

Ternary Complexes of Copper(II) Containing 2,2'-Bipyridyl & Some Diaminocarboxylic Acids

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Stability constants of the complexes of the types CuAB and CuABH have been determined pH metrically at 37°C and $I=0.15 M$ (NaClO₄) where A = 2,2'-bipyridyl (bipy) and B = DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine(Orn). The probable structures of the CuAB and CuABH complexes are discussed in terms of their stability constant data. The results clearly suggest that the site of protonation in the CuABH complexes is the terminal amino group of the ligand B.

In recent years, considerable attention has been paid to the binary and ternary complexes of transition metal ions containing 2,2'-bipyridyl¹⁻⁵ because of the similarity of the ligand with biologically important ligands like porphyrines and purines. The present note deals with the ternary complex formation tendency of 2,2'-bipyridyl (bipy) (A) with Cu(II) in presence of three diaminocarboxylic acids, viz., DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine (Orn) (B). All the studies have been carried out by pH metry at 37°C and $I=0.15 M$ (NaClO₄). The stability constant data for the binary complex systems Cu(II)-dapa, Cu(II)-daba and Cu(II)-Orn(B) at these experimental conditions were reported elsewhere⁶. However, the comparative data at these experimental conditions for the Cu(II)-bipy(A) system are not available.

The ligands used in this work 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. The methods of preparation and determination of copper perchlorate and of other reagents were described earlier⁶. The pH titrations were carried out at 37°C and $I=0.15 M$ (NaClO₄) using the apparatus and procedure described previously^{7,8}. Calculations were carried out with the aid of MINQUAD-75 computer programme⁹ on an IBM-370 computer. The revised binary stability constant data for the system Cu(II)-bipy (A) and the previously reported⁶ data for the binary systems Cu(II)-dapa, Cu(II)-daba and Cu(II)-Orn(B) are included in Table 1. The results obtained for the ternary complex systems are given in Table 2.

The charges of all the complex species reported in this note are neglected for clarity.

The Cu(II)-bipy(A)-dapa, -daba and -Orn(B) systems showed the presence of two ternary complexes (CuABH and CuAB) in addition to the binary complexes HA, CuA, CuA₂, HB, H₂B, H₃B, CuBH, CuB₂H₂, CuB₂H and also CuB and CuB₂ in the dapa and daba (B) ligand systems. It appears reasonable to suggest that the extra proton in the CuABH complexes in all the title ternary systems resides at the secondary ligand (B) because in the Cu(II)-bipy (A) binary system, no protonated species were detected. The same view is confirmed by noting that the log βCuABH, pK^H CuABH and log K_{CuABH}^{CuA} values (Table 2) follow the trends of the log β_{HB} or log β_{CuBH} values (Table 1) for the Cu(II)-dapa, -daba or -Orn(B) binary systems. It has been well established previously by several

Table 1—Stability Constants for the Proton and Cu(II) Complexes of bipy, dapa, daba and Orn at 37°C and $I=0.15 M$ (NaClO₄)

Parameter	ligands, B			
	^a bipy	^b dapa	^a daba	^b Orn
log β _{HB}	4.51(1)	9.37(2)	9.93(2)	10.22(1)
log β _{H₂B}	...	15.98(3)	18.02(4)	18.85(2)
log β _{H₃B}	...	17.37(5)	19.88(6)	20.99(4)
log β _{CuBH}	...	15.37(4)	16.99(3)	17.67(2)
log β _{CuB}	6.56(3)	10.61(4)	10.94(3)	...
log β _{CuB₂H₂}	...	30.16(5)	32.92(4)	34.32(3)
log β _{CuB₂H}	...	25.32(6)	26.89(4)	26.12(6)
log β _{CuB₂}	12.43(5)	20.18(5)	19.15(6)	...

Standard deviations are given in parentheses

^abipy becomes primary ligand (A) in the ternary systems (Table 2), ^bref. 6.

Table 2—Stability Constants for the Cu(II)-bipy (A)—Secondary Ligand (B) Ternary Systems at 37°C and $I=0.15 M$ (NaClO₄)

Parameter	Secondary ligand, B		
	dapa	daba	Orn
log β _{CuABH}	21.75(6)	23.57(11)	24.58(11)
log β _{CuAB}	17.29(4)	17.42(5)	17.34(7)
pK^H CuABH	4.46	6.15	7.24
log K_{CuABH}^{CuA}	6.38	6.58	6.91
log K_{CuABH}^{CuA}	15.19	17.01	18.02
Δ log K_{CuABH}	-0.18	+0.02	+0.35
log X_{CuABH}	0.91	1.79	2.41
log K_{CuAB}^{CuA}	10.73	10.86	10.78
log K_{CuAB}^{CuB}	6.68	6.48	—
Δ log K_{CuAB}	+0.29	-0.08	—
log X_{CuAB}	1.95	3.26	—

Standard deviations are given in the parentheses.

