

## Stability and structure of Cu(II) and Zn(II) ternary complexes with L-glutamic acid and some diaminocarboxylic acids

M SIVASANKARAN NAIR\*, S THEODORE, D MANICKAM,  
P THILLAI ARASU and C NATARAJAN†

Department of Chemistry, Madurai Kamaraj University, P. G. Centre, Palayamkottai 627002, India

† Department of Inorganic Chemistry, Madurai Kamaraj University, Madurai 625 021, India

MS received 20 November 1989; revised 6 April 1990

**Abstract.** The computer-based analysis of the pH titration data obtained in the M–A–B [M = Cu(II)/Zn(II), A = L-glutamic acid (Glu) and B = DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine (Orn)] ternary complex systems showed the presence of the mixed species of stoichiometry MABH and/or MAB in addition to various binary species due to ligands A and B. The results indicate the glycine-like mode of binding of Glu (A) primary ligand in both the Cu(II) and Zn(II) mixed ligand systems. The extra proton in the MABH type of species is associated with the secondary ligand (B), possibly with the terminal amino groups. However, in the dapa secondary ligand systems, the results also indicate the possibility of the attachment of the extra proton to the  $\alpha$ -amino group. The dapa, daba and Orn secondary ligands (B) coordinate the metal in a tridentate manner in the mixed species of stoichiometry MAB.

**Keywords.** Ternary complexes; stability constants; glutamic acid; diaminocarboxylic acid.

### 1. Introduction

Investigations on the coordination chemistry of potentially tridentate ligands are of great interest to many workers because such studies are closely connected with peptide and protein complex chemistry (Sigel 1971–1983; Eichhorn 1973). Studies on metal complexes containing diaminocarboxylic acids are of special interest because the third donor group in these ligands is a nitrogen atom which is able to coordinate with hydrogen ions in the intermediate pH range. Hence there is significant competition between hydrogen ions and metal ions for coordinating with the third donor group resulting in a number of complex equilibria. The present studies are aimed at finding the types of ternary species formed by Cu(II) and Zn(II) in the presence of a potentially tridentate L-glutamic acid (Glu) primary ligand (A) and some diaminocarboxylic acid secondary ligands (B) and to assess the donor groups involved in coordination. The diaminocarboxylic acids used are DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine (Orn). The individual binary systems involving the above ligands under the present experimental conditions have already been reported (Nair and Santappa 1981; Nair *et al* 1986).

\* For correspondence

## 2. Experimental

The ligands used in this work were Fluka products of *puris* quality. The compounds dapa and Orn were used in monoprotonated form while daba was used in diprotonated form. Copper perchlorate, zinc perchlorate and other reagents were prepared and estimated as described earlier (Nair *et al* 1982, 1986). The pH titration was carried out at 37°C and with  $I = 0.15$  NaClO<sub>4</sub>. The apparatus and procedure used have been described earlier (Nair *et al* 1987, 1988). Calculations were made with the aid of the SCOGS computer program (Sayce 1968, 1971; Sayce and Sharma 1972) on a Siva PC-XT/386 with MS-DOS working system. The binary stability constants used for the computation of the ternary complex stability constants are shown in table 1, and the results obtained are given in table 2. The charges of all the complex species reported in this paper are omitted for clarity.

**Table 1.** Stability constants for the proton and Cu(II)/Zn(II) complexes of Glu, dapa, daba and Orn binary systems.

Temperature = 37°C;  $I = 0.15$  (NaClO<sub>4</sub>)

