NOTE

pH-Metric Studies on Mixed Ligand Complexes of Cd(II) with 2,2'- Bipyridylamine as Primary Ligand and Diamines as Secondary Ligand

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The formation of ternary chelates of Cd(II) with 2,2'-bipyridyl-amine as primary ligand (A) and diamines such as ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, N-N-diethyl ethylene-diamine, N-N-dimethyl ethylenediamine as secondary ligand (L) has been carried out pH-metrically at $30 \pm 0.1°C$. The ionic strength was maintained at $\mu = 0.2$ M dm^{-3}. Stability constants have been evaluated and discussed in terms of basicity of ligand, statistical and stereochemical factors.

Key Words: pH-metric, Mixed ligand, Complexes, Cd(II), 2,2'-Bipyridylamine, Diamines.

Mixed ligand complexes of Cd(II) with 2,2'-bipyridylamine and diamines such as ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, N-N-diethyl ethylenediamine, N-N-dimethyl ethylenediamine have been carried out pH-metrically. The investigations on mixed ligand complexes have been stimulated due to their analytical applications, formation as intermediates in ligand displacement reactions and possible significance as model for biological processes[1–3]. Ternary complexes also play an important role in various fields such as chemotherapy[4–6] and catalysis[7]. The formation, stabilities and reactivities of their complexes is a very active and challenging field of research[8–10]. Joshi *et al*[11–13] have studied some biologically relevant binary and ternary metal chelates of Cu(II), Ni(II), Zn(II), Cd(II) with 2,2'-bipyridylamine and bidentate amino acids.

Ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, N-N-diethyl ethylene-diamine, N-N-dimethyl ethylenediamine (AnalaR), sodium perchlorate (Fluka), 2,2'-bipyridylamine (Fluka), perchloric acid (Baker analyzed) and sodium hydroxide (AnalaR) were used.

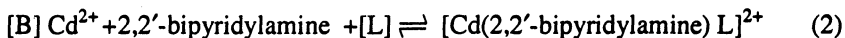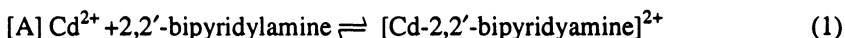A stock solution of Cd(ClO$_4$)$_2$ was prepared and standardized with disodium

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salt of EDTA[14]. Carbonate-free sodium hydroxide solution was used for carrying out titration. Digital pH-meter 361 with readability of ± 0.01 was used for pH measurement. Modified form of Irving-Rossotti titration technique has been used[15]. The 1 : 1 : 1 molar ratio of Cd, A and L was maintained. The ionic strength was maintained 0.2 M dm^{-3} using NaClO$_4$.

Mixed ligand complexes of type Cd-2,2′-bipyridylamine-diamine and 2,2′-bipyridylamine, first coordinate with Cd(II) and then with diamines. The formation of mixed ligand complex MAL can be represented as follows:
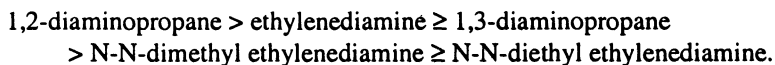
[A] Cd^{2+} +2,2′-bipyridylamine $\rightleftharpoons$ [Cd-2,2′-bipyridyamine]$^{2+}$ (1)

[B] Cd^{2+} +2,2′-bipyridylamine +[L] $\rightleftharpoons$ [Cd(2,2′-bipyridylamine) L]$^{2+}$ (2)

Mixed ligand formation constant

$$\log K_{MAL}^{MA} = \log K_{Cd-2,\,2'-bipy\,AL}^{Cd-2,\,2'-bipy\,A} = \frac{[Cd-2,2'-bipy\,A]}{[Cd-2,2'-bipy\,A]^{2+}\cdot[L]}$$

From potentiometric curves, it is observed that the formation of [Cd-2,2′-bipy A]$^{2+}$ complex takes place at lower pH and is stable up to higher pH where the combination of secondary ligand takes place.

Separation between secondary ligand [L] and Cd + 2,2′-bipy A + L mixed ligand starts after pH 5.75. The secondary ligand combines with Cd(II) after the formation of [Cd-2,2′-bipy A]$^{2+}$ is complete. It can be considered that the secondary ligand combines with [Cd(2,2′-bipy A]$^{2+}$ just as it does with [Cd(aq)$_2$]$^{2+}$ in binary systems.

The modified form of Irving-Rossotti titration technique for such systems is therefore valid[15]. n, pL values were calculated using the equation given by Irving-Rossotti[16].

More precise values of log $K_{Cd-bipy\,AL}^{Cd-bipy\,A}$ were calculated by the method of linear plot[17]. The values are presented in Table-1. The values of log $K_{Cd\cdot AL}^{Cd\cdot A}$ are in the following order:

1,2-diaminopropane > ethylenediamine ≥ 1,3-diaminopropane
> N-N-dimethyl ethylenediamine ≥ N-N-diethyl ethylenediamine.

The sequence is explained in terms of basicity of secondary ligand. All secondary ligands used are bidentate in nature. 1,3-Diaminopropane forms a six-membered chelate ring, while other ligand forms a five-membered chelate ring with Cd(II). Thus complexes of 1,3-diaminopropane are expected to be less stable. Therefore mixed ligand formation constant value of 1,3-diaminopropane is lower than 1,2-diaminopropane and ethylenediamine.

Formation constant of N,N-dimethyl ethylenediamine is lower then N,N-diethyl ethylenediamine because of steric effect. Presence of two —C$_2$H$_5$ groups on two chelate ring nitrogen atoms has decreased the value of stability constant of [Cd-2,2′-bipyA.N,N-diethyl ethylenediamine] than [Cd-2, 2′ bipyA.N,N dimethyl ethylenediamine].

TABLE-1

DISSOCIATION CONSTANT OF FREE LIGAND AND STABILITY CONSTANTS OF Cd(II) TERNARY COMPLEXES.

Temperature: $30\pm0.1^\circ$C and strength: $\mu = 0.2$ M dm^{-3} (NaClO$_4$)

Ligand (L)	pK_1^H	pK_2^H	log $K_{Cd-2,2'-bipy\,AL}^{Cd-2,2'-bipy\,A}$
Ethylenediamine	9.85	6.94	6.20
1,2-diaminopropane	10.04	6.65	6.39
1,3-diaminopropane	10.90	8.85	6.06
N-N-diethyl ethylenediamine	10.40	6.94	5.76
N-N-dimethyl ethylenediamine	9.99	6.48	5.85

2,2'-bipy A = 2,2'bipyridylamine.

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