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Stability of copper(II) complexes of sulfur and selenium antioxidants

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The data was analyzed and speciation models determined using ICP-OES. The copper solutions were then titrated with sulfur and selenium antioxidants in aqueous conditions. Binding of sulfur and selenium antioxidants in 1:2 ratios of metal:ligand with metal concentrations at 1.0 mM were added to bring the solution pH down to 2-3 and were bubbled with 0.1 M HClO₄. 0.1 M HCl was added to the titration solutions to maintain a constant ionic strength of 0.1 M NaClO₄. Precipitation occurred above pH=7.

**Results and Discussion**
- For all of the Cu²⁺ amino acid solutions analyzed, models indicated that three species were present through the titration – CuL⁺, Cu₂L⁺, and a constant ionic strength of 0.1 M NaClO₄.
- For the Cu²⁺-methimazole solution, two species were identified, [Cu(MetIm)₂]⁺ and [Cu₂(MetIm)₂]⁺ (Figure 4), but precipitation occurs at pH=6, indicating a high stability for the 1:2 complex as the solution approaches biological concentrations.
- A weak correlation trend exists between the stability of the ML₂ species and the antioxidant abilities of the amino acids (Figure 7).
- Little difference is observed in stability of Cu²⁺-amino acid complexes (Table 1), regardless of the thioether/selenoether moiety, likely indicating primarily O and N interactions with the metal center.
- Glycine, the only amino acid tested without sulfur or selenium, had the highest stability for the ML₂ species.
- For the methimazole compounds, the dmit only weakly associates with Cu²⁺, but the [Cu₂(MetIm)₂]⁻ and [Cu₂(MeCys)₂]⁻ species are very stable.

**Antioxidant Capability vs. Stability**

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>LH (pKᵢ)</th>
<th>LH₂ (pKᵢ)</th>
<th>CuL (log β)</th>
<th>Cu₂L (log β)</th>
<th>IC₅₀ (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gly</td>
<td>2.28±0.04</td>
<td>9.67±0.02</td>
<td>8.26±0.01</td>
<td>15.10±0.05</td>
<td>22.2±1.1</td>
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<tr>
<td>Met</td>
<td>2.09±0.01</td>
<td>9.20±0.01</td>
<td>7.96±0.05</td>
<td>14.65±0.07</td>
<td>11.0±0.02</td>
</tr>
<tr>
<td>SeMet</td>
<td>2.05±0.01</td>
<td>9.29±0.02</td>
<td>8.02±0.02</td>
<td>14.6±0.02</td>
<td>25.1±0.01</td>
</tr>
<tr>
<td>MeCys</td>
<td>2.02±0.05</td>
<td>8.79±0.02</td>
<td>8.06±0.05</td>
<td>14.47±0.06</td>
<td>10.0±0.02</td>
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<tr>
<td>SeMeCys</td>
<td>2.3±0.2</td>
<td>8.86±0.02</td>
<td>8.1±0.01</td>
<td>14.5±0.03</td>
<td>8.64±0.02</td>
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<tr>
<td>Dmit</td>
<td></td>
<td></td>
<td>1.9±0.1</td>
<td></td>
<td>1500±0.3</td>
</tr>
<tr>
<td>Metim</td>
<td>11.3±0.01</td>
<td>-</td>
<td>10.8±0.1</td>
<td>20.1±0.1</td>
<td>102±3.0</td>
</tr>
</tbody>
</table>

**References**

**Acknowledgements**
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