Interaction of N-[Tris(hydroxymethyl)methyl]glycine with some Transition Metal Complexes in Aqueous Solution

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Equilibrium study of the reaction between Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} or Pb^{II} with 1,10-phenanthroline (phen) and N-[tris(hydroxymethyl)methyl]glycine (H_3L) by potentiometric titration technique in aqueous solution at 30° and at an ionic strength 0.01 M (KNO_3) provided evidence of formation of ternary (1 : 1 : 1) complexes $M(phen)(H_2L)^+$. Cu^{II} formed two different species $Cu(phen)(H_2L)^+$ and $Cu(phen)_2(HL)$. Trends of $\triangle \log K$ values and the tentative structures of the different species have been discussed.

N-[Tris (hydroxymethyl) methyl] glycine (Tricine) forms complexes with several metal ions[1-3]. The present communication deals with the study of interaction of tricine (H_3L) with Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} or Pb^{II} in the presence of 1,10-phenanthroline, hereafter Phen. Results have been compared with those of the corresponding values for the complexes of glycine under identical conditions.

Experimental

AnalaR grade chemicals were employed. Nitric acid, aqueous solutions of Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Pb^{II} and Cd^{II} nitrates in standard nitric acid and potassium hydroxide solution were prepared in double-distilled CO_2-free water and standardised as usual[4]. Aqueous solutions of KNO_3, phen and tricine were prepared by direct weighing.

pH-measurements were made using a Philips PR 9405 M pH meter with a glass electrode and an SCE connected to the cell by means of a salt birdge at a constant temperature of 30 ± 0.1° in an inert atmosphere of nitrogen and at an ionic strength of 0.1 M (KNO_3).

The following six mixtures, (i) $0.02M$ HNO_3 ; (ii) (i) + $0.01M$ phen, (iii) (ii) + $0.01M$ metal nitrate, (iv) (i) + $0.01M$ tricine/glycine, (v) (iv) + $0.01M$ metal nitrate, and (vi) (iii) + $0.01M$ tricine, each of total volume 50 cm³ were titrated with $0.20M$ KOH solution. The ionic strength, $\mu =$ $1.0M$ was maintained constant by adding the required amount of KNO_3. Moles of alkali (a) required per mole of ligand at different pH were calculated from pH vs volume curves (Fig. 1).

Results and Discussion

The acid dissociation constants ($K_{H_3L}^H$, $K_{H_2L}^H$) of tricine and the stability constants ($K_{MH_2L}^M$, K_{MHL}^M

and K^{CuH_2L}) of binary complexes were calculated by the method of Chaberek and Martell[5], and Nayan and Dey[6]. The stability constants of the ternary complexes were calculated by the method of Thompson and Loraas[7]. Results are presented in Table 1.

The curve F (Fig. 1) corresponding to the ternary systems follows the same path as that of the
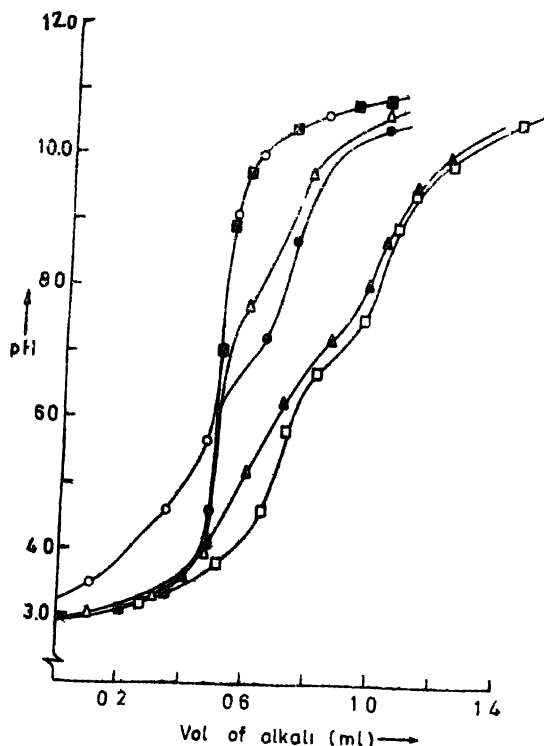

Fig 1. Titration curves of binary and ternary systems of Cu^{II} ion: (■) acid curve, (○) phen. (●) 1 : 1 Cu^{II}—phen, (△) tricine, (▲) 1:1:1 Cu^{II}—phen—tricine, and (□) 1 : 1 Cu^{II}—tricine.

