Indian Journal of Chemistry
Vol. 35A, September 1996, pp. 793-795

Multiple equilibrium studies on some zinc(II) mixed ligand complex systems

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Received 21 November 1995; revised 11 March 1996

Multiple equilibrium studies involved in some Zn(II) ternary systems viz. Zn(II)-L-cysteine (cys)/D-pencillamine (pen)/L-cysteic acid (cya) (A)-DL-2,3-diaminopropionic acid (dapa), DL-2,4-diaminobutyric acid (daba) and DL-ornithine (orn) (B) by the computer analysis of the *p*H titration data have shown the presence of $ZnABH_2$, ZnABH or ZnAB type ternary species. The trends in the results demonstrate the possibility of attachment of an extra proton in the ZnABH species to be with ligand (B). In the $ZnABH_2$ species, one proton resides with ligand (A) and the other with ligand (B). The mode of coordination of cys, pen, dapa, daba and orn ligands in the ZnAB type species is similar to their coordination in the corresponding binary species. However, in the ZnAB and ZnABH species in the Zn(II)-cya(A)-dapa, daba and orn (B) systems, cya (A) ligand binds the metal in a glycine-like mode though it is monodentate in its ZnA and ZnA_2 binary species.

There has been a large number of reports on the complex forming properties of L-cysteine and D-pencillamine which are biologically and therapeutically of significance[1,2]. Both these ligands are soft and form thermodynamically more stable complexes with transition metal ions such as Ni(II) and Zn(II). However, Cu(II) complexes with cysteine and pencillamine are readily oxidised and the oxidative product of L-cysteine is L-cysteic acid. The present note deals with the multiple equilibrium studies of Zn(II) ternary complex systems involving L-cysteine (cys), D-pencillamine (pen) and L-cysteic acid (cya) (A) and three diaminocarboxylic acids namely 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 *p*H titrimetry at 37°C and I = 0.15 *M* ($NaClO_4$).

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Experimental

All the experimental details have been described earlier[3]. All the calculations have been done with the aid of MINIQUAD-75 computer program[4] on a Cyber 180/830A computer. During the computer analysis of the *p*H titration data in the ternary systems, the binary stability constants under the present experimental conditions (Table 1) have been kept as non-refinable parameters. The various type of ternary complexes detected in the ternary systems under study along with their stability constants are reported in Table 2.

Results and discussion

Stability and structure of ZnAB type complexes

The log K^{ZnA}_{ZnAB} values in Table 2 in the Zn(II)-cys(A)-dapa, daba and orn (B), and Zn(II)-pen (A)-dapa, and orn (B) systems correspond to the tridentate binding of the ligand (B) in the ZnAB type ternary species. The log K^{ZnB}_{ZnAB} values of 9.66 and 10.23 respectively in the Zn(II)-cys/pen (A)-orn (B) systems bear favourable comparison with the corresponding log K^{Zn}_{ZnA} values of 9.64 and 10.33 in the Zn(II)-cys(A)/pen (A) binary systems suggesting the same mode of binding of cys/pen (A) ligands, i.e., via N-amino and S-mercapto groups in both ZnA binary and ZnAB ternary species (B = orn). The above parameter could not be computed in the Zn(II)-cys (A)-dapa and daba (B), and Zn(II)-pen (A)-daba (B) systems because in the Zn(II)-dapa and daba binary systems, the log K^{Zn}_{ZnB} values are not available in the present experimental conditions (Table 1). However, the trends in the log β_{ZnAB} values in Table 2 in the Zn(II)-cys (A)-dapa, daba and orn (B) systems demonstrate that both cys/pen (A) ligands should bind the metal in a bidentate manner via N-amino and S-mercapto groups in the ZnAB species in the Zn(II)-cys (A)-dapa and daba (B), and Zn(II)-cys/pen (A)-orn (B) systems also as in the case of ZnAB species in the Zn(II)-cys/pen (A)-orn (B) systems. Thus, ZnAB species in the Zn(II)-cys/pen (A)-dapa and orn (B) and Zn(II)-cys (A)-daba (B) systems would respectively contain three five, two five and one seven, and two five and one six-membered chelates.

