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# Ternary Cu(II) complexes involving N-(1-naphthyl)ethylenediamine, ethylenediamine (N–N donors) and a series of amino acids ($N–O^-$ donors)

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**Abstract.** The dissociation constants for N-(1-naphthyl)ethylenediamine (NEN) and the formation constants for binary (ML) and ternary metal complexes (MLA), where M = Cu(II), L = alanine, phenylalanine, tryptophan, lysine, arginine, serine, threonine, aspartic acid or histidine and A = NEN or ethylenediamine (EN) have been determined by pH titrations and are reported at 35°C ($\mu = 0{\cdot}2$ M $KNO_3$). The relative stability of the ternary complexes are discussed in terms of statistical effects and the nature of ligands in the coordination sphere of the metal ion.

**Keywords.** Ternary complexes; N-(1-naphthyl)ethylenediamine; ethylenediamine; aminoacid–copper complexes.

## 1. Introduction

In the present investigation the formation and stability of ternary Cu(II) complexes containing N-(1-naphthyl)ethylenediamine (NEN) or ethylenediamine (EN) as the (N–N) donor ligands and a series of amino acids, alanine (Ala), phenylalanine (Phe), tryptophan (Trp), lysine (Lys), arginine (Arg), serine (Ser), threonine (Thr), histidine (His) or aspartic acid (Asp), as the ($N–O^-$) donors are reported at 35°C ($\mu = 0{\cdot}2$ M $KNO_3$). The effect of the naphthyl substituent on the dissociation constants of NEN and on the stability and formation of the binary and ternary complexes have been evaluated by comparing the relevant data for systems containing NEN or EN determined under identical experimental conditions.

## 2. Materials and methods

N-(1-naphthyl)ethylenediamine dihydrochloride, ethylenediamine dihydrochloride and the various amino acids were obtained from Sigma, USA. Arginine, lysine, aspartic acid and histidine were used in the triprotonated form while all other ligands were used in the diprotonated form.

The pH metric titrations were carried out in a double-walled titration cell maintained at 35°C ($\mu = 0{\cdot}2$ M $KNO_3$). For the determination of dissociation

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contants of NEN/EN, the formation constants for the binary Cu(II) complexes and various ternary Cu(II) complexes, the following solutions were titrated with standard carbonate-free NaOH: (I) 0·002 M NEN/EN; (II) Sol I + 0·002 M Cu(II); (III) Sol II + 0·002 M amino acid.

Details of the experimental procedure are given in our earlier publication (Koteswar Rao and Srinivas Mohan 1989). The acid dissociation constants for diprotonated NEN/EN, the binary constants for Cu(II)–NEN/EN complexes and the ternary constants for the various amino acids–Cu(II)–NEN/EN systems were calculated from the pH data using the Computer program SCOGS (Sayce 1968). The relevant uncomplexed and complexed metal species were taken into consideration for computation.

## 3. Results

The stepwise dissociation constants $pK_a$ and $pK_{2a}$ for diprotonated NEN/EN were calculated from the data for solution (I) by taking into consideration the species $H_2A$, HA and A and are listed in table 1. Formation constants for the binary complexes ($K^{M}_{MA}$) involving Cu(II) and diprotonated NEN/EN were calculated from data for solution (II) taking into consideration the species $H_2A$, HA, A, M and MA and are listed in table 1. In systems involving NEN, ternary complex formation (MLA) takes place in a stepwise manner involving the initial formation of Cu(II)–amino acid complex (ML) followed by the addition of NEN (A). Ternary formation constants ($K^{ML}_{MLA}$) were calculated by taking into consideration the species HA, A, ML and MLA. Formation constants for ternary complexes containing two moles of NEN could not be

**Table 1.** Dissociation constants[a,b] binary[b] and ternary constants[b] of Cu(II) complexes containing N-(1-naphthyl)ethylenediamine or ethylenediamine (A) and various amino acids (L).