Parameters	Copper(II)				Zinc(II)			
	Glu <sup>a</sup>	dapa <sup>b</sup>	daba <sup>b</sup>	Orn <sup>b</sup>	Glu <sup>c</sup>	dapa <sup>d</sup>	daba <sup>d</sup>	Orn <sup>d</sup>
$\log \beta_{HB}$	9.63(2)	9.37(2)	9.93(2)	10.22(1)				
$\log \beta_{H_2B}$	15.35(5)	15.98(3)	18.02(4)	18.85(2)				
$\log \beta_{H_3B}$	17.62(9)	17.37(5)	19.88(6)	20.99(4)				
$\log \beta_{MBH}$	—	15.37(4)	16.99(3)	17.67(2)	—	13.61(4)	14.22(4)	14.56(2)
$\log \beta_{MB}$	8.52(8)	10.61(4)	10.94(3)	—	5.39	—	—	6.69(3)
$\log \beta_{MB_2H_2}$	—	30.16(5)	32.92(4)	34.32(3)	—	25.70(3)	27.04(16)	27.83(11)
$\log \beta_{MB_2H}$	—	25.32(6)	26.89(4)	26.12(6)	—	—	21.47(4)	—
$\log \beta_{MB_2}$	15.61(10)	20.18(5)	19.15(6)	—	9.38	13.70(2)	13.44(4)	—

L-glutamic acid becomes the primary ligand, A in the ternary systems.

Source: <sup>a</sup>Unpublished data from our lab; <sup>b</sup>Nair and Santappa (1981); <sup>c</sup>Sillen and Martell (1971);

<sup>d</sup>Nair *et al* (1982).

**Table 2.** Stability constants of Cu(II)/Zn(II)–L-glutamic acid (A)–dapa, daba and Orn (B) ternary systems.

Temperature = 37°C;  $I = 0.15$  (NaClO<sub>4</sub>)

Parameters	Cu(II)–L-glutamic acid-B system			Zn(II)–L-glutamic acid-B system		
	Ligand B			Ligand B		
	dapa	daba	Orn	dapa	daba	Orn
$\log \beta_{MABH}$	25.03(9)	25.56(8)	—	19.48(9)	—	—
$\log \beta_{MAB}$	—	17.23(9)	16.70(9)	10.72(13)	11.29(9)	11.56(9)
$pK_{MABH}^H$	—	8.33	—	8.76	—	—
$\log K_{MABH}^{MA}$	16.51	17.04	—	14.09	—	—
$\log K_{MABH}^{MBH}$	9.66	8.57	—	5.87	—	—
$\log Q$	15.66	15.63	—	10.11	—	—
$\Delta \log K_{MABH}$	1.14	0.05	—	0.48	—	—
$\log X_{MABH}$	4.29	2.59	—	3.88	—	—
$\log K_{MAB}^{MA}$	—	8.71	8.18	5.33	5.9	6.17
$\log K_{MAB}^{MB}$	—	6.29	—	—	—	4.87
$\Delta \log K_{MAB}$	—	–2.23	—	—	—	–0.52
$\log X_{MAB}$	—	–0.30	—	–1.64	–0.24	—

