Ternary Complexes in Solution, XX\textsuperscript{1,2}

Stability of the Mixed-Ligand Cu\textsuperscript{2+} Complexes Formed with 1,2-Diaminobenzene and Oxalate or Salicylate

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Ternary complexes, Mixed-ligand complexes, Cu(II) complexes, 1,2-Diaminobenzene, Oxalate, Salicylate

The stability constants of the ternary Cu\textsuperscript{2+} complexes containing 1,2-diaminobenzene and oxalate or salicylate have been calculated from potentiometric titration curves published by G. K. Chaturvedi and J. P. Tandon (Z. Naturforsch. 23b, 303 [1968]; 25b, 26 [1970]). A comparison of the results with data of the literature reveals that the qualities of 1,2-diaminobenzene in ternary complexes correspond to those of ethylenediamine, while the qualities of both amines differ considerably from those of 2,2'-bipyridyl, which has a stability-enhancing effect.

Ternary complexes containing an aromatic amine and an O-ligand\textsuperscript{3} are known to be especially stable\textsuperscript{4-6}. Furthermore, if the O-ligand has an extended \(\pi\)-system as in pyrocatecholate, compared for example with oxalate, the stability is further increased\textsuperscript{8}. To see if a similar influence occurs in N-ligands we now compared the stability of mixed-ligand Cu\textsuperscript{2+} complexes containing 1,2-diaminobenzene with the ones containing ethylenediamine\textsuperscript{4,7}. In addition, it appeared appropriate to consider also the known stabilities of ternary complexes having the aromatic 2,2'-bipyridyl as N-ligand\textsuperscript{4,6} in the reasoning.

The aim of these several comparisons could relatively easily be achieved, as Chaturvedi and Tandon\textsuperscript{8,9} had recently published the potentiometric titration curves of the systems 1,2-diaminobenzene-Cu\textsuperscript{2+}-oxalate\textsuperscript{8} and -salicylate\textsuperscript{8} without a mathematical evaluation of their data. We have now used these experimental results and calculated the stability of the complexes, Cu(Dab)(oxalate) and Cu(Dab)(salicylate) (cf. 3).

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Calculations

To improve the exactness of the evaluation of the experimental data the figures published by Chaturvedi and Tandon\textsuperscript{8,9} were photographically enlarged in a distortion free manner. Then the amount of NaOH could be defined that corresponded to a neutralization degree of one. Taking this value and the ionic product of water, \(pK_{\text{H}2O} = 13.38\) (cf. 10), from the measured degree of neutralization we could calculate the acidity constants of those ligands which had been titrated by Chaturvedi and Tandon. The other acidity constants which were needed for the evaluation of the mixed-ligand system had to be taken from the literature\textsuperscript{11-14}. However, here it should be noted that an error in the acidity constants will not show up in \(\log X\) and \(\log K\), the constants used for the characterization of the ternary complexes.

