Ag(I) COMPLEXES
OF SOME ω'-AMINOALKYLPYRIDINIUM COMPOUNDS

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The stability constants of the Ag(I) complexes of some ω'-aminoalkylpyridinium compounds are determined by a pH-metrical method, at 25°C and in 0.5 M KNO₃. The results are compared with those obtained in a similar investigation of the Ag(I) complexes of ω-aminocarboxylic acids. In both cases complexes of the same type are formed and only quantitative differences can be observed.

INTRODUCTION

The interest of studying the donor properties of positively charged ligands has been outlined by Quagliao and coworkers [1, 2]. In the present investigation the stability constants of the Ag(I) complexes of the ligands (I) are determined.

(I) \[ \text{NH}_2-(\text{CH}_2)_n^+\text{N} \] \[ n = 2, 3, 4, \text{and} \ 5 \]
\[ (\beta L^+, \gamma L^+, \delta L^+ \text{Le,L}^+/\text{eL}^+) \]

These ligands are obtained as the dinitrate salts (II)

(II) \[ (\text{NH}_3^+-(\text{CH}_2)_n^+\text{N}) (\text{NO}_3)_2 \] \[ n = 2, 3, 4, \text{and} \ 5 \]
\[ (\beta \text{HL(NO}_3)_2, \gamma \text{HL(NO}_3)_2 \]
\[ \delta \text{HL(NO}_3)_2, \text{eHL(NO}_3)_2 \]

In earlier investigations [3] the stability constants of the Ag(I) complexes of the ω-aminocarboxylic acids were determined. These constants are compared with the results of this work.

EXPERIMENTAL

Preparation of the ligands

The synthesis of the ligands may be exemplified by the procedure used for the synthesis of the 2'-aminoethylpyridinium cation. Potassiumphtalimide and an excess of ethylenedibromide were heated according to Putochin [4], giving 2'-phtalimideethylbromide. 2'-Phtalimide-ethylpyridiniumbromide was obtained as described
by Gabriel [5] and Boese [6] by heating 2'-phtalimide-ethylbromide with a slight excess of pyridine. The phtalimide group was hydrolized by refluxing with concentrated HBr. Phtalic acid precipitated and was removed and 2'-aminoethylpyridiniumbromide-hydrobromide was obtained after evaporation of HBr in vacuum. Finally the dibromide salt was converted into its dinitrate with an equivalent quantity of AgNO₃. The other ligands were prepared in the same way using the appropriate α, ω dibromides. All ligands were purified by recrystallisation from methanol.

Anal. Calc. for $\beta$HL(NO₃)₂: C, 33.98%; H, 4.84%; N, 22.57%. Found: C, 34.03%; H, 4.66%; N, 22.56%.

Calc. for $\gamma$HL(NO₃)₂: C, 36.66%; H, 5.35%; N, 21.57%. Found: C, 36.61%; H, 5.56%; N, 21.31%.

Calc. for $\delta$HL(NO₃)₂: C, 39.45%; H, 6.02%; N, 20.28%. Found: C, 39.04%; H, 6.02%; N, 20.23%.

Calc. for $\varepsilon$HL(NO₃)₂: C, 41.40%; H, 6.21%; N, 19.30%. Found: C, 41.66; H, 6.28; N, 19.15%.

pH measurements and calculation of acidity and stability constants

pH measurements are carried out as described before [3]. The acidity constants $pK_{HL^2+}$ of the different ligands and the formation function $\bar{n}$ of the Ag(I) complexes are determined using the same methods and under the same experimental circumstances as mentioned in the previous paper [3].

Stability constants of the Ag(I) complexes are obtained from the formation function $\bar{n}$ using Sillen's [7] curve fitting method and using a least squares procedure.

Results and discussion

Over the concentration range investigated, the coordination number of Ag(I) with these ligands was found to be 2.

Values of $pK_{HL^2+}$, of log $k_1$ with $k_1 = \frac{(AgL^{2+})}{(Ag^+)(L^+)}$, of log $k_2$ with $k_2 = \frac{(AgL_2^{3+})}{(AgL^{2+})(L^+)}$ and of log $K_2 = \log k_1 k_2$ are given in Table I

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$pK_{HL^2+}$</th>
<th>log $k_1$</th>
<th>log $k_2$</th>
<th>log $K_2$</th>
<th>log $k_1/k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$L⁺</td>
<td>6.98</td>
<td>2.08</td>
<td>2.38</td>
<td>4.46</td>
<td>-0.30</td>
</tr>
<tr>
<td>$\gamma$L⁺</td>
<td>9.08</td>
<td>2.91</td>
<td>3.10</td>
<td>6.01</td>
<td>-0.20</td>
</tr>
<tr>
<td>$\delta$L⁺</td>
<td>9.91</td>
<td>3.24</td>
<td>3.37</td>
<td>6.61</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\varepsilon$L⁺</td>
<td>10.43</td>
<td>3.49</td>
<td>3.73</td>
<td>7.22</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

The values for log $k_1$, log $k_2$ and log $K_2$ are the mean values of those obtained by the two different computation methods. It is striking that the properties of the Ag(I)
complexes of these positively charged ligands do not depart from those of the Ag(I) complexes of negatively charged ligands such as aminocarboxylic acids [3].

Indeed, \( \log (k_1/k_2) \) is negative here as in the case of the aminocarboxylic acids and even the maximum value of \( \log (k_1/k_2) \) is found for the ligand with four methylene groups in both cases alike. It is suggested therefore that the electrostatic effect mentioned by Datta and Grzybowski [8] is rather small at an ionic strength of 0.5. Another property of the Ag(I) complexes with primary amines is the linear relationship between \( pK_{HL^{2+}} \) and \( \log k_1 \). This is illustrated in figure 1. The equation of the straight line is \( pK_{HL^{2+}} = 2.515 \log k_1 + 1.731 \).

Fig. 1 — The linear relationship between \( pK_{HL^{2+}} \) and \( \log k_1 \).
The difference $\Delta \text{pK}$ between $\text{pK}_{\text{HL}}$ values for the aminocarboxylic acids and $\text{pK}_{\text{HL}^2}$ for the corresponding aminoaalkylpyridinium cations decreases with increasing length of the aliphatic chain.

The same remark holds for $\Delta \log k_1$ and $\Delta \log k_2$ as is shown in Table II.

\begin{table}
\centering
\begin{tabular}{cccc}
Number of methylene groups in the ligand & $\Delta \text{pK}$ & $\Delta \log k_1$ & $\Delta \log k_2$ \\
\hline
2 & 3.19 & 1.29 & 1.41 \\
3 & 1.38 & 0.55 & 0.65 \\
4 & 0.75 & 0.33 & 0.42 \\
5 & 0.34 & 0.10 & 0.22 \\
\end{tabular}
\end{table}

From this table it can be seen that the pyridinium group is a more electronegative substituent than the carboxylic group. As a conclusion one can say that aliphatic amines bearing a positive charge do not form Ag(I) complexes of a different type than those formed between Ag(I) and aliphatic amines bearing a negative charge. Only quantitative difference are observed, resulting from the fact that, in general, positively charged substituents have a greater electron-withdrawing power than negatively charged substituents.

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