As in the Zn(II)-cys (A)-dapa/daba (B) systems described above, one can expect the tridentate binding of dapa/daba (B) ligands in the ZnAB

Table 1—Experimental parameters for the proton and Zn(II) complexes of cys, pen, cya (ref. 5) dapa, daba and orn (B) (ref. 7)
[Temp. = 37°C; I = 0.15 *M* ($NaClO_4$)]

Parameters	cys	pen	cya	dapa	daba	orn
$\log \beta_{HB}$	10.31 (2)	10.89 (1)	8.41 (1)	9.37 (2)	9.93 (2)	10.22 (1)
$\log \beta_{H_2B}$	18.53 (7)	18.89 (5)	10.56 (4)	15.98 (3)	18.02 (4)	18.85 (2)
$\log \beta_{H_3B}$	19.93 (8)	20.80 (9)	—	17.37 (5)	19.88 (6)	20.99 (4)
$\log \beta_{ZnBH}$	—	14.93 (9)	—	13.61 (4)	14.22 (4)	14.56 (2)
$\log \beta_{ZnB}$	9.64 (9)	10.33 (3)	3.77 (9)	—	—	6.69 (3)
$\log \beta_{ZnB_2H_2}$	29.93 (5)	31.31 (3)	—	25.70 (3)	27.04 (16)	27.83 (11)
$\log \beta_{ZnB_2H}$	24.63 (9)	25.99 (3)	—	—	21.47 (4)	—
$\log \beta_{ZnB_2}$	17.81 (9)	20.19 (1)	6.02 (8)	13.70 (2)	13.44 (4)	—

Table 2—Experimental parameters for the Zn(II)-cys/pen/cya (A)-dapa, daba and orn (B) ternary systems
[Temp. = 37°C; I = 0.15 *M* ($NaClO_4$)]

Parameters	Zn(II)-cys (A)-B systems ligand B			Zn(II)-pen (A)-B systems ligand B			Zn(II)-cya (A)-B systems ligand B		
	dapa	daba	orn	dapa	daba	orn	dapa	daba	orn
$\log \beta_{ZnABH_2}$	—	30.11 (9)	30.78 (9)	—	30.67 (9)	31.44 (9)	—	25.52 (9)	25.95 (6)
$\log \beta_{ZnABH}$	23.24 (9)	24.37 (9)	24.05 (9)	23.79 (6)	—	24.65 (9)	17.86 (9)	18.91 (9)	18.92 (9)
$\log \beta_{ZnAB}$	16.34 (7)	17.18 (9)	16.35 (9)	16.96 (9)	—	16.92 (9)	11.13 (7)	11.45 (7)	—
$pK^{H}_{ZnABH_2}$	—	5.74	6.73	—	—	6.79	—	6.61	7.03
pK^{H}_{ZnABH}	6.90	7.19	7.70	6.83	—	7.73	6.73	7.46	—
$\log K^{ZnBH}_{ZnABH}$	9.63	10.15	9.49	10.18	—	10.09	4.25	4.69	4.36
$\log K^{ZnA}_{ZnAB}$	6.70	7.54	6.71	6.63	—	6.59	—	—	—
$\log K^{ZnB}_{ZnAB}$	—	—	9.66	—	—	10.23	—	—	—
$\Delta \log K_{ZnABH}$	−0.01	0.51	−0.15	−0.15	—	−0.24	—	—	—
$\Delta \log K_{ZnAB}$	—	—	0.02	—	—	−0.10	—	—	—

species in the Zn(II)-cya (A)-dapa and daba (B) systems also. The ligand cya is monodentate in its ZnA and ZnA_2 binary species[5]. Assuming monodentate binding of cya (A), and tridentate binding of dapa/dapa (B) ligands, the log β_{ZnAB} value in the Zn(II)-cya (A)-dapa/daba (B) systems can be calculated as *ca.* 10 log units. But the experimental values obtained are 11.15 and 11.45 respectively in the above two systems. These higher values demonstrate that cya (A) binds the metal in the ZnAB ternary species in a bidentate manner i.e., in a glycine-like mode though it is monodentate in its ZnA and ZnA_2 binary species. Thus, ZnAB species in these two systems would respectively contain three five-membered, and two five- and one six-membered chelates.

The values for the parameter $\Delta \log K_{ZnAB}$ obtained in the Zn(II)-cys/pen (A)-orn (B) systems are higher than the statistical values[6] indicating marked stabilities for the ternary complex compared to the binary analogues. This parameter could not be calculated in other systems because of the non-availability of certain binary constants in the present experimental conditions. In all the systems, appreciable amount of metal ion has been found to be present in the form of ZnAB ternary species. For example, in the Zn(II)-cys (A)-dapa (B) system, both in 1 : 1 : 2 and 1 : 2 : 1 solutions, *ca.* 70% of the total metal ion has been found to be present in the form of ZnAB species.