T = 35°C; $\mu$ = 0·2 M ($KNO_3$)

| | | NEN | | EN | | |
|---|---|---|---|---|---|---|
| Ligands | $\log K^{M}_{MA}$ | $\log K^{ML}_{MLA}$ | $\Delta \log K$ | $\log K^{ML}_{MLA}$ | $\Delta \log K$ | $\Delta(\Delta \log K)$ |
| N-(1-naphthyl)-ethylenediamine | 5·51 | | | | | |
| Ethylenediamine | 10·32 | | | | | |
| Alanine | | 5·28 | −0·23 | 9·70 | −0·62 | +0·39 |
| Phenylalanine | | 5·28 | −0·31 | 9·81 | −0·51 | +0·20 |
| Tryptophan | | 5·30 | −0·21 | 9·82 | −0·50 | +0·29 |
| Threonine | | 5·25 | −0·26 | | | |
| Lysine[c] | | 5·13 | −0·38 | 9·63 | −0·69 | +0·31 |
| Arginine[c] | | 5·18 | −0·33 | 9·71 | −0·61 | +0·28 |
| Aspartic acid | | 5·30 | −0·21 | 9·33 | −0·99 | +0·78 |
| Histidine | | 5·18 | −0·33 | 8·87 | −1·45 | +1·12 |

[a]NEN: $pK_a$ = 1·32; $pK_{2a}$ = 8·97, EN: $pK_a$ = 6·96, $pK_{2a}$ = 9·73

[b]All constants accurate to ±0·02

[c]Values refer to protonated ternary complexes (MHLA)

determined since solutions containing a 1:1:2 molar ratio of amino acid–Cu(II)–NEN respectively were found to undergo hydrolysis and result in precipitation at higher pH values. In systems involving EN, ternary complex formation was observed to take place by the simultaneous addition of EN and the amino acid to Cu(II). The cumulative formation constants $K^{M}_{MLA}$ were calculated by taking into consideration the species $H_2L$, HL, L, $H_2A$, HA, A, M, ML, MA and MLA. For triprotonated amino acids Asp, His, Lys or Arg, the $H_3L$ species was also considered. The stepwise formation constants $K^{ML}_{MLA}$ which were calculated from the cumulative ternary constants and the corresponding binary constants ($K^{M}_{ML}$) determined under identical experimental conditions (Prasad and Srinivas Mohan 1987; Prasad *et al* 1987) are listed in table 1. The influence exerted by a ligand (L or A) which is already bound to the metal ion on the binding of a second ligand (A or L) has been quantitatively assessed in terms of the parameter $\Delta \log K$ (Bhattacharya 1981) and these values are listed in table 1.

## 4. Discussion

Due to the inductive effect of the naphthyl ring the dissociation of a proton from the substituted nitrogen atom of NEN ($pK_a$) is 5·6 units lower than the corresponding constant for EN (table 1). The $pK_{2a}$ value of NEN is decreased to a much smaller extent ($\sim$ one unit) since it refers to the dissociation of a proton from the unsubstituted nitrogen atom. The decreased basicity of NEN is reflected in the stability of its binary Cu(II) complex which is about five log units lower relative to the Cu(II)–EN binary complex. The large difference in values for these binary constants indicates that while EN is bidentate, NEN is monodentate and is bound to Cu(II) through the unsubstituted nitrogen atom with the higher basicity.

The statistically expected $\Delta \log K$ values for the binding of a bidentate amino acid to square planar Cu(II) already bound to monodentate NEN or bidentate EN are $-0{\cdot}3$ and $-0{\cdot}6$, respectively. The experimental $\Delta \log K$ values (table 1) are in this range. However, for ternary sytems containing the tridentate amino acids His and Asp, these values are relatively more positive for systems involving NEN than for the corresponding systems containing EN. This trend is more clearly reflected in the $\Delta(\Delta \log K)$ values (table 1) obtained from the expression,

$$\Delta(\Delta \log K) = \Delta \log K_{NEN} - \Delta \log K_{EN},$$

which support the view that ternary complexes containing monodentate NEN are more stable since the various amino acids bind Cu(II) without a change in denticity, whereas ternary systems containing bidentate EN and the tridentate amino acids Asp and His have lower stability due to decreased denticity viz. bidentate in ternary relative to tridentate in binary Cu(II) complexes (Martin 1979).

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## References

Bhattacharya P K 1981 *J. Sci.-Ind. Res.* **40** 382
Koteswar Rao A and Srinivas Mohan M 1989 *Proc. Indian Acad. Sci. (Chem. Sci.)* **101** 1
Martin R B 1979 in *Metal ions in biological systems* (ed.) H Sigel (New York: Marcell Dekker) vol. 9, chap. 1
Prasad K, Rao A K and Srinivas Mohan M 1987 *J. Coord. Chem.* **46** 251
Prasad K and Srinivas Mohan M 1987 *J. Coord. Chem.* **16** 1
Sayce I G 1968 *Talanta* **15** 1397