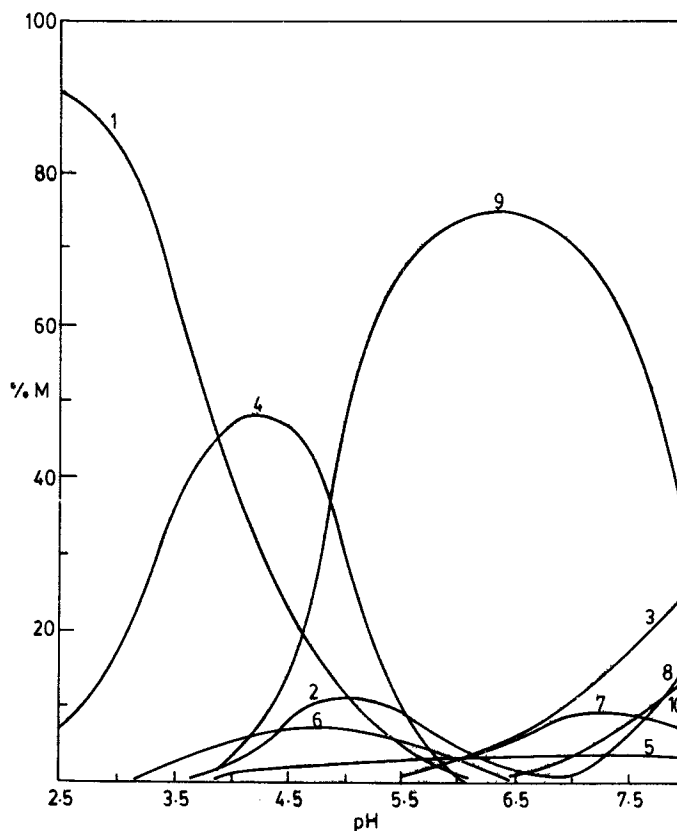
### 3. Results and discussion

#### 3.1 Copper(II)-Glu (A)-dapa, daba, and Orn(B) ternary systems

The best-fit computer model (Sayce 1968) for the Cu(II)-Glu (A)-dapa (B) system showed the presence of CuABH ternary species in addition to the binary species HA, H<sub>2</sub>A, H<sub>3</sub>A, CuA, CuA<sub>2</sub>, HB, H<sub>2</sub>B, H<sub>3</sub>B, CuBH, CuB, CuB<sub>2</sub>H<sub>2</sub>, CuB<sub>2</sub>H and CuB<sub>2</sub>. The Cu(II)-Glu (A)-daba (B) system gives rise to the formation of two ternary species CuABH and CuAB in addition to the binary species of the types mentioned under the dapa secondary ligand system, while in the Cu(II)-Glu (A)-Orn (B) system only the CuAB type of ternary species was detected in addition to the binary species HA, H<sub>2</sub>A, H<sub>3</sub>A, CuA, CuA<sub>2</sub>, HB, H<sub>2</sub>B, H<sub>3</sub>B, CuBH, CuB<sub>2</sub>H<sub>2</sub> and CuB<sub>2</sub>H.

The  $\log K_{\text{CuABH}}^{\text{CuA}}$  values obtained in the Cu(II)-Glu (A)-daba (B) system (table 2) follow the same trend as the  $\log \beta_{\text{HB}}$  and  $\log \beta_{\text{CuBH}}$  values (table 1), suggesting the attachment of an extra proton in the CuABH species to the daba secondary ligand (B), possibly to its terminal amino group as in the case of the protonated binary species in the Cu(II)-daba (B) system (Nair and Santappa 1981). The possibility of the site of protonation in the CuABH species being the Glu primary ligand (A) may be ruled out because in the Cu(II)-Glu (A) binary system no protonated binary species was detected (Kamakshi 1989). Thus the CuABH species in the above system would contain two five-membered chelate rings due to the glycine-like mode of binding of Glu (A) and the protonated daba (B) ligands. The  $\log K_{\text{CuABH}}^{\text{CuA}}$  value of 16.51 obtained in the Cu(II)-Glu (A)-dapa (B) system is higher by about 0.9 log units than the  $\log \beta_{\text{CuBH}}$  of 15.40 obtained in the Cu(II)-dapa (B) binary system. This may be attributed to the possibility of attachment of the extra proton to the  $\alpha$ -amino group as well, as already suggested for the CuBH dapa complex. Thus the CuABH complex in the Cu(II)-Glu (A)-dapa (B) system would have two equilibrium structures with two different modes of binding of dapa (B): one in which  $\alpha$ -amino-carboxyl chelation is involved and the terminal amino group is protonated; and the other which contains terminal amino-carboxyl chelation with the  $\alpha$ -amino group being protonated. These structural aspects are reflected in the  $\log K_{\text{CuABH}}^{\text{CuBH}}$  values (table 2). The value of 8.57 obtained for this parameter in the Cu(II)-Glu (A)-daba (B) system is comparable to the  $\log \beta_{\text{CuA}}$  value expected for the glycine-like mode of binding of Glu (A) ligand (Nair *et al* 1987, 1988). However this parameter is higher in the dapa secondary ligand system by about one log unit compared to that value expected for the glycine-like mode of binding of Glu. Hence at a first glance one may be tempted to conclude that Glu should be terdentate in the CuABH species in the Cu(II)-Glu (A)-dapa (B) system. However by considering the fact that for the CuABH species in this system two equilibrium structures are possible as discussed above, one can say that the resulting enhanced stability should be reflected in the  $\log K_{\text{CuABH}}^{\text{CuAH}}$  and  $\log K_{\text{CuABH}}^{\text{CuA}}$  value, i.e., under such a situation one can expect higher  $\log K_{\text{CuABH}}^{\text{CuBH}}$  values.