Stability and structure of ZnABH and $ZnABH_2$ type complexes

The log β_{ZnABH} values in Table 2 in the Zn(II)-cys/cya (A)-dapa, daba and orn (B) systems and Zn(II)-pen (A)-dapa and orn (B) systems follow the trends of the basicity of ligand (B), indicating the site of protonation in the ZnABH species in these ternary systems to be with the ligand (B), possibly with its terminal amino group as is the case with dapa, daba and orn (B) ZnBH binary species[7]. The protonated dapa, daba and orn ligands (B) in the ternary species would bind the metal in a glycine-like mode. The log K^{ZnBH}_{ZnABH} va-

lues in Table 2 in the above ternary systems bear favourable comparison with the corresponding log K^{Zn}_{ZnA} values in the Zn(II)-cys/pen (A) binary systems suggesting the bidentate binding of cys/pen (A) ligands via amino and mercapto groups in the ZnABH species also as their binding in the ZnA cys/pen binary species. However, the values obtained for the above parameter in the Zn(II)-cya (A)-dapa, daba and orn (B) systems (Table 2) are higher compared to the log K^{Zn}_{ZnA} value of 3.77 in the Zn(II)-cya (A) binary system, where cya is monodentate[5]. This suggests that in the ZnABH species in these ternary systems, cya (A) binds the metal in a bidentate mode i.e., in a glycine-like mode.

The $\Delta \log K_{ZnABH}$ values obtained in the Zn(II)-cys (A)-dapa, daba and orn (B) and Zn(II)-pen (A)-dapa and orn (B) systems are higher than the statistical values[6] demonstrating marked stabilities for the ZnABH ternary complexes compared to their binary analogues. This is also reflected in the species distribution plots where appreciable amount of metal ion has been found to be present in the form of ZnABH species. Thus, in both 1 : 2 : 1 and 1 : 1 : 2 solutions in the Zn(II)-cys (A)-daba (B) system, *ca.* 30% of the metal ion has been found to be present in the form of ZnABH species. The $\Delta \log K_{ZnABH}$ values in the cya (A) ligand systems could not be calculated because stability constant value for the bidentate binding of cya in its binary species is not available[5].

The second proton in the $ZnABH_2$ species in the Zn(II)-cys/pen (A)-daba and orn (B) systems would reside with the cys/pen (A) ligand, possibly with its amino group as is the case in their protonated binary species[5]. This protonated (A) ligand would bind the metal through the mercapto and carboxylato groups. As outlined above, the protonated (B) ligand binds the metal in a glycine-like mode. Thus $ZnABH_2$ species in all these systems would contain one six and one five-membered chelate rings, which is the preferred arrangement for the first-row transition metal ions in general. In the $ZnABH_2$ species in the Zn(II)-cya (A)-daba and orn (B) systems also, one proton can be attached with cya (A) ligand and the other would reside with the terminal amino group of daba/orn (B) system. The $pk^{H}_{ZnABH_2}$ values in Table 2 in both these systems are higher than the pK_a value for the carboxylate and sulphonic acid groups of cya (A) ligand, but slightly lesser than that value for the amino group. This demonstrates that the site of protonation in the cya (A) ligand in $ZnABH_2$ species in the above two systems is the amino group of the ligand and the protonated cya (A) ligand can bind the metal through carboxylate group. The slightly lesser $pK^{H}_{ZnABH_2}$ value compared to the pK_a value of the amino group of free ligand indicates a decrease in the basicity during complex formation. In all the systems, appreciable amount of Zn(II) has been found to be present in the form of $ZnABH_2$ species. Thus, a maximum of 23% of the total metal ion has been found in this species form in the Zn(II)-pen (A)-orn (B) system.

References

1 Gergely A & Sovago I, *Metal ions in biological systems*, edited by H Sigel (New York, Marcel Dekker) 1979, Vol 9, p. 77.

2 Hung Z X, Dai X Y, Hua X & Chag X, *Chin J Chem*, (1990) 128.

3 Nair M S, Arasu P T, Pillai M S & Natarajan C, *Trans Met Chem*, 20 (1995) 132.

4 Gans P, Vacca A & Sabatini A, *Inorg Chim Acta*, 18 (1976) 237.

5 Nair M S, Arasu P T, Pillai M S & Natarajan C, *Talanta*, 40 (1993) 1411.

6 Sigel H, *IUPAC Coordination Chemistry* 20, edited by D Banerjea (Oxford, Pergamon Press), 1980, p. 27.

7 Nair M S, Pillai M S & Ramalingam S K, *J Chem soc Dalton Trans*, (1986) 1.