Preliminary Complexation Studies of Bis-(8-Hydroxyquinoline)-substituted Tetraaza-15-crown-5 with Various Metal Ions

Xian X. Zhang, Jerald S. Bradshaw, R. Todd Bronson, Paul B. Savage and Reed M. Izatt

Department of Chemistry and Biochemistry
Brigham Young University
Provo, UT 84602

Dr. Kelvin Higa (Program Director)
Office of Naval Research
800 No. Quincy Street
Arlington, VA 22217-5000

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Complexation of bis(8-hydroxyquinoline)-substituted tetraaza-15-crown-5 (1) (see our Technical Report No. 6) with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ was evaluated potentiometrically in aqueous solution (0.10 M Me₄NCl) at 25°C. Ligand 1 formed very stable complexes with these metal ions. The UV-Vis spectra of 1 and its complexes were examined in an aqueous acetic acid buffer solution (pH 4.7). The 1-Cu²⁺ complex provided a new absorption band at 258 nm.
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X. X. Zhang, Jerald S. Bradshaw, R. T. Bronson, Paul B. Savage, and Reed M. Izatt

Department of Chemistry and Biochemistry
Brigham Young University, Provo, UT 84602

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PRELIMINARY COMPLEXATION STUDIES OF
BIS(8-HYDROXYQUINOLINE)-SUBSTITUTED TETRAAZA-
15-CROWN-5 WITH VARIOUS METAL IONS

Xian X. Zhang, Jerald S. Bradshaw, R. Todd Bronson,
Paul B. Savage, and Reed M. Izatt

Department of Chemistry
Brigham Young University, Provo, UT 84602
Results and Discussion

A series of new 8-hydroxyquinoline- and 8-aminoquinoline-substituted tetraaza-15-
(-16)-crown-5 ethers (1-4 and 5-8, respectively) have been prepared in our laboratory. These
new ligating agents were designed to selectively bind transition and post-transition metal ions
with a concomitant modulation in the absorption and fluorescent spectra of the compounds. This
report gives a preliminary account of the complexation of ligand 1 with various metal ions.

Protonation and Complexation Studies of Ligand 1. Protonation constants of 8-
hydroxyquinoline-containing tetraazacrown ether 1 and stability constants for the interactions of
1 with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ were determined by a potentiometric titration
technique at 25°C in aqueous solution. The ionic strength was kept constant with 0.10 M
tetramethylammonium chloride. The overall reactions are expressed by the general equation:

\[ pM^{2+} + qH^+ + rL^2- \rightleftharpoons [M_pH_qL_r]^{(2p+q-2r)} \]  \hspace{1cm} (1)

where M is the metal ion and L is the ligand. The overall equilibrium constant can be defined as

\[ \beta_{pqr} = \frac{[M_pH_qL_r]^{(2p+q-2r)}}{[M^{2+}]^p[H^+]^q[L^2-]^r} \] \hspace{1cm} (2)

The values of the protonation constants of the ligands and stability constants of the metal ion
complexes (log \( \beta_{pqr} \)) are listed in Tables 1 and 2, respectively.

Four protonation constants can be calculated for compound 1. The first two protonation
constants (log \( K_1 = 9.55 \) and log \( K_2 = 7.30 \) (16.85 - 9.55), Table 1) and the last two constants
Table 1. Logarithms of Protonation Constants of Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log β</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺ + L²⁻ ⇌ HL⁻</td>
<td>9.55 ± 0.05</td>
</tr>
<tr>
<td>2H⁺ + L²⁻ ⇌ H₂L</td>
<td>16.85 ± 0.08</td>
</tr>
<tr>
<td>3H⁺ + L²⁻ ⇌ H₃L⁺</td>
<td>19.87 ± 0.09</td>
</tr>
<tr>
<td>4H⁺ + L²⁻ ⇌ H₄L₂⁺</td>
<td>21.31 ± 0.14</td>
</tr>
</tbody>
</table>

(log K₃ = 3.02 and log K₄ = 1.44) are close to each other. A large decrease in protonation constants is seen between the second and the third protonation steps. Since the first protonation constant of 1 (log K₁ = 9.55) is hydroxyquinoline (9.65 at 25 °C, μ = 0.1),³ the first two protonation constants of 1 are due to protonation of OH groups of the 8-hydroxyquinoline portion and the last two forming a neutral complex with a divalent cation which may be coordinated by both the 8-hydroxyquinolines and the macroring.

Data in Table 2 show that each metal ion studied forms several types of complexes with the ligand. The 1:1 complexes ML (p = 1, q = 0, r = 1 in eq. 1) and M(OH)L⁻ (p = 1, q = -1, r = 1) are observed in each case. The complexes of ligand 1 with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ are very stable in aqueous solution. The large stability constants (log βₘₐₙ > 12 and log βₘₙ₁ > 15) are shown in Table 2. The most stable complexes were observed for Cu²⁺. The values of log β₉ and log β₉₁ are 15.5 and 18.6, respectively. Cd²⁺ also forms very stable complexes with ligand 22 (log β₉₁ = 15.3 and log β₉₁₁ = 17.5). Therefore, not only the fully deprotonated form of 22 (L²⁻) but also the monoprotonated ligand (HL⁻) forms very stable complexes with the metal ions studied (except for Co²⁺). In the case of Co²⁺, the complex CoHL⁺ was not detected. However, Co²⁺ forms a 1:2 (M:LB) complex with 1 (log β₉₂ = 20.2). A dinuclear complex with Cu²⁺, Cu₂L₂⁺, was also observed. The equilibrium constants of the complexes containing hydrolysis products of the metal ions, M(OH)L⁻, range from 6.44 (log β₉₉₉OH) to 9.62 (log
Table 2. Overall Stability Constants* of Metal Ion Complexes with Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>r</th>
<th>Cu²⁺</th>
<th>Co²⁺</th>
<th>Ni²⁺</th>
<th>Zn²⁺</th>
<th>Cd²⁺</th>
<th>Pb²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>15.52 ± 0.08</td>
<td>12.34 ± 0.04</td>
<td>13.46 ± 0.03</td>
<td>12.41 ± 0.03</td>
<td>15.33 ± 0.02</td>
<td>13.65 ± 0.03</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>18.55 ± 0.12</td>
<td>16.15 ± 0.18</td>
<td>15.55 ± 0.09</td>
<td>17.50 ± 0.05</td>
<td>16.93 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>8.53 ± 0.19</td>
<td>6.44 ± 0.06</td>
<td>7.49 ± 0.12</td>
<td>6.49 ± 0.05</td>
<td>9.62 ± 0.07</td>
<td>8.22 ± 0.08</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>18.92 ± 0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td>20.19 ± 0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>-3.59 ± 0.25</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

*The equilibria of the reactions are defined by the general equation:

\[ pM^{2+} + qH^+ + rL^{2-} \rightleftharpoons M_{p}H_{q}L_{r}^{(2p+q-2r)} \]

\( M = \text{metal; } L = \text{ligand. A minus } q \text{ value refers to OH}^{-} \text{ group.} \)
\( \beta_{\text{Cