

Ternary Transition Metal Chelates of 1,10-Phenanthroline & A Biological Buffer (Bicine)

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Solution equilibria of the system Cu(II), Ni(II), Co(II), Zn(II), Cd(II) or Mn(II)-1,10-phenanthroline(phen)-N,N-bis-(2-hydroxyethyl)glycine (bicine) have been studied pH-metrically and the formation of various protonated 1:1:1 mixed ligand complex species inferred from the potentiometric titration curves. The formation constants of the resulting species have been calculated at $30 \pm 1^\circ\text{C}$ ($\mu = 0.1 \text{ M KNO}_3$). The lower values of formation constants of the mixed ligand chelates than those of binary complexes have been discussed. The order of the stabilities with respect to the metal ions has been found to be: Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Mn(II).

The importance of transition metal ions in the biological systems and the phenomenon of chelation are well recognised. However, an accurate elucidation of the chelation process is apparently complicated in metabolic reactions where a variety of equilibria involving a number of metal ions and donor molecules coexist. Yet, studies on complexation reactions between biologically important metal ions and donor molecules *in vitro* are desirable. The advantages of investigations involving two or more different ligands are also evident, as complexation equilibria in such systems would be much closer to those existing in metabolic reactions.

The activity of the biologically important ligand 1,10-phenanthroline (phen) (A) on fungi, gram-positive, gram-negative and acid fast organism has been described¹⁻⁴. As compared to the phenanthroline base and its binary complexes, the ternary complexes involving phenanthroline are much more active. Because the activities of the metal chelates in biological systems are directly proportional to their concentrations, the formation constant data may be utilized to calculate the same. The present paper deals with the determination of formation constants of the systems M(II)-phen-bicine in solution at 30°C and at ionic strength 0.1 M (KNO_3), where M(II) is Cu(II), Ni(II), Co(II), Zn(II), Cd(II) or Mn(II). In order to compare the results, the binary complexes of the parent compound glycine as well as bicine have also been investigated under the same experimental conditions.

Materials and Methods

Solutions were prepared using reagent grade chemicals and doubly distilled water, either by direct weighing or by standardisation employing usual methods. The following solutions were prepared: (a)

0.01 *M* nitrates of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II) in 0.02 *M* nitric acid; (b) 1.0 *M* potassium nitrate; (c) 0.02 *M* nitric acid; (d) 0.2 *M* potassium hydroxide; (e) 0.01 *M* 1,10-phenanthroline (E. Merck); (f) secondary ligand (L): 0.01 *M* glycine (E. Merck) and bicine (B D H biochemical reagents).

All the measurements were carried out at 30°C using Philips precision pH-meter (PR 9405M) with a glass-calomel electrode assembly. The sensitivity of the pH-meter was $\pm 0.05 \text{ pH}$ units. The instrument was standardised against standard buffers of 4.0 and 9.2 pH values. The instrument was rechecked after each experiment.

The concentrations of the titration mixtures in binary and ternary complexing systems for pH-metric titrations were adjusted as described earlier⁵. The total initial volume was maintained at 50.0 cm^3 ; in each case the ionic strength was maintained at 0.1 M by adding the requisite amount of KNO_3 solution. These mixtures were titrated individually against standard KOH solution (0.2 M).

Calculations

The acid dissociation constants of bicine and glycine and the formation constants of binary metal ligand complexes were determined by Chaberek and Martell's method⁶ and are recorded in Table I.

Though the formation of metal-bicine complexes takes place at lower pH values in the metal-bicine (1:1) titrations, the mixed ligand titration curve departs from the secondary ligand titration curve only after the complete formation of $1:1 (\text{M-phen})^{2+}$ complex species and before the formation of hydroxo species. Thus, the mixed ligand complex formation takes place in stepwise reactions as follows:

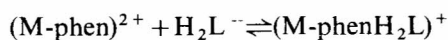


Table I—Formation Constants of binary Complexes of Glycine and bicine

[$\mu = 0.1 \text{ M KNO}_3$; $t = 30 \pm 1^\circ\text{C}$]