workers^{6,10,11} that in the CuBH or Cu(BH)B (dapa, daba or Orn) complexes, the extra proton is attached to the terminal amino group of the respective ligands, the ligand being bound to the metal in a glycine-like mode. Again, the $\log K_{CuABH}^{CuBH}$ values given in Table 2 are comparable to the $\log \beta_{CuA}$ value given in Table 1 for the Cu(II)-bipy (A) binary system. This demonstrates that bipy is bidentate in the ternary complexes as also in CuA binary complex. Thus, the CuABH complex species in all the title systems contains two five-membered chelate rings with the extra proton residing on the terminal amino group of the secondary ligand, B. Comparison of the calculated values of $\Delta \log K_{CuABH}$ and $\log X_{CuABH}$ (Eqs 1-4) given in Table 2 with the respective statistically expected values^{1,2} of -0.6 and $+0.6$ clearly demonstrates marked stabilities of the CuABH ternary complexes compared to the binary complexes. The positive $\Delta \log K_{CuABH}$ values in the daba and Orn(B) ligand systems show that these ligands prefer to add on to CuA (bipy) binary complex rather than to the aquated Cu(II).

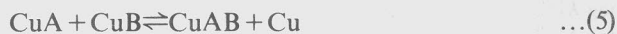


$$\Delta \log K_{CuABH} = \log \beta_{CuABH} - (\log \beta_{CuA} + \log \beta_{CuBH}) \dots(2)$$

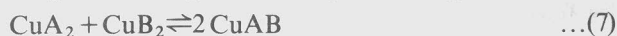


$$\log X_{CuABH} = 2 \log \beta_{CuABH} - (\log \beta_{CuA_2} + \log \beta_{CuB_2H_2}) \dots(4)$$

The $\log K_{CuAB}^{CuB}$ values in Table 2 for all the title systems are comparable to the $\log \beta_{CuA}$ value of 6.56 in the Cu(II)-bipy (A) binary system suggesting that bipy is bidentate in the CuAB complexes. The $\log K_{CuAB}^{CuA}$ values of 10.73, 10.86 and 10.78 respectively in the Cu(II)-bipy (A) -dapa, -daba and -Orn (B) systems are of the order expected for the terdentate binding of dapa, daba and Orn (B) ligands. Since the $\log \beta_{H,B}$ values are in the order: dapa > daba > Orn (Table 1), one should expect a higher $\log K_{CuAB}^{CuA}$ values for the Orn (B) ligand system than that in the ternary system with B = daba. The reverse trend (Table 2) observed may be accounted for by the steric factors since two five- and one seven-membered chelate rings are present in the ternary system with B = Orn compared to the two five- and one six-membered chelate rings in the system with B = daba. The $\Delta \log K_{CuAB}$ and $\log X_{CuAB}$ (Eqs 5-8) values in Table 2 clearly indicate the enhanced stabilities for the ternary complexes CuAB on statistical grounds^{1,2}. Again, the positive $\Delta \log K_{CuAB}$ values (Table 2) indicate that the secondary ligand B prefers to add on to the CuA binary complex rather than to the aquated Cu(II) ion.



$$\Delta \log K_{CuAB} = \log \beta_{CuAB} - (\log \beta_{CuA} + \log \beta_{CuB}) \quad \dots(6)$$



$$\log X_{CuAB} = 2 \log \beta_{CuAB} - (\log \beta_{CuA_2} + \log \beta_{CuB_2}) \quad \dots(8)$$

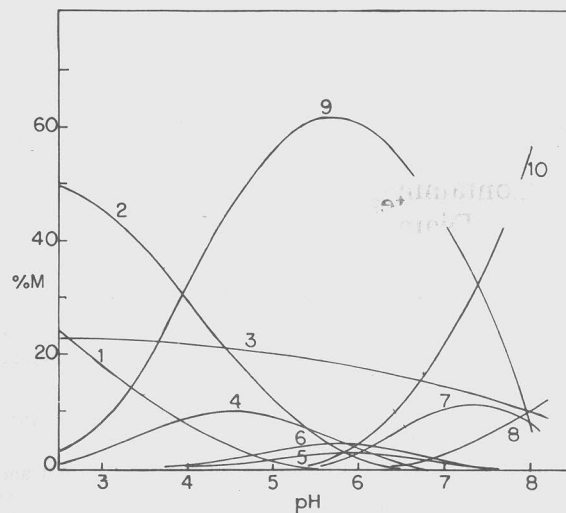


Fig. 1—Distribution diagram for the Cu(II)-bipy(A)-daba(B) ternary system at a Cu:A:B ratio of 1:1:1 [(1) Unbound Cu(II), (2) CuA, (3) CuA₂, (4) CuBH, (5) CuB, (6) CuB₂H₂, (7) CuB₂H (8) CuB₂, (9) CuABH and (10) CuAB]

The distribution of various binary and ternary complexes (as percentages of total metal) as a function of pH has been calculated for all the title ternary systems; a representative distribution is shown in Fig. 1. The marked stabilization of ternary relative to the binary complexes is reflected in the species distribution plots, i.e., the ternary complexes occur in very high concentrations compared with the binary complexes in all the systems studied, where the concentration of the ternary species exceeded the statistically expected 50% of the total metal. The respective amounts of the total metal found in the form of CuAB complexes in the ternary systems with B = dapa, daba and Orn are 82, 56 and 58% at pH 8.00 and there is a steady increase in their formation with increase in pH.

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