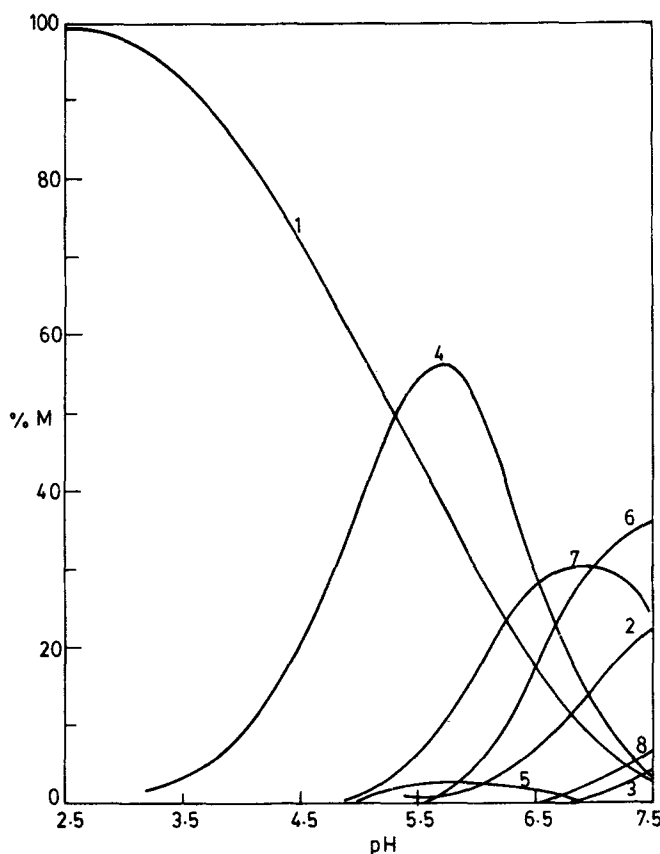
The  $\log Q$  values ( $\log Q = \log \beta_{\text{CuABH}} - \log \beta_{\text{HB}}$ ) obtained in the Cu(II)-Glu (A)-dapa and daba (B) systems also suggest the glycine-like mode of binding of the protonated secondary ligands. However since  $\log \beta_{\text{H}_3\text{B}}$  value is higher for daba compared to that for dapa, one should expect higher  $\log Q$  values for the daba secondary ligand system. But the observed trend is in the reverse direction (table 2). This may again be accounted for by considering the two equilibrium structures of CuABH species in the Cu(II)-Glu (A)-dapa (B) system.



**Figure 1.** Distribution diagram for the copper(II)-L-glutamic acid (A)-daba (B) ternary system ( $C_M = C_A = C_B = 0.003$ ). (1) Unbound metal; (2) CuA; (3) CuA<sub>2</sub>; (4) CuBH; (5) CuB; (6) CuB<sub>2</sub>H<sub>2</sub>; (7) CuB<sub>2</sub>H; (8) CuB<sub>2</sub>; (9) CuABH; and (10) CuAB.