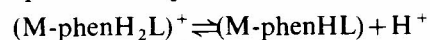
Metal ion	Glycine	Bicine	
	$\log K_{ML}$	$\log K_{(MH_2L)^+}$	$\log K_{(MHL)}$
H ⁺	$pK_1 = 2.35$; $pK_2 = 9.78$	$pK_1 = 2.48$	$pK_2 = 8.00$
Cu(II)	8.56 ± 0.02	8.06 ± 0.02	7.07 ± 0.02
Ni(II)	6.01 ± 0.02	6.12 ± 0.01	—
Co(II)	5.06 ± 0.01	5.11 ± 0.01	5.19 ± 0.01
Zn(II)	5.40 ± 0.01	5.23 ± 0.02	—
Cd(II)	—	4.63 ± 0.03	—
Mn(II)	3.41	2.91	—

The formation constant of the protonated mixed ligand complex is given by:

$$K_{MAH_2L^+} = \frac{[M\text{-phenH}_2L^+]}{[(M\text{-phen})^{2+}][H_2L^-]}$$

These constants were calculated by the method of Thompson and Loraas⁷.

In the next step of the titration curves, the protonated mixed ligand complex loses one of its protons and the formation of the uncharged complex species takes place:



The equilibrium constant of the above reaction is given by the equation,

$$K_{M\text{-phenHL}} = \frac{[M\text{-phenHL}][H^+]}{[M\text{-phenH}_2L^+]}$$

Considering the whole amounts of the metal ions and the ligands to be consumed in the formation of M-phenHL species, the above equilibria can be treated as proton dissociation of the ligand and the values of the dissociation constant $K_{M\text{-phenHL}}$ can be evaluated by an algebraic method⁸.

The free energies of formation (ΔG°) were calculated from the following equation:

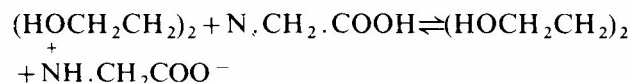
$$\Delta G^\circ = -RT \ln K_{M\text{-phenH}_2L}$$

where $K_{M\text{-phenH}_2L}$ ($x = 1$ or 2) is the formation constant of the complex; R is the gas constant and T is the absolute temperature.

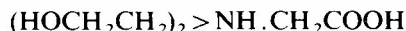
Results and Discussion

Proton ligand complexes

Bicine possesses the following zwitterionic structures:



In the initial stage of titration the following species will be formed by protonation:



The dissociation constants of glycine and bicine corresponding to cationic group $>\text{NH}^+$, and the carboxylic acid group $-\text{COOH}$ have been reported in Table I. N,N-Dihydroxyethyl glycinate ion is less basic than glycinate ion.

Binary metal complexes

In metal-bicine systems, the reaction mixtures are initially colourless but in the cases of Cu(II), Co(II) and Mn(II) systems, the mixtures attain colours during titration. Mixtures in the cases of Ni(II), Zn(II) and Cd(II) systems remain colourless throughout.

The titration curves of Cu(II) or Co(II)-bicine (1:1) system have two inflections. The first inflection is due to the formation of 1:1 Cu(II) or Co(II)-bicine chelate and the second inflection is due to either the dissociation of a proton from the hydroxyethyl group or from the coordinated water molecule as discussed later.

A comparison of the formation constants of M(II)-glycine and M(II)-bicine chelates shows equal or higher affinity of bicine for metal ions, indicating the participation of the hydroxyethyl groups in chelate formation. For metal ions with coordination number 4, bicine behaves as a tridentate ligand while with metals with coordination number 6, it acts as a tetradentate ligand. At higher pH, the solution with Zn(II), Cd(II) or Mn(II) becomes turbid. Values of stepwise formation constants corresponding to various equilibria are recorded in Table I.

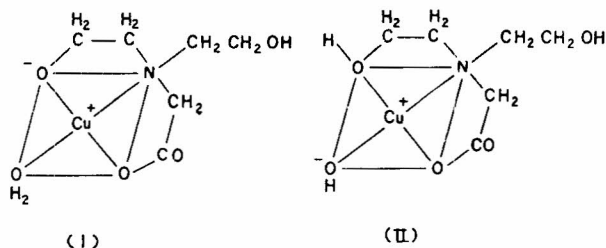
The absence of polynuclear species was confirmed by using several concentrations of the reactants, the results obtained were identical.

