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Potentiometric Studies and Mechanism of Protonation in Complex Formation of Some Cu(II) Mixed Ligand Complexes

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Modified form of Irving-Rossotti titration technique is used to determine the formation constants for Cu(II) mixed ligand complexes at 1 : 1 : 1 optimum molar concentration of metal, primary ligand (A) and secondary ligand (L). The formation constant values of binary complexes are compared with ternary complexes. The $\Delta \log K_T$ values are negative suggests favourable formation of ternary complexes. The variation of $\Delta \log K_T$ values has been explained in terms of $M \rightarrow L\pi$ interaction, size of chelate ring and steric factors. Stability constants have been evaluated and discussed in terms of basicity of ligand, statistical and stereochemical phenomenon. A mechanism of protonation in complex formation is suggested.

Key Words: Potentiometric, Mechanism, Cu(II), Mixed ligand complexes.

INTRODUCTION

Studies of formation constants of mixed ligand system (MAL) where A = 2,2′-bipyridyl or 2,2′-bipyridylamine and L-amino acids or polyhydroxy phenols has been carried out by earlier workers[1–4]. Copper is one of the elements which is used in highest concentration than any of the non-ferrous transition metals especially bound by the protein metallothionein[5, 6]. Extensive data on the stability of transition metal complexes in solution are available by using different experimental techniques[7–9].

In the present communication mixed ligand formation constants of type $\log K^{Cu\cdot A}_{Cu\cdot A\cdot L}$ are reported where A = 2,2′-bipyridylamine and L = ethylene diamine or 1,2-diaminopropane or 1,3-diaminopropane, N,N-diethyl ethylene diamine or N,N-dimethyl ethylenediamine.

EXPERIMENTAL

Ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, N,N-diethyl ethylenediamine N,N-dimethyl ethylenediamine (AnalaR), Sodium perchlorate

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(Fluka), 2,2′-bipyridylamine (Fluka), perchloric acid (Baker analysed) and sodium hydroxide (AnalaR) were used.

A stock solution of $Cu(ClO_4)_2$ was prepared and standardised with EDTA solution[10]. Carbonate free sodium hydroxide solution was used for carrying out titrations. Digital μ pH-meter 361 with readability ±0.01 was used for pH-metric measurements. Modified form of Irving-Rossotti titration technique has been used[11, 12]. The 1 : 1 : 1 molar ratio of Ni, A and L was maintained in the solution. The ionic stength of the solution was maintained at 0.2 M dm^{-3} using sodium perchlorate. Five sets of the solution were prepared containing:

(I) Known amount of $HClO_4$,
(II) Free $HClO_4$ + known amount of primary ligand,
(III) Free $HClO_4$ + known amount of primary ligand + known amount of metal perchlorate,
(IV) Free $HClO_4$ + known amount of secondary ligand,
(V) Free $HClO_4$ + known amount of primary ligand + known amount of secondary ligand + known amount of metal perchlorate.

Total of each mixture was raised to 50 mL using double distilled water. From titration data (Fig. 1) $\bar{n}H, \bar{n}$ and pL were calculated using Excel computer programme on the basis of literature method[13, 14]

