	36.39 (4)	-	-	-	26.50 (7)
$\log \beta_{\text{CuABH}}$	-	29.59 (9)	29.83 (6)	-	-	-	22.79 (6)
$\log \beta_{\text{CuAB}}$	15.43 (8)	21.12 (9)	21.42 (6)	-	12.38 (7)	17.17 (3)	18.46 (5)
$\log \beta_{\text{CuAB}_2}$	-	-	-	14.62 (8)	16.00 (8)	-	-
$pK^{\text{H}}_{\text{CuABH}_2}$	-	5.50	6.56	-	-	-	3.79
$pK^{\text{H}}_{\text{CuABH}}$	-	8.47	8.41	-	-	-	4.30
$\log K^{\text{CuBH}}_{\text{CuABH}}$	-	7.52	5.91	-	-	-	8.41
$\log K^{\text{CuA}}_{\text{CuAB}}$	6.83	12.52	12.82	-	3.78	8.57	9.86
$\log K^{\text{CuB}}_{\text{CuAB}}$	7.31	5.68	3.34	-	8.17	7.93	8.19
$\log K^{\text{CuAB}}_{\text{CuAB}_2}$	-	-	-	-	3.62	-	-
$\log K^{\text{CuA}}_{\text{CuAB}_2}$	-	-	-	6.02	7.40	-	-
$\log K^{\text{CuB}}_{\text{CuAB}_2}$	-	-	-	8.33	8.45	-	-
$\Delta \log K_{\text{CuABH}}$	-	-1.08	-2.69	-	-	-	-0.19
$\Delta \log K_{\text{CuAB}}$	-1.29	-2.92	-5.26	-	-0.43	-0.67	-0.41
$\Delta \log K_{\text{CuAB}_2}$	-	-	-	-0.27	-0.15	-	-
$\log X_{\text{CuABH}}$	-	-	-	-	-	-	3.59
$\log X_{\text{CuAB}}$	1.72	4.41	-	-	2.63	3.60	3.85
$\log X_{\text{CuAB}_2}$	-	-	-	3.79	4.51	-	-

the CuABH₂ species in the Cu(II)-cya(A)-dopm(B) system also. The higher $\log \beta_{\text{CuABH}_2}$ value of 1.4 log units in the dopa (B) ligand system is due to the fact that in the former system coordination of the dopa ligand results in the formation of a 5-membered chelate, while in the latter system dopm with its hydroxo groups protonated coordinates the metal only through its amino group resulting in no chelate ring.

(ii) *Cu(II)-cya (A)-Bimz, Him, Hist and His (B) ternary systems* — The various types of ternary species identified in the title ternary systems are given in Table 4. The $\log K^{\text{CuB}}_{\text{CuAB}}$ values obtained in the Cu(II)-cya (A)-Him/Hist/His (B) systems (Table 4) correspond to the glycine-like mode of binding of cya

in the CuAB species. The $\log K^{\text{CuA}}_{\text{CuAB}}$ value of 3.78 in the Him primary ligand system indicates the monodentate binding of Him in the CuAB species and the fourth position of this species would be occupied by the solvent water molecule and this water molecule will be replaced by the unidentate Him ligand in the CuAB₂ type species. In the CuAB₂ species in the Cu(II)-cya (A)-Bimz(B) system also, the metal ion would have a coordination number of four due to the glycine-like mode of binding of a cya and monodentate binding of two Bimz ligands.

The $\log \beta_{\text{CuAB}}$ value of 18.46 in the Cu(II)-cya(A)-His(B) system is higher than that value of 17.17 in the Hist(B) ligand system. This indicates tridentate binding of His(B) in the CuAB species in the former

system. Since in the Cu(II)-His(B) and not in the Cu(II)-cya(A) system the protonated binary species has been identified (Table 1) it can be expected that in the CuABH species in the Cu(II)-cya(A)-His(B) system the extra proton is attached with the His (B) ligand, possibly with its primary amino group¹². As in the case of NiABH₂ species in the Ni(II)-cya(A)-His(B) reported earlier¹², it may be expected that in the CuABH₂ species in the Cu(II)-cya(A)-His(B) system also one proton would be attached with the primary amino group of His(B) and the other would reside with the amino group of cya (A) ligand.

(iii) *Cu(II)-cya(A)-2aba, 3aba, 4aba and ahba (B) ternary systems* — The Cu(II)-cya (A)-2aba, 3aba, and 4aba (B) systems showed the presence of CuAB ternary species, while in the corresponding ahba(B) system, CuABH ternary species has been detected. The log β_{CuAB} values in the former three systems (Table 4) bear favourable comparison with those values reported in the corresponding ternary systems involving DL-alanine primary ligand¹⁰. This indicates that cya (A) ligand binds the metal in a glycine-like mode in its CuAB species. The log $K_{\text{CuAB}}^{\text{CuB}}$ values in these systems clearly suggest the bidentate binding of 2aba, 3aba and 4aba ligands in their respective CuAB species. Thus the CuAB species in the above three systems would respectively contain 5 and 5,5

and 6 and 5 and 7 membered chelate rings. The $\Delta \log K$ and $\log X$ values²¹ (Table 5) for the CuAB species in the 3aba (B) ligand system is more positive compared to that in the 2aba (B) ligand system indicating high stability for the Cu(II) ternary chelates containing 5 and 6-membered chelates compared to 5 and 5 membered chelates. The more negative $\Delta \log K$ value in the 4 aba (B) ligand system indicates lesser stability for the 5 and 7 membered chelates due to steric factors.

The detection of CuABH species in the Cu(II)-cya(A)-ahba(B) system is rather surprising because in the individual Cu(II).cya(A) and Cu(II)-ahba(B) binary systems, no protonated binary species has been detected (Table 2). Since the other derived constants could not be calculated, it is not possible to find out the mode of coordination in this species.

(iv) *Cu(II)-cya(A)-dp, tp, dapa, baba and orn(B) ternary systems* — The various types of ternary species detected in these systems are reported in Table 5. The log β_{CuAB} values of 17.84 and 16.95 respectively in the Cu(II)-cya(A)-dp and tp(B) systems bear favourable comparison with those values of 17.91 and 17.30 respectively in the Cu(II)-gly(A)-en and tp(B) systems^{22,23} demonstrating the glycine-like mode of binding of cya and diamine-like binding of dp and tp in their respective CuAB species. The log

Table 5 — Stability constants in the Cu(II)-cya(A)-secondary ligand(B) ternary system at 37°C and $I=0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$. Standard deviations are given in parentheses.

Parameters	Secondary ligand, B								
	2 aba	3 aba	4 aba	ahba	dp	tp	dapa	daba	orn
$\log \beta_{\text{CuABH}_2}$	-	-	-	-	-	-	26.92 (7)	-	-
$\log \beta_{\text{CuABH}}$	-	-	-	25.85 (9)	-	22.57 (7)	23.28 (8)	24.40 (5)	24.86 (8)
$\log \beta_{\text{CuAB}}$	15.12 (9)	14.50 (9)	12.92 (8)	-	17.84 (3)	16.95 (4)	18.46 (6)	17.71 (5)	-
$pK_{\text{CuABH}_2}^{\text{H}}$	-	-	-	-	-	-	7.91	7.41	7.19
$pK_{\text{CuABH}}^{\text{H}}$	-	-	-	-	-	5.62	4.82	6.69	-
$\log K_{\text{CuAB}}^{\text{CuA}}$	6.52	5.90	4.32	-	9.24	8.35	9.86	9.11	-
$\log K_{\text{CuAB}}^{\text{CuB}}$	7.02	7.34	6.85	-	7.39	7.48	7.85	6.77	-
$\Delta \log K_{\text{CuABH}}$	-	-	-	-	-	-	-0.69	-1.19	-1.41
$\Delta \log K_{\text{CuAB}}$	-1.58	-1.26	-1.75	-	-1.21	-1.12	-0.75	-1.83	-
$\log X_{\text{CuABH}}$	-	-	-	-	-	-	1.82	1.30	0.82
$\log X_{\text{CuAB}}$	0.53	1.52	-	-	1.77	2.40	2.16	1.69	-

β_{CuAB} value of 18.46 in the Cu(II)-cya(A)-dapa(B) system is higher than that of 17.84 in the dp(B) ligand system. Similarly the same parameter obtained in the dapa(B) ligand system is higher than that value of 16.95 in the tp(B) ligand system. These trends indicate the tridentate binding of both dapa and dapa in the ternary complexes. The glycine-like mode of binding of dapa and dapa ligands may be ruled out because the $\log \beta_{\text{CuAB}}$ value obtained in both these systems are higher than that value of 15.12 in the Cu(II)-cya(A)-2aba(B) system. However, the difference of (i) 0.6 log units between the $\log \beta_{\text{CuAB}}$ values in the Cu(II)-cya(A)-dapa and dp(B) systems and (ii) 0.7 log units in the dapa and tp(B) ligand systems indicate that the binding of the third donor group viz. carboxylato group in both dapa and dapa ligands in the ternary species is weak.