Both  $\Delta \log K_{\text{CuABH}}$  and  $\log X_{\text{CuABH}}$  (Sigel 1980; Nair *et al* 1986) obtained in the Cu(II)-Glu (A)-dapa and daba (B) systems are more positive compared to statistical values, demonstrating a marked stability in the CuABH species. This trend is also reflected in the % distribution plots where more than 75% of the total metal is found to be present in the form of the CuABH species (figure 1).

The  $\log K_{\text{CuAB}}^{\text{CuB}}$  value of 6.29 obtained in the daba secondary ligand system suggests that Glu should bind the metal in a glycine-like mode. This parameter could not be calculated in the Orn secondary ligand system because the  $\log \beta_{\text{CuB}}$  value is not available. The  $\log K_{\text{CuAB}}^{\text{CuA}}$  values obtained (table 2) in the Cu(II)-Glu (A)-daba and Orn(B) systems are slightly higher than the values expected for the glycine-like mode of binding of these ligands in the CuAB type of species suggesting their terdentate mode of binding. Thus the CuAB species in the daba and Orn secondary ligand systems would contain two five- and one six-membered, and two five- and one seven-membered rings respectively. Among these, the latter species should be less stable due to steric factors. The  $\Delta \log K$  and  $\log X$  (Sigel 1980) values obtained for the CuAB species in the Cu(II)-Glu (A)-daba (B) system (table 2) do not suggest enhanced stabilities as compared to the binary analogues. The species distribution plots also suggest the same trend. For example, only about 15% of the total metal was found to be present in the form of the CuAB species in the daba secondary



**Figure 2.** Distribution diagram for the zinc(II)-L-glutamic acid (A)-dapa (B) ternary system ( $C_M = C_A = C_B = 0.003$ ). (1) Unbound metal; (2) ZnA; (3) ZnA<sub>2</sub>; (4) ZnBH; (5) ZnB<sub>2</sub>H<sub>2</sub>; (6) ZnB<sub>2</sub>; (7) ZnABH; and (8) ZnAB.

ligand system. However, from the % distribution plot (figure 1) it may be inferred that a high percentage of the metal should be present in the form of a CuAB-type of ternary species at higher pH ranges because there is steady increase in its formation above pH 7.

### 3.2 Zinc(II)-Glu (A)-dapa, daba and Orn (B) ternary systems

The best-fit computer model obtained in the ternary systems show that in the dapa secondary ligand system the ZnABH and ZnAB species are important, while in the daba and Orn secondary ligand systems only the ZnAB-type of ternary species is important in addition to the various species due to ligands A and B (table 1).

From the trends in the  $\log K_{ZnAB}^{ZnA}$  and  $\log Q$  values obtained (table 2) in the Zn(II)-Glu (A)-dapa (A) system, and by the same argument as in the case of the CuABH species in the corresponding Cu(II) ternary system, it may be concluded that the extra proton in the ZnABH species is with the dapa ligand possibly with the terminal or the  $\alpha$ -amino group. The  $\log K_{ZnABH}^{ZnBH}$  value indicates the glycine-like mode of binding of Glu (A) ligand in the ZnABH species. Thus, among the two equilibrium structures for this species one would contain two five-membered chelate rings whereas the other would have one five- and one six-membered ring. The  $\Delta \log K$  value obtained

for this species is positive which demonstrates that the protonated dapa secondary ligand prefers to add on to the ZnA Glu binary species rather than to the aquated Zn(II) ion. Both the  $\Delta \log K$  and  $\log X$  (table 2) values (Sigel 1980) indicate enhanced stability for the ZnABH species as compared to the binary analogues. The electrostatic interaction between the uncoordinated  $-\text{COO}^-$  group of the Glu primary ligand and the  $-\text{NH}_3^+$  group of the protonated dapa secondary ligand would give enhanced stability for the ZnABH species. As shown in figure 2 about 32% of the total metal was found to be present in the form of the ZnABH species.