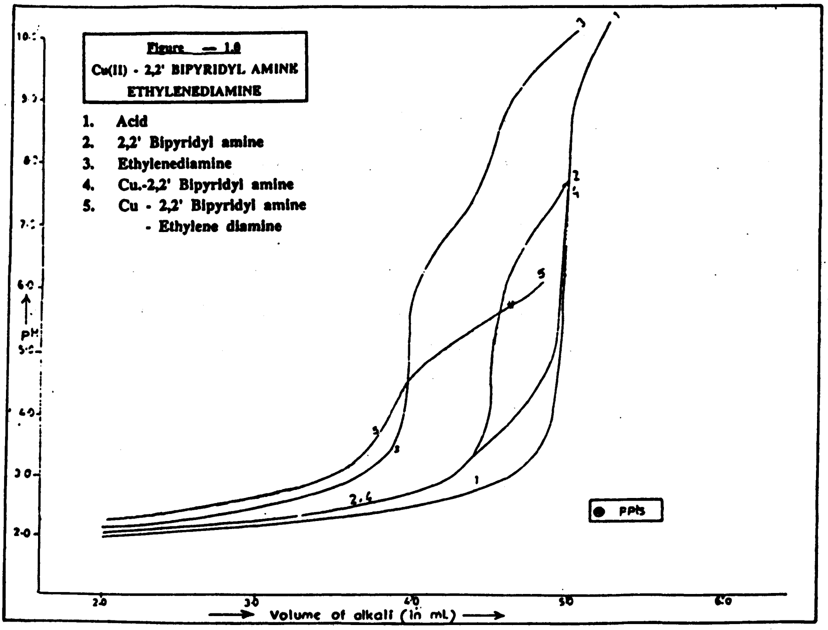


Fig. 1. Cu-2,2′-Bipyridylamine ethylenediamine

RESULTS AND DISCUSSION

The proton ligand and metal ligand formation constants of ligand and divalent copper ion with diamines were calculated by measuring the magnitude of the proton displacement during titration in presence and in absence of metal ion against standard sodium hydroxide respectively. The proton ligand, binary ligand and mixed ligand formation constants are presented in Table-1. The proton ligand formation constant values are same as reported earlier[15]. The metal ligand binary formation constant values are in the order of 1,3-diaminopropane > 1,2-diaminopropane > ethylenediamine > N,N-dimethyl ethylene diamine > N,N-diethyl ethylene diamine. The formation of mixed ligand complex can be represented as follows:

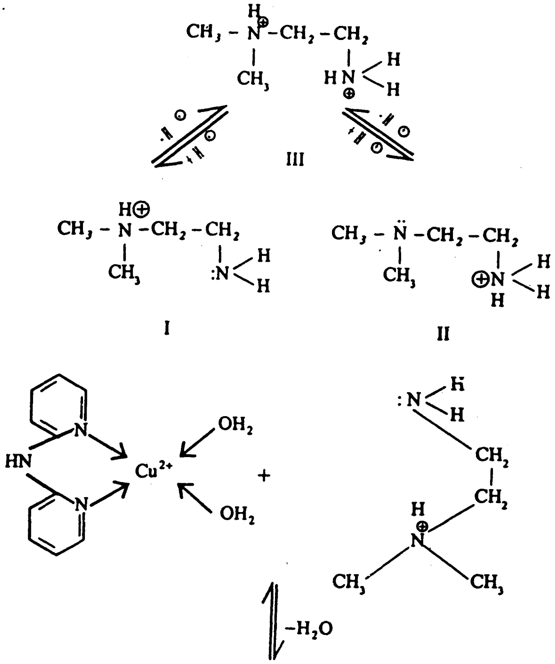
$$[\mathrm{Cu(bipyridylamine)}] + \mathrm{L} \rightleftharpoons [\mathrm{Cu(bipyridylamine)L}]$$

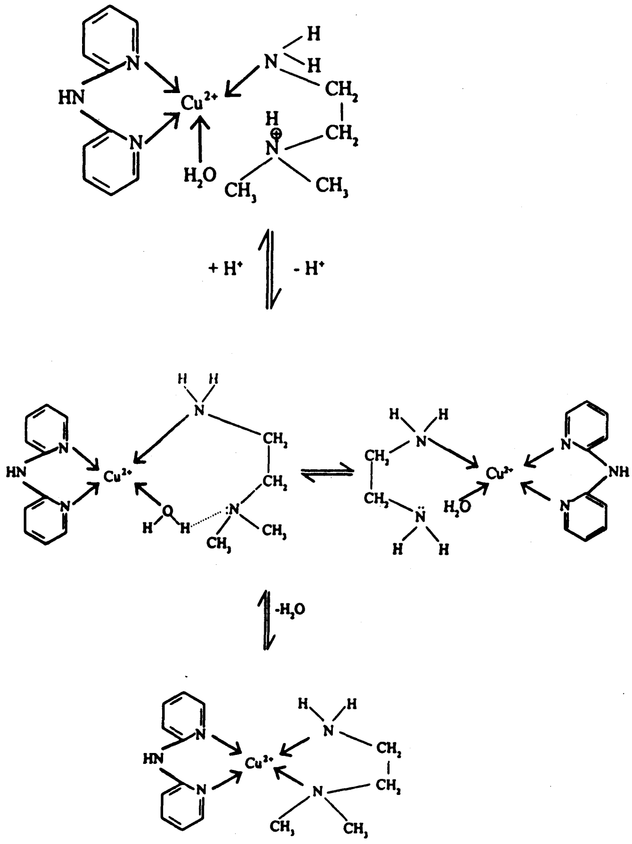
$$K^{\mathrm{Cu.bipyA}}_{\mathrm{Cu.bipyA\cdot L}} = \frac{[\mathrm{Cu\cdot bipyA\cdot L}]}{[\mathrm{Cu\cdot bipyA}][\mathrm{L}]}$$

where A = 2,2′-bipyridylamine

L = ethylene diamine or 1,2-diaminopropane, 1,3-diaminopropane, N,N-diethyl ethylene diamine or N,N- dimethyl ethylene diamine.