In the CuABH species in the Cu(II)-cya(A)-tp(B) system the site of protonation can be with one of the amino groups of tp(B) ligand since no protonated binary species has been detected in the Cu(II)-cya(A) binary system. The $\log \beta_{\text{CuABH}}$ values of 23.28, 24.80 and 24.86 respectively in the Cu(II)-cya(A)-dapa, dapa and orn(B) systems follow the trends of the $\log \beta_{\text{CuBH}}$ values. This demonstrated that the extra proton in the CuABH species in the above three systems resides with the respective (B) ligands. In the CuABH₂ species in the Cu(II)-cya(A)-dapa(B) system, logically it can be concluded that one proton resides with the dapa(B) ligand and the other will be attached with the cya(A) ligand.

(v) *Species distribution plots* — For all the ternary systems under investigation, similar pH versus %Cu plots were drawn. The diprotonated species, CuABH₂ have been found to be maximum favoured in the lower pH ranged, followed by the monoprotated CuABH complexes. With the increase in pH, CuAB ternary species becomes appreciable and more than 50% of the total metal ion has been found to be present in the form of this species in almost all the systems. In order to demonstrate these qualitative trends, the diagram obtained in the Cu(II)-cya(A)-dopa(B) system is given in Fig.1.

(vi) *Spectral measurements* — The λ_{max} value of 585 nm for the CuAB species in the Cu(II)-cya(A)-dp(B) system is comparable to that value of 584 nm in the Cu(II)-2aba-dp system. Both these values are comparable to the λ_{max} value of 585 nm in the Cu(II)-gly-en system²⁰. Again, the λ_{max} value of 593 nm for the CuAB species in the Cu(II)-cya-tp system is

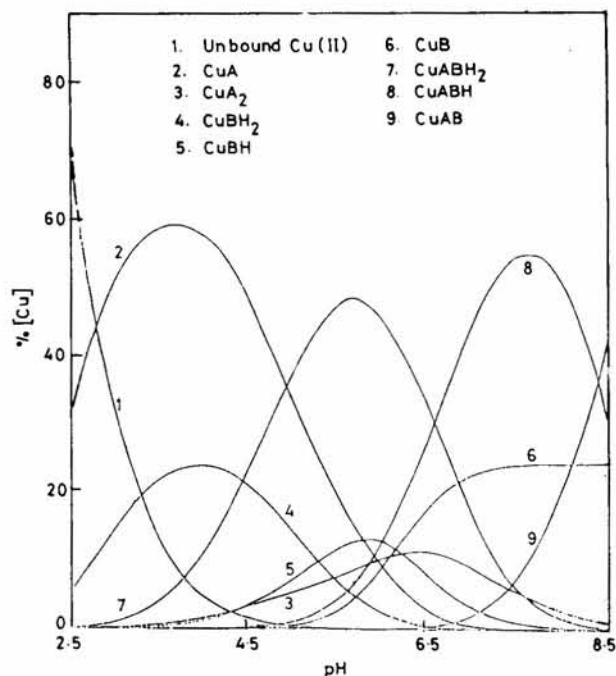


Fig.1 — Distribution diagram for the Cu(II)-L-cysteic acid (A)-dopa(B) system at a Cu-A-B ratio of 1:1:1

comparable to that value of 594 nm in the Cu(II)-2aba-tp system. These trends demonstrate well the glycine-like mode of binding of cya ligand in the CuAB species. The λ_{max} values of 587 and 604 nm respectively in the Cu(II)-cya-dapa and baba systems are lesser than that values of 621 nm in the Cu(II)-cya-2aba system indicating higher ligand field strength for the dapa and dapa ligands suggesting tridentate and not glycine-like mode of binding of dapa/dapa(B) ligands. However, a comparable λ_{max} value in the dapa and dp(B) system indicate that the ligand field strength around Cu(II) remains practically unchanged in going from the CuAB complex in the Cu(II)-cya-dapa system to the dp(B) system. This indirectly suggests that the binding of the carboxylato group of dapa(B) ligand is very weak. By considering the tridentate binding of dapa ligand in the Cu(II)-cya-dapa system, one could expect lesser λ_{max} value in this system compared to that in the corresponding tp(B) system. But the value observed is 10 nm higher in the dapa ligand system. This can be accounted by considering the fact that glycine-like mode of binding of cya(A), and diamine-like mode of binding of tp(B) in the CuAB species in the latter system give rise to 5 and 6 membered chelate rings, which is the preferred arrangement for Cu(II). In the dapa(B) ligand

system because of the tridentate binding of this ligand the CuAB species would contain two 5 and one 6 membered chelates, which should be slightly less favoured compared to the former arrangement. This justifies higher λ_{\max} value in the Cu(II)-cya(A)-daba(B) system.

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