The glycine-like mode of binding of Glu is well-demonstrated by the  $\log K_{\text{ZnAB}}^{\text{ZnB}}$  value of 4.87 obtained in the Zn(II)–Glu (A)–Orn (B) system because this value is comparable to the  $\log \beta$  value for the ZnA glycine species (Sillen and Martell 1971). This parameter could not be calculated for the dapa and daba secondary ligand systems because the stability constant data for the ZnB (B = dapa and daba) are not available. The fact that the  $\log \beta_{\text{ZnAB}}$  value obtained in the Zn(II)–Glu (A)–dapa, daba, and Orn (B) are comparable after due allowance for the basicity difference among the secondary ligands suggest that Glu should bind Zn(II) in a glycine-like mode. The  $\log K_{\text{ZnAB}}^{\text{ZnA}}$  value of 6.17 obtained in the Zn(II)–Glu (A)–Orn (B) system is comparable to the  $\log \beta_{\text{ZnB}}$  value of 6.69 in the Zn(II)–Orn (B) binary system suggesting the tridentate binding of Orn in the ZnAB species. Though such a comparison is not possible in the case of dapa and daba secondary ligand systems because of the non-availability of the  $\log \beta_{\text{ZnB}}$  values in the Zn(II)–dapa and daba (B) binary systems (table 1), it may be noted from table 2 that the  $\log K_{\text{ZnAB}}^{\text{ZnA}}$  values obtained in the Zn(II)–dapa, daba and Orn (B) systems follow the trend of  $\log \beta_{\text{H}_3\text{B}}$  values. This indicates the possibility of the terdentate binding of dapa, daba, and Orn secondary ligands in the respective ZnAB species. The  $\Delta \log K_{\text{ZnAB}}$  value obtained in the Orn secondary ligand system suggest enhanced stability for the ZnAB species. The  $\log X_{\text{ZnAB}}$  values obtained in the Zn(II)–Glu (A)–dapa and daba (B) systems (table 2) do not show marked stabilities for the ZnAB type of species. However  $\log X_{\text{ZnAB}}$  in the Orn secondary ligand system and  $\Delta \log K_{\text{ZnAB}}$  in the dapa and daba secondary ligand systems could not be computed because the stability-constant data for the ZnB<sub>2</sub> and ZnB species respectively are not available (table 1). The maximum amount of the metal present in the form of ZnAB type of species was found to be only about 8% in the Zn(II)–Glu (A)–dapa, daba and Orn (B) systems in the pH range of 7.00. However, it may be seen from figure 2 that the concentration of the ZnAB type of species should be higher at higher pH values.

## References

- Eichhorn G L 1973 *Inorganic biochemistry* (Amsterdam: Elsevier) vols 1 and 2  
 Nair M S, Chalapathi K V, Santappa M and Murugan P K 1982 *Inorg. Chem.* **21** 2418  
 Nair M S, Pillai M S and Ramalingam S K 1986 *J. Chem. Soc., Dalton Trans.* 1  
 Nair M S and Santappa M 1981 *J. Chem. Soc., Dalton Trans.* 992  
 Nair M S, Sivasankar B and Rengaraj K 1987 *Indian J. Chem.* **A26** 52  
 Nair M S, Sivasankar B and Rengaraj K 1988 *Indian J. Chem.* **A27** 48  
 Sayce I G 1968 *Talanta* **15** 1397  
 Sayce I G 1971 *Talanta* **18** 653  
 Sayce I G and Sharma V S 1972 *Talanta* **19** 831  
 Sigel H 1971–1983 *Metal ions in biological systems* (New York: Marcel Dekker) vols 1–12  
 Sigel H 1980 *IUPAC coordination chemistry – 20* (Oxford: Pergamon Press) p. 27  
 Sillen L G and Martell A E 1971 *Stability constants of metal ion complexes* (London: Chem. Soc.) No. 25