TABLE 1—FORMATION CONSTANTS OF METAL COMPLEXES OF
GLYCINE AND TRICINE

$\mu = 0.1\ M\ KNO_3$, temp $= 30 \pm 1°$

Metal	$\log K^{M}_{M(H_2L)}$	$\log K^{M(phen)}_{M(phen)(H_2L)}$	$\Delta \log K_M$
Ni^{II}	5.45 (6.01)	5.16	0.29
Co^{II}	4 71 (5 06)	4 65	0.06
Zn^{II}	5.29 (5 40)	4.81	0.48
Cd^{II}	– (4 70)	–	–
Pb^{II}	3 28 (3.41)	3.91	−0.63
Cu^{II}	7.30 (8.56)	6.06	1.24

$\log K^{CuH_2L}_{CuHL}$	$\log K^{Cu(phen)H_2L}_{Cu(phen)HL}$	$\Delta \log K_{Cu}$
−7.12	−6.70	−0.42

Values in the parenthesis correspond to those with glycine.

pK^{H}_{NH+} (Tricine : 8.18, Glycine : 9.78) Limits of error =
$\pm (0\ 01 - 0.03)$ in log scale.

curve C which corresponds to the binary Cu–phen system. This shows the complete formation of $(Cu–phen)^{2+}$ in the first step. The curve F then separates from the curve C showing the coordination of the second ligand tricine to the binary complex $(Cu–phen)^{2+}$. The curve F corresponding to Cu^{II} ion shows an additional inflection after the complete formation of the ternary Cu(phen)-(H_2L) complex indicating the loss of a proton from the coordinated tricine molecule to form the Cu-(phen)(HL) complex according to the equilibrium,

$$[Cu(phen)H_2L]^+ \rightleftharpoons Cu(phen)HL + H^+.$$
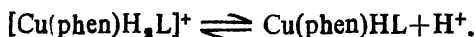
Tricine, which is a zwitterionic amino acid, is expected to have two proton dissociation constants corresponding to the cationic $\equiv \overset{+}{N}H$ group, and the carboxylic acid group, COOH. But under the present experimental conditions, only $K_2(\equiv \overset{+}{N}H)$ values could be evaluated. The higher value of this proton dissociation constant as compared to glycine arises probably due to inductive electron attraction by the hydroxyl oxygen.

Titration curves (Fig. 1) of binary metal-tricine mixtures revealed the formation of 1 : 1 complexes with Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} or Pb^{II}. Complexation of Cd^{II} could not be completed due to the appearance of turbidity.

The titration curve for Cu^{II}-tricine system showed two inflections corresponding to the release of two protons in steps. The second proton is released either from the chelating ligand (H_2L) or from the coordinated water molecule. The higher values of the formation constants of the glycinate complexes than those of the corresponding tricinate complexes are due to the weaker basicity of the amino nitrogen of tricinate as compared to that of the glycinate.

Titration curves of the ternary M(II)–phentricine mixtures of Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} or Pb^{II} show only one inflection but titration of Pb^{II}, Cd^{II} system could not be completed due to the appearance of turbidity. Cu^{II} ternary system shows two inflections, the first one due to the release of proton from the tricine molecule as a result of complexation with Cu^{II} ion and the second one due to the deprotonation of coordinated tricine. The formation constant values of the two species of ternary complexes of Cu^{II} ion indicates that a more stable complex is formed after the release of proton than the protonated complex itself.

Due to the lower basicity of tricine, its metal ion affinity is lowered as compared to glycinate ion (Table 1). Tricine behaves as tridentate ligand in the case of binary complex formation. Since mixed ligand complex formation takes place in steps, the possibility of binding of the secondary ligand tricine to metal ion is only through O/N, showing the bidentate nature of the ligand. Hence the stability of the resulting ternary complex decreases.

Hexacovalent metal ions show a less negative $\Delta \log K$ value, and this may be due to the participation of the two $[(OHCH_2)C-]$ groups in coordinating to metal ions both in binary as well as in ternary complexes. Based on this, it may be proposed that tricine also behaves as tetradentate ligand.

Acknowledgement

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