Next, the stability constants of the binary complexes, \(K_{\text{CuL}}\text{CuL}\) and \(K_{\text{CuL}}\text{CuL}\) had to be determined. As there were only titration curves published of the Cu:L = 1:1 systems, we proceeded in the following way. At constant ionic strength the difference of \(\log K_{\text{CuL}}\text{CuL} - \log K_{\text{CuL}}\text{CuL}\) is rather independent on the temperature\textsuperscript{15}; hence, we took these differences at \(I = 0.1\), namely 1.02 for 1,2-dia-
minobenzene\textsuperscript{16} and 1.1 for oxalate\textsuperscript{14} from the literature. Now we calculated from the titration data \( \log K_{\text{CuL}}^\text{Cu} \) under the assumption of \( \log K_{\text{CuL}}^\text{Cu} = -5.0 \), \textit{i.e.} under neglect of \( \text{CuL}_2 \), and then, by subtracting the mentioned differences we obtained values for \( \log K_{\text{CuL}}^\text{Cu} \). By taking into account this latter value we were now able to repeat the calculation for \( \log K_{\text{CuL}}^\text{Cu} \), and then obtained also a new value for \( \log K_{\text{CuL}}^\text{Cu} \). This iteration procedure was repeated until the values of the constants did not change anymore. As the following example of the copper(II)-1,2-diaminobenzene system (at 32\textdegree) shows, this was quickly achieved (in parenthesis is given the value used for \( \log \): \( \log K_{\text{CuL}}^\text{Cu} = 4.25 \pm 0.10 \) (—5.0); 4.06\pm0.06 (3.23); 4.12\pm0.07 (3.04); 4.10\pm0.07 (3.10); 4.11\pm0.07 (3.08); hence the final result was \( \log K_{\text{CuL}}^\text{Cu} = 4.11\pm0.07 \) and \( \log K_{\text{CuL}}^\text{Cu} = 3.09 \). The given range of error is three times the standard deviation; the same holds for the error limits in the Tables. In the case of salicylate we used the value of \( \log K_{\text{CuL}}^\text{Cu} \) determined by \textsc{Perre}n et al.\textsuperscript{1}*. Now we could compute, based on the experimental data of \textsc{Chaturvedi} and \textsc{Tandon}\textsuperscript{\textit{a},\textit{b}} the stability constant \( \beta_{\text{Cu}(Dab)(OL)} \) by taking into account the species \textit{H}+, \textit{H}_2(Dab)\textsuperscript{2+}, \textit{H}(Dab)\textsuperscript{+}, \textit{Dab}, \textit{Cu}(Dab)\textsuperscript{2+}, \textit{Cu}(Dab)\textsuperscript{2+}, \textit{H}_2(OL), \textit{H}(OL)\textsuperscript{−}, \textit{OL}\textsuperscript{2−}, \textit{Cu}(OL), \textit{Cu}(OL)\textsuperscript{2−}, \textit{Cu}^{2+} \text{and Cu}(Dab)(OL) (\textit{cf.}\textsuperscript{2}).

Results and Discussion

The acidity constants of the ligands and the stability constants of their binary Cu\textsuperscript{2+} complexes are given in Table I. Table II contains the constants of the mixed-ligand Cu\textsuperscript{2+} complexes formed by 1,2-diaminobenzene and oxalate or salicylate. For the ternary complexes the overall constant \( \beta_{\text{Cu}(Dab)(OL)} \) according to equilibrium (1) was computed\textsuperscript{2}. The constant \( \log K_{\text{Cu}(Dab)(OL)}^\text{Cu} \) according to equilibrium (2) was calculated from Eqn. (3). Of course, one may consider the reaction between Cu(OL) and Dab, too; the corresponding equilibrium constant was calculated according to Eqn. (4) and is also listed in Table II.

\[
\begin{align*}
\text{Cu} + \text{Dab} + \text{OL} & = \text{Cu}(\text{Dab})(\text{OL}) \quad \beta_{\text{Cu}(\text{Dab})(\text{OL})} = \frac{[\text{Cu}(\text{Dab})(\text{OL})]}{[\text{Cu}][\text{Dab}][\text{OL}]} \quad (1) \\
\text{Cu}(\text{Dab}) + \text{OL} & = \text{Cu}(\text{Dab})(\text{OL}) \quad K_{\text{Cu}(\text{Dab})(\text{OL})}^\text{Cu} = \frac{[\text{Cu}(\text{Dab})(\text{OL})]}{[\text{Cu}(\text{Dab})][\text{OL}]} \quad (2) \\
\log K_{\text{Cu}(\text{Dab})(\text{OL})}^\text{Cu} & = \log \beta_{\text{Cu}(\text{Dab})(\text{OL})} - \log K_{\text{Cu}(\text{Dab})} \quad (3) \\
\log K_{\text{Cu}(\text{Dab})(\text{OL})}^\text{Cu} & = \log \beta_{\text{Cu}(\text{Dab})(\text{OL})} - \log K_{\text{Cu}(\text{Dab})} \quad (4)
\end{align*}
\]

