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Stability Constants of the Ternary Complexes of Copper(II) with Dipicolinic Acid and Amino Acids

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The stability constants of mixed-ligand complexes of the type (CuXY) where X = 2,6-pyridinedicarboxylic acid (dipicolinic acid) as the primary ligand and Y = DL-α-alanine, β-alanine, glycine or glutamic acid as secondary ligand have been determined in aqueous solution using pH-metric technique. The stability constants have been evaluated at 25°C and at 0.1 M ionic strength. Copper (II) formed 1 : 1 : 1 mixed-ligand complexes with dipicolinic acid and amino acids. The preferential formation of the ternary complexes over the binary complexes have been discussed in terms of equilibrium constants.

INTRODUCTION

Much work has been done on the mixed-ligand complexes[1–6], in which two kinds of ligands are involved in chelation. The effect of the chelate rings, steric factors and metal ion activity have been evaluated in the formation of a ternary complex from the aquated metal ion and the chelating agents.

Mixed-ligand complexes of metal ions have been extensively studied in recent years[7–9] following the recognition that these play an important role in biological process. The formation of ternary complexes is statistically more favoured and frequently they are of favoured stability also.[10] Mixed-ligand complexes formed by biologically active ligands like amino acids and polypeptides can serve as model systems for the study of the more complicated phenomena occurring in biological systems. Ternary complexes of various metal ions involving amino acids, diamines and carboxylic acids have been extensively studied[11–13]. There have been some reports of complexes of metal ions with DL-aspartic acid as the primary ligand and few amino acids as the secondary ligands[14–17]. The aim of the present work is undertaken to explain the preferential formation of ternary complexes of copper(II) over the binary complexes and some structural aspects of copper(II) with dipicolinic acid as the primary ligand and DL-α-alanine, β-alanine, glycine and glutamic acid as secondary ligands.

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EXPERIMENTAL

Dipicolinic acid, glycine, DL-α-alanine, β-alanine, glutamic acid (B.D.H.) and $Cu(ClO_4)_2$ (Fisher Reagent Grade) were used without further purification. All the solutions were made in deionized water. The metal salt solution was standardized by EDTA titration and purities of all the compounds were assessed by potentiometric method.

pH-measurements were made at 25°C in 0.1M ($NaClO_4$) ionic strength on a Systronic pH-meter, model LI-120, equipped with saturated calomel electrode and sealed glass electrode. The reproducibility was within 0.02 pH units. All the titrations were carried out under an atmosphere of nitrogen in a thermostated bath.

RESULTS AND DISCUSSION

The proton-ligand and metal-ligand stability constants were determined by Irving and Rossotti[18]. The pKa values were obtained from intercepts of the linear plots of log $[n_A/(1 - \bar{n}_A)]$ vs pH (where $\bar{n}_A$ is the average number of protons per ligand). Metal-ligand stability constants were obtained from half-integral values of plots of $\bar{n}_A$ vs pL. The values given in Table 1 reveal that there is good agreement between our values and those reported in literature[17].

TABLE–1
IONIZATION CONSTANTS OF THE LIGANDS AND STABILITY CONSTANTS OF BINARY COMPLEXES OF COPPER(II)

Sl. No.	Ligand	pK_1	pK_2	log K_{MX1}	log K_{2MX}
		Observed (Literature)	Observed (Literature)	Observed (Literature)	Observed (Literature)
1.	DL-α-Alanine	2.45 (2.35*)	9.60 (9.61*)	9.19 (8.12*)	6.83 (6.71*)
2.	β-Alanine	3.57 (3.60*)	10.21 (10.16*)	7.06 (7.04*)	5.43 (5.54*)
3.	Glutamic acid	4.12 (4.07*)	9.38 (9.41**)	7.86 (7.87*)	6.26 (6.29**)
4.	Glycine	2.42 (2.33*)	9.62 (9.53*)	8.40 (8.19*)	7.11 (6.85*)
5.	Dipcolinic acid	2.43 (—)	4.79 (—)	9.14 (—)	— (—)

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The stability constants of mixed-ligand complexes (log K_{MXY}) were calculated by following expressions obtained by the modification of Thompson and Loraa's method[19]

$$\log K_{MXY} = \frac{T_M^{-1/2} A.X}{1/8\, A^3 \cdot X}$$

when $T_M = T_X = T_Y$

where

$$A = \frac{2T_X + 2T_Y - T_{OH} - H^+}{\dfrac{4H^2}{K_1K_2 + K'_1\,K'_2} + \dfrac{2(H)}{K_2 + K'_2}}$$

T_{OH} is the concentration of NaOH. K_1K_2 and $K'_1\,K'_2$ are the first and second dissociation constants of the two ligands and A is the initial concentration of $HClO_4$.

It is interesting to observe that in the case of mixed-ligand titrations shows higher pH of precipitation than individual metal complex titrations, reveals the formation of mixed-ligand complex. The shapes and positions of titration curves confirm simultaneous formation of ternary complexes as suggeted by Martell[20].

It is observed that $\Delta \log K$ is positive indicates the formation of ternary complexes over binary ones [$\Delta \log K = \log (K_{MX1} + \log K_{MY1}) - \log \beta_{MXY}$]. For the stability of mixed-ligand complexes indicated by magnitude of disproportion constnat, $K_{DMXY} > 0.6$. The values of β_{MXY}, K_{DMXY}, K_{2MXY}, K_{2MYX} and $\Delta \log K$ were calculated for such systems and are listed in Table 2.

TABLE–2

COPPER(II)-DIPICOLINIC ACID-LIGAND(Y) SYSTEM: STABILITY CONSTNATS* OF TERNARY COMPLEXES

Temp = 25°C; $\mu = 0.1$ M($NaClO_4$)

Sl. No.	Ligand (Y)	$\log \beta_{MXY}$	$\log K_{DMXY}$	$\log K_{2MXY}$	$\log K_{2MYX}$	$\Delta \log K$
1.	DL-α-Alanine	12.98	2.99	3.84	4.79	4.35
2.	β-Alanine	12.15	2.42	3.01	5.09	4.05
3.	Glutamic acid	12.00	2.40	2.86	4.14	5.00
4.	Glycine	11.92	4.38	2.78	3.52	5.62

*The general accuracy of the results is ± 0.1 log unit.

The over-all stability constant, β_{MXY}, for the ternary systems with dipicolinic acid and amino acids of copper(II) were found to be higher than those of nicotinic acid and amino acids. This may be due to the positions of both the —COOH group (in dipicolinic acid) in the pyridine ring with respect to the nitrogen which is favourable condition for the coordination with the metal ion.

The positive values of $\Delta \log K$ of dipicolinic acid and amino acids with copper (II) and relatively higher indicating the preferential formation of the ternary complexes to a greater degree.

It is, however, interesting to note that the comparison of K_{2MXY} and K_{MX1}, ternary complexation is favoured over binary ones. Furthermore, it can be seen from Table 2 for all the ligands investigated the order of β_{MXY} was DL-α-alanine > β-alanine > glutamic acid > glycine. The β_{MXY} values of the β-alaninate complex is less than the corresponding value of the DL-α-alanine due to the less favoured six-membered ring formed by β-alanine compared to the five-membered ring formed by DL-α-alanine.

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