Formation of Copper(II) Complexes of 1,3-Diamino-2-propanol in Aqueous Solution

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Copper(II) Complexes, 1,3-Diamino-2-propanol

The complex formation between Cu²⁺ ions and 1,3-diamino-2-propanol has been studied potentiometrically at 25 °C, constant ionic strength equal to 0.1 M NaClO₄ and pH 5–11. The nature of the complexes has been established by examining the standard deviations and values of the agreement index R of different models.

Introduction

The exceptional behaviour of 1,3-diamino-2-propanol in the formation of copper(II) complexes has been noted in earlier communications in the literature. X-ray investigations have shown that this ligand can form both mono- and trinuclear complex species, and exist in such species in both neutral (HL) and dissociated (L⁻) form.

The values of the stability constants of the complexes CuL⁺ and Cu₂L₂⁺ have been reported in earlier solution equilibria studies.

The purpose of the present work was twofold: (a) to find out if bis complexes are formed in alkaline solutions, and (b) to determine the nature of the possible protonated, hydrolyzed, or polynuclear complex species formed.

Experimental

Reagents. 1,3-Diamino-2-propanol was a reagent from Ega-Chemie KG. The concentration of the aminoalcohol solution was determined by neutralization titrations.

Apparatus and methods. A Radiometer PHM 52 potentiometer equipped with a Beckman N 40495 glass electrode and a calomel reference electrode was used for the measurements. In the latter electrode the electrolyte was 0.1 NaCl solution.

Results and Discussion

The apparatus and experimental conditions used in the potentiometric titrations have been described in detail elsewhere.

The concentration of the ligand varied between 1 × 10⁻⁴ M and 1 × 10⁻² M. Several titrations with different total concentrations of the metal and ligand were carried out. The ratio C_L : C_{Cu} was varied between 1 and 7.

The thermostated mixtures of copper(II) perchlorate, 1,3-diamino-2-propanol, hydrochloric acid (whose concentration was more than twice the total concentration of the aminoalcohol in every titration), and sodium perchlorate were titrated with 0.1 M sodium hydroxide solution. All measurements were carried out under nitrogen atmosphere at 25.0 ± 0.1 °C, and both the solutions to be titrated and the titrant were 0.1 M in regard to sodium perchlorate.

Calculations. The values log K₁ = 9.578 and log K₂ = 8.003 at 1 = 0.1 (NaClO₄) and 25 °C were used for the protonation constants of the ligand.

The stability constants of the complexes were computed with the programmes SCOOGS and MINIQUAD on an Univac 1108 computer. The programme MINIQUAD calculates also an agreement index R and a x² statistic which is a measure of the normality of the distribution of the residuals (f_{obs}−f_{calc}). The acceptable value of x² at the 95% confidence level for 6 degrees of freedom, should be less than 12.6.

The protonation constant of the hydroxyl group of 1,3-diamino-2-propanol is not easily ascertained, and only an approximate value 14.06 (determined...
spectrophotometrically at \( I = 0.162 \) (NaCl) and 30 °C is available in the literature. This protonation constant cannot be determined potentiometrically in aqueous solution by means of neutralization titrations because the potentials of the neutralization steps do not stabilize. For this reason the ligand was treated as a diprotic acid in the calculations, and the formation constants of species in which the proton of the hydroxyl group was assumed to dissociate from the ligand were determined by calculating the stability constants of hydrolyzed complex compounds.

All the titration curves of copper(II) ions with 1,3-diamino-2-propanol recorded in this study show dramatic inflections where \( C_B \) (the concentration of added sodium hydroxide) is exactly 3 \( C_Cu \). This suggests the formation of a \((CuL)_n^{n+}\) complex. To determine the value of \( n \), successive calculations with different models were carried out for each set of titration data. Table I shows some of the values needed to find \( n \). The data required for their calculation were obtained from the buffer region where \( C_B \) lies between 0 and 3 \( C_Cu \). As one can see from the standard deviations of the constants and the values of \( R \), the best fits are obtained with the model where \( n = 1 \). On the other hand, according to the HAMILTON test, there is no difference between two models if the ratio \( R_2/R_1 \) is less than 1.5–2. Thus, applying this test to the present systems, there is practically no difference between models where \( n = 1 \) and \( n = 2 \) in titrations where \( C_L \) is \( 0.111 \times 10^{-3} \) and \( 0.222 \times 10^{-3} \) M. Attempts to add other species than \((CuL)_n^{n+}\) to the model in the pH region between 5 and 7 were unsuccessful. Table II shows values calculated from data obtained up to pH 11. The best standard deviations and R values were obtained for a model consisting of the species \( Cu^{2+}, CuH_2L_2^{2+}, CuHL_2^{+}, \) and \( CuL_2 \). In titrations where the ratio \( C_L:C_Cu \) is small, the species \( Cu(OH)L \) is also detected in the pH region where \( C_B \) is greater than 3 \( C_Cu \). In such titrations the formation of bis complexes is very small, as one can see from Fig. 1 a. Fig. 1 b shows the distribution of various complex species in one individual titration where an excess of the ligand was present in the solution to be titrated.