Table I. Negative log acidity constants of the ligands and log stability constants of their binary complexes

\begin{table}
\begin{center}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Ligand (L) & T(\textdegree) & pK\textsubscript{H}\textsubscript{L} & pK\textsubscript{H}\textsubscript{L} & log K\textsubscript{Cu} & log K\textsubscript{Cu} \\
& & & & Cu & CuL \\
\hline
1,2-Diaminobenzene & 32 & 0.6\textsuperscript{b} & 4.69\pm0.04 & 4.11\pm0.07 & 3.09 \\
& 37 & 0.6\textsuperscript{b} & 4.52\pm0.03 & 3.98\pm0.08 & 2.96 \\
Oxalate & 37 & 1.12\textsuperscript{c} & 3.68\pm0.09 & 4.66\pm0.09 & 3.56 \\
Salicylate & 32 & 3.05\pm0.06 & 13.0\textsuperscript{d} & 10.16\pm0.07 & 8.07\textsuperscript{d} \\
\hline
\end{tabular}
\end{center}
\textsuperscript{a} Calculated with the experimental data published by \textsc{Chaturvedi} and \textsc{Tandon}. The experimental data at 32\textdegree \textsuperscript{C} are taken from Fig. 1 in ref. 8; those at 37\textdegree \textsuperscript{C} are from Fig. 1 in ref. 9. \textsuperscript{b} From ref. 11; \textit{I} = 0.4, \textit{T} = 25\textdegree \textsuperscript{C}. \textsuperscript{c} From ref. 12; \textit{I} = 1, \textit{T} = 32\textdegree \textsuperscript{C}. \textsuperscript{d} From ref. 14; \textit{I} = 0.15, \textit{T} = 37\textdegree \textsuperscript{C}.
\end{table}

Table II. Log stability constants of the ternary 1,2-diaminobenzene-Cu\textsuperscript{2+}-oxalate and -salicylate complexes

\begin{table}
\begin{center}
\begin{tabular}{|c|c|c|c|c|}
\hline
Ligand (OL) & T(\textdegree) & \log \beta_{\text{Cu}(\text{Dab})(\text{OL})} & \log K_{\text{Cu}(\text{Dab})(\text{OL})}^\text{Cu} & \log K_{\text{Cu}(\text{Dab})(\text{OL})}^\text{Cu} \\
& & & & Cu(OL)(Dab) \\
\hline
Oxalate & 37 & 8.22\pm0.13 & 4.24 & 3.56 \\
Salicylate & 32 & 13.88\pm0.35 & 9.77 & 3.72 \\
\hline
\end{tabular}
\end{center}
\textsuperscript{a} \textit{Cf.} footnote \textsuperscript{a} of Table I.
\end{table}
There are two convenient ways to characterize the stability of mixed-ligand complexes. One is according to Eqn. (5), where $\Delta \log K$ corresponds to equilibrium (6). The other is based on log $X$ (Eqn. 7) and equilibrium (8). Generally, one would expect to observe negative values for $\Delta \log K$ (Eqn. 5), since usually it holds\(^6\) that $K_{\text{Cu(OL)}}^{\text{Cu(Dab)}} > K_{\text{Cu(Dab)}}^{\text{Cu(OL)}}$ (cf. Table I). The method using equilibrium (7) for characterization is somewhat more "objective", as the value expected for $X$ can be deduced from statistical arguments\(^7\): $X = 4$, i.e., $\log X = 0.6$.

\[
\Delta \log K = \log K_{\text{Cu(Dab)}}^{\text{Cu(OL)}} - \log K_{\text{Cu(OL)}}^{\text{Cu(Dab)}} = \log K_{\text{Cu(OL)}}^{\text{Cu(Dab)}} - \log K_{\text{Cu(Dab)}}^{\text{Cu(OL)}} \quad (5)
\]

\[
\text{Cu(Dab)} + \text{Cu(OL)} \rightleftharpoons \text{Cu(Dab)OL} + \text{Cu} \quad (6)
\]

\[
\log X = 2 \log \rho_{\text{Cu(Dab)}^{\text{Cu(OL)}}} - (\log \rho_{\text{Cu(Dab)}} + \log \rho_{\text{Cu(OL)}}) \quad (7)
\]

\[
\text{Cu(Dab)}_2 + \text{Cu(OL)}_2 \rightleftharpoons 2 \text{Cu(Dab)OL} \quad X = \frac{[\text{Cu(Dab)OL}^2]}{[\text{Cu(Dab)}][\text{Cu(OL)}]} \quad (8)
\]