The mixed ligand formation constants of 1 : 1 : 1 ternary complexes of Cu(II)-2,2′-bipyridylamine-diamines were calculated considering that 1 : 1 $[\mathrm{Cu(2,2'\text{-}bipyridyl\cdot A)}]^{2+}$ is completely formed[14–16] before coordination of secondary ligand takes place. The formation of Cu(II)-2,2′-bipyridylamine-diamine is expected to take place by the following mechanism.





The values of log $K^{Cu\cdot A}_{Cu\cdot A\cdot L}$ are in the following order:

1,3 diaminopropane > 1,2 diaminopropane > ethylene diamine >
N,N dimethyl ethylenediamine > N,N diethyl ethylenediamine.

This order followed is same as in case of binary complexes.

This sequence is explained in terms of stereochemical structure and basicities of secondary ligands. All secondary ligands used are bidentate in nature. 1,3-Diaminopropane forms a six-member chelate ring while all others form five member chelate ring with copper(II). pK_1^H value for 1,3-diaminopropane is highest among the group of diamines selected. Mixed ligand formation constant values for [Cu-2,2′-bipyridylamine ethylene diamine], [Cu-2,2′-bipyridylamine 1,3-diaminopropane] and [Cu-2,2′-bipyridylamine. 1,2-diaminopropane] follow the sequence which is in agreement with proton ligand formation constants of ligands. Complex of [Cu-2,2′-bipyridylamine-N,N-diethyl ethylenediamine] has lower formation constant value than [Cu-2,2′-bipyridylamine-N,N-dimethyl ethylenediamine] although the basicity of N,N-dimethyl ethylenediamine is lower than N,N-diethyl ethylenediamine. The presence of two —C_2H_5 groups on two chelating nitrogen atoms has lowered the value of formation constant. Mixed ligand complexes of ethylenediamine have higher value of formation constants than N,N-dimethyl ethylenediamine and N,N-diethyl ethylenediamine complexes; steric hindrance due to presence of either —C_2H_5 or —CH_3 group can be a probable reason.

TABLE-1
DISSOCIATION CONSTANTS OF FREE LIGAND, FORMATION CONSTANTS OF Cu(II) BINARY AND TERNARY COMPLEXES AT TEMPERATURE 30 ± 0.1°C, IONIC STRENGTH $\mu = 0.2$ mol dm^{-3} ($NaClO_4$)

Ligand L	pk_1^H	pk_2^H	$\log k_{Cu \cdot L}^{Cu}$	$\log k_{Cu \cdot L_2}^{Cu \cdot L}$	$\log k_{cuCdotbipyA \cdot L}^{Cu \cdot bipyA}$	$\Delta \log K_T$
Ethylene diamine	9.85	6.94	10.33	8.95	10.11	−0.22
1,2-diamino propane	10.04	6.65	10.79	9.09	10.33	−0.46
1,3-diamino propane	10.09	8.85	13.59	11.03	13.41	−0.18
N,N-diethyl ethylenediamine	10.04	6.94	8.23	6.76	8.01	−0.22
N,N-dimethyl ethylenediamine	9.99	6.48	8.83	7.14	8.71	−0.12

where $\Delta \log K_T = \log k_{MAL}^{MA} - \log k_{ML}^{M}$, bipyA = 2,2′-bipyridylamine.

The relative stabilities of mixed ligand complexes is compared to corresponding binary complexes and can be quantitatively expressed in terms of $\Delta \log K_T$[17]. $\Delta \log K_T = \log K_{Cu \cdot A \cdot L}^{Cu \cdot A} - \log K_{Cu \cdot L}^{Cu}$. The advantages of using $\Delta \log K_T$ for comparison of stabilities of binary and mixed ligand complexes have been reviewed[18]. The $\Delta \log K_T$ values are negative indicating greater stability of complexes.

The $\log K_{Cu \cdot A \cdot L}^{Cu \cdot A}$ are significantly higher than $\log K_{Cu \cdot L_2}^{Cu \cdot L}$ values, while lower than $\log K_{Cu \cdot L}^{Cu}$ values. The reason can be the special nature of 2,2′-bipyridylamine. Besides N → Mσ bonding there exists strong M → Nπ interaction due to back donation of electrons from metal *dπ* orbitals to vacant delocalized *pπ* orbitals over the bipyridylamine molecule. As a result of π-interaction in M—N bond, the concentration of electrons around the metal ions in the $[M(bipyridylamine)]^{2+}$ complex does not increase significantly and the electronegativity of metal ion in $[M(bipyridylamine)]^{2+}$ remains same as $[M(H_2O)_n]^{2+}$.

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