As mentioned above, the ligand was considered as a diprotic acid in the calculation of the constants given in Tables I and II. Thus, the following equilibrium constants are found:

Table I. Some calculated values used in determining \( n \) in the complex \((CuL)_n^{n+}\). The data were obtained in the pH region 5–7.

<table>
<thead>
<tr>
<th>( C_{Cu} (10^{-2} \text{ M}) )</th>
<th>( C_L (10^{-2} \text{ M}) )</th>
<th>( n )</th>
<th>( \log(\beta_{(CuL)_n^{n+}}) )</th>
<th>( R )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.111</td>
<td>1</td>
<td>3.703(15)</td>
<td>0.0050</td>
<td>6.2</td>
</tr>
<tr>
<td>0.201</td>
<td>0.667</td>
<td>2</td>
<td>10.699(22)</td>
<td>0.0060</td>
<td>10.4</td>
</tr>
<tr>
<td>0.222</td>
<td>0.044</td>
<td>3</td>
<td>17.588(47)</td>
<td>0.0091</td>
<td>5.9</td>
</tr>
<tr>
<td>0.100</td>
<td>0.044</td>
<td>1</td>
<td>3.776(18)</td>
<td>0.0072</td>
<td>4.7</td>
</tr>
<tr>
<td>0.222</td>
<td>0.667</td>
<td>2</td>
<td>10.660(38)</td>
<td>0.0087</td>
<td>6.8</td>
</tr>
<tr>
<td>0.201</td>
<td>0.111</td>
<td>3</td>
<td>17.585(84)</td>
<td>0.0138</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table II. Stability constants calculated from five different sets of data in the pH region 5–11.

<table>
<thead>
<tr>
<th>( C_L:C_Cu )</th>
<th>( \log(\beta_{Cu^{2+}}) )</th>
<th>( \log(\beta_{Cu(OH)L}) )</th>
<th>( \log(\beta_{CuH_2L_2^{2+}}) )</th>
<th>( \log(\beta_{CuHL_2^{+}}) )</th>
<th>( \log(\beta_{CuL_2}) )</th>
<th>( R )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.11</td>
<td>3.702(15)</td>
<td>-6.54(5)</td>
<td>-3.45(fix)</td>
<td>6.35(fix)</td>
<td>0.0026</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>2.22</td>
<td>3.784(10)</td>
<td>-6.60(9)</td>
<td>-3.45(fix)</td>
<td>6.7(7)</td>
<td>0.0028</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>3.31</td>
<td>3.777(13)</td>
<td>-3.494(13)</td>
<td>6.39(3)</td>
<td>15.05(12)</td>
<td>0.0008</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>4.41</td>
<td>3.776(5)</td>
<td>6.31(8)</td>
<td>15.2(3)</td>
<td>0.0010</td>
<td>7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.65</td>
<td>3.713(12)</td>
<td>6.32(12)</td>
<td>15.12(8)</td>
<td>0.0023</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean values | 3.75 | -6.6 | -3.44 | 6.34 | 15.1 |
Fig. 1. Relative concentrations of the various complex species during two titrations of solutions containing copper(II) ions and 1,3-diamino-2-propanol [titrant 0.1 M NaOH, I = 0.1 (NaClO₄), t = 25 °C, C_{Cu} = 1.00 \times 10^{-3} \text{M}, C_L = 1.11 \times 10^{-3} \text{M (a) and 3.33 \times 10^{-3} M (b)}].

\[
\begin{align*}
\beta_{\text{CuL}^+} &= K(\text{Cu}^{2+} + \text{HL} = \text{CuL}^+ + \text{H}^+) \\
\beta_{\text{Cu(OH)L}} &= K(\text{Cu}^{2+} + \text{HL} + \text{H}_2\text{O} = \text{Cu(OH)L} + 2\text{H}^+) \\
\beta_{\text{CuH}_2\text{L}_2^{2+}} &= K(\text{Cu}^{2+} + 2\text{HL} = \text{CuH}_2\text{L}_2^{2+}) \\
\beta_{\text{CuHL}_2^{2+}} &= K(\text{Cu}^{2+} + 2\text{HL} = \text{CuHL}_2^{2+} + \text{H}^+) \\
\beta_{\text{CuL}_2} &= K(\text{Cu}^{2+} + 2\text{HL} = \text{CuL}_2 + 2\text{H}^+)
\end{align*}
\]

If the ligand is considered as a triprotic acid, and the value 14.06 is used for the protonation constant of the hydroxyl group, the values of the stability constants for the complexes CuL⁺, Cu(OH)L, CuH₂L₂²⁺, CuHL₂²⁺, and CuL₂ are, respectively, 17.81, 7.5, 34.46, 24.68 and 43.2.

The system of divalent copper and 1,3-diamino-2-propanol is very complicated. This aminoalcohol is able to form several different complex species with the Cu²⁺ ion, as can be seen from the present and earlier solid state investigations⁶-⁷. The nature of the complexes depends greatly on the conditions (i.e. ionic strength, total concentrations, and pH); hence, the results of this study are valid only for the conditions studied (a relatively low ionic strength and small total concentrations of the copper ions and aminoalcohol).