By using the results of Tables I and II, the values for $\Delta \log K$ and log $X$ were calculated. These data are listed in Table III, together with some results taken from the literature. Examples 1 to 5 of Table III demonstrate quite clearly the stability enhancing effect, brought about by the $\pi$-acceptor qualities of the aromatic amine\(^4\)\(^5\). In addition, it is obvious from comparing the value for log $X$ of 3 with 1 or 2 and 5 with 4 that the $\pi$-system of the O-ligand is also of influence. This suggests that cooperative effects between the two ligands within a ternary complex may occur\(^4\). A comparison of systems 1 and 2 shows that salicylate is nearly as effective an O-ligand as is pyrocatecholate. Hence, a comparison of 4 to 7 reveals quite clearly that the qualities of 1,2-diaminobenzene correspond exactly to those of the simple aliphatic ethylenediamine. In other words, the $\pi$-system of the benzene ring is without any remarkable influence on the stability of these ternary complexes. This result is in contrast to the observations made with the "analogous" O-ligands, pyrocatecholate and oxalate; these O-ligands form mixed-ligand Cu\(^{2+}\) complexes with different stabilities\(^8\).

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\(^{2}\) Part XVIII: Ch. F. NAUMANN and H. SIGEL, J. Amer. Chem. Soc. 96, 2750 [1974].

\(^{3}\) Abbreviations: The terms, "N-ligand" and "O-ligand", are used for ligands containing O or N as donor atoms. L, general ligand; OL, ligand with O as donor atoms; Dab, 1,2-diaminobenzene. Charges are omitted in all equations.


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Table III. Comparison of the stability of some ternary Cu\(^{2+}\) complexes (I = 0.1).

<table>
<thead>
<tr>
<th>No.</th>
<th>Amine</th>
<th>Ligand (OL)</th>
<th>$T(°C)$</th>
<th>$\Delta \log K$</th>
<th>log $X$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,2'-Bipyridyl</td>
<td>Pyrocatecholate</td>
<td>25</td>
<td>+0.43</td>
<td>6.15</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Salicylate</td>
<td>25</td>
<td>+0.27</td>
<td>5.7</td>
<td>5, 18</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Oxalate</td>
<td>25</td>
<td>+0.7</td>
<td>4.9</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Ethylenediamine</td>
<td>Pyrocatecholate</td>
<td>25</td>
<td>−0.76</td>
<td>2.65</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Oxalate</td>
<td>25</td>
<td>−0.79</td>
<td>0.94</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>1,2-Diaminobenzene</td>
<td>Salicylate</td>
<td>32</td>
<td>−0.4</td>
<td>2.3</td>
<td>a</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Oxalate</td>
<td>37</td>
<td>−0.4</td>
<td>1.3</td>
<td>a</td>
</tr>
</tbody>
</table>

\(^a\) This work.
The ionic product of water at 37 °C and I = 0 is $10^{13.62}$ (extrapolated from the data of A. K. Covington, R. A. Robinson, and R. G. Bates, J. Chem. Educ. 44, 635 [1967]). This value was corrected for an ionic strength of 0.1 by subtraction of 0.25 log units (cf. H. Hauer, E. J. Billo, and D. W. Margerum, J. Amer. Chem. Soc. 93, 4173 [1971]), hence we obtained $pK_{H_2O} = 13.38$. The same value was used at 32 °C.

11 K. Wüthrich and S. Fallab, Chimia 17, 356 [1963].


16 H. Sigel, unpublished results.


20 For a general discussion of the driving forces leading to the formation of mixed-ligand complexes see refs. 5 and 6.