Protonated ternary metal complexes

Type MAH_2L^+ : Protonated ternary complexes of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II) have been studied. With Mn(II), turbidity occurs in the ternary systems before the complete formation of 1:1:1 chelate. For other systems complete formation of 1:1:1

chelate takes place. The formation constants ($\log K_{\text{MAHL}^+}$) and the free energies of formation (ΔG°) of the protonated ternary complexes of bicine have been listed in Table 2.

From a comparison of the formation constants of binary and ternary complexes of bicine, it is observed that for Cu(II)-phen-bicine system, $\log K_{\text{MAHL}^+}$ is much lower than the corresponding value for binary complex, while for other systems it is nearly equal or lower. In Cu(II)-phen-bicine chelate, bicine behaves as a bidentate ligand, because Cu(II) has coordination number four and two of these are already filled by the primary ligand (phen), while in the binary systems bicine acts as a tridentate or tetradentate ligand (structure I or II).



For metal ions with coordination number six, the values of formation constants of ternary complexes are also lower than those of binary complexes, even though the hydroxyethyl groups are taking part in complexation reactions in both the cases. This may be due to steric hindrance.

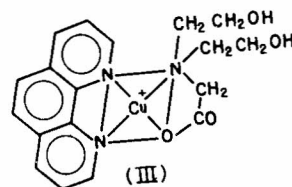
The order of the stabilities of the ternary complexes with respect to metal ion is: Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Mn(II).

Type MAHL: In the titration curves for ternary systems with Cu(II) or Co(II), one more inflection is found after the complete formation of 1:1:1 ternary chelate; also, the intensity of colour of the solutions increases during the titrations. The additional release of proton may either be due to hydroxocomplex formation or the removal of one proton from the coordinated ligand. The first possibility is ruled out because no precipitate is formed during the titration. Hence, the second alternative is acceptable as no other hydrogen is present. The formation constants of the

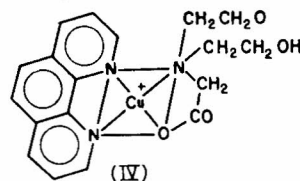
complexes formed and the free energies of formation are given in Table 2.

Chelate structure

A comparison of the formation constants of binary chelates of metal ions reported in Table 1 indicates that in spite of the lower basicity, the chelating tendency of bicine is increased due to the participation of the hydroxyethyl groups of the ligand in complexation. For metal ions with coordination number 4, only one hydroxyethyl group may be involved in chelation according to molecular models. Hence, there is an ambiguity for the structures (I & II) formed after the hydrolysis of 1:1 M(II)-bicine chelate, where M(II) is Cu(II) or Co(II). The Cu(II)-bicine chelate structure may be I or II; or they may be in equilibrium with each other. The structure of the ternary complex may be represented by (III).



The titration curves show a further dissociation of a proton from the above ternary chelate; it may be argued that this release of proton is from the hydroxyethyl group of bicine molecule because no other dissociable hydrogen is present. Hence, the structure of the species may be represented by (IV).



On the basis of this argument it may be suggested that the loss of proton from bicine 1:1 Cu(II)-bicine chelate is from the hydroxyethyl group and not from the H₂O molecule attached to Cu(II). Therefore, structure (I) is preferred to (II) for the 1:1 complex.

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Table 2—Formation Constants and Free Energy of Formation of Ternary Complexes

Metal ion	$\log K_{(\text{MAHL})^+}$	$-\Delta G^\circ_{(\text{MAHL})^+}$ (kcal/mol)	$\log K_{\text{MAHL}}$	$-\Delta G^\circ_{(\text{MAHL})}$ (kcal/mol)
Cu(II)	5.90 ± 0.01	8.17	5.51 ± 0.02	7.63
Ni(II)	5.50 ± 0.01	7.62	—	—
Co(II)	4.49 ± 0.02	6.22	4.91 ± 0.02	6.80
Zn(II)	4.28 ± 0.02	5.93	—	—
Cd(II)	4.15 ± 0.01	5.75	—	—
Mn(II)	2.80 ± 0.03	3.88	—	—