Spectroscopy as a tool to detect multinuclear Cu(II)-triethanolamine complexes in aqueous solution

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Supplementary Information
A speciation curve representing the expected prevalence of monomeric versus dimeric species based on literature stability constants

![Speciation curve](image)

**Figure S1.** Speciation simulation for an aqueous solution containing [CuSO$_4$] = 0.058 mol/L and [TEA] = 0.295 mol/L, based on the model shown in Table S2.

**Table S1.** Cumulative stability constants for Cu$^{2+}$ complexes defined as (Cu)$_p$(TEA)$_q$(OAc)$_r$(NH$_3$)$_s$H$_t$ ↔ pCu + qTEA + rOAc + sNH$_3$ + tH used in HYSS2006$^{[1]}$ for modelling the speciation of the different samples. Charges were omitted for simplicity. The log $\beta$ value for the species followed by (s) is the solubility product of the related precipitate 1-4.

<table>
<thead>
<tr>
<th>Species</th>
<th>Log $\beta_{pqrs}$</th>
<th>Cu</th>
<th>TEA</th>
<th>OAc</th>
<th>NH$_3$</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(TEA)</td>
<td>3.85</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu(TEA)(OH)</td>
<td>-1.74</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>Cu(TEA)(OH)$_2$</td>
<td>-9.21</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>TEAH</td>
<td>7.81</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>-15.2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>Cu(OH)$_2$ (s)</td>
<td>9.1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

**dimeric TEA complexes**

<table>
<thead>
<tr>
<th>Species</th>
<th>Log $\beta_{pqrs}$</th>
<th>Cu</th>
<th>TEA</th>
<th>OAc</th>
<th>NH$_3$</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$(TEA)$_2$(OH)$_2$</td>
<td>-1.1</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>Cu$_2$(TEA)$_2$(OH)$_3$</td>
<td>-8.2</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-3</td>
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<tr>
<td>Cu$_2$(TEA)$_2$(OH)$_4$</td>
<td>-16.6</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-4</td>
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</tbody>
</table>

**References**

Measurement of $T_1$ and $T_2$ relaxation constants.

Relaxation time constants of the TEA proton resonances were measured on two samples using the standard inversion recovery delay and CPMG sequences in the Bruker library. All measurements were performed at 20°C on a Bruker Avance II 500.13 MHz spectrometer equipped with a $^1$H-$^{13}$C-$^{31}$P TXI probehead. For the inversion recovery experiment, the interscan delay was set to 2 s and the recovery delay was varied from 4 µs to 1 s, sampled over 16 data points. For the CPMG experiment, the interscan delay was 2.5 s and a spin echo duration of 1 ms was used. The number of spin echoes varied from 0 to 400 for the sample at pH 1.69 and from 2 to 16 for the sample at pH 9.57, in both cases sampled over 8 data points. Data fitting was performed using the relaxation module within TopSpin 3.2.

Sample composition:

Sample 1: 0.055 mol.L$^{-1}$ CuSO$_4$, Cu/TEA = 1:5.25, pH = 1.7
Sample 2: 0.055 mol.L$^{-1}$ CuSO$_4$, Cu/TEA = 1:5.25, pH = 9.6

<table>
<thead>
<tr>
<th>pH</th>
<th>$T_1$ (CH$_2^a$) / ms</th>
<th>$T_1$ (CH$_2^b$) / ms</th>
<th>$T_2$ (CH$_2^a$) / ms</th>
<th>$T_2$ (CH$_2^b$) / ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.69</td>
<td>161.9</td>
<td>151.0</td>
<td>124.1</td>
<td>122.8</td>
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<tr>
<td>9.57</td>
<td>7.0</td>
<td>8.6</td>
<td>4.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

$N(CH_2^aCH_2^bOH)_3$
NMRD $R_1$ curves, $R_2$ values at 60 MHz, and fitted curves.

$R_1$ curves of a CuSO$_4$ reference solution and of Cu-TEA samples at pH 1.3 and 2.7. Additional $R_2$ values at 60 MHz. Fitted $R_1$ curve of the CuSO$_4$ reference and predicted $R_2$ curve.

$R_1$(s$^{-1}$)

- Cu TEA pH 1.33
- Cu TEA pH 2.7
- $R_2$ pH 1.33
- $R_2$ pH 2.7
- CuSO$_4$
- $R_2$ CuSO$_4$
- Fit $R_1$
- Fit $R_2$

d=0.33 nm
D=2.8 $10^{-9}$ m$^2$s$^{-1}$
r=0.28 nm
$\tau_R$= 15 ps
$\tau_M$=200 ps
$\tau_{S0}$ = 1.4 ns
$\tau_V$ = 0.5 ps
q = 6
$g$ Landé = 2.14
$R_1$ curves of Cu-TEA samples at pH 1.3, 6.1, 8.1 and 8.6.
$R_1$ curves of Cu-TEA samples at pH 8.6 and 10.0.
$R_1$ curves of Cu-TEA samples at pH 11.4, 10.9, and 12.4. Additional $R_2$ value measured at 60 MHz for pH 12.4. Fitted $R_1$ curve at pH 12.4 and predicted $R_2$ curve.

d=0.33 nm  
D=2.8 $10^{-9}$ m$^2$s$^{-1}$  
r=0.28 nm  
$\tau_R$=20 ps  
$\tau_M$=10 ns  
$\tau_{SO}$=1.22 $10^{-9}$ s  
$\tau_V$=3 ps  
A/h=1.43 $10^6$ rads$^{-1}$  
Q=2.  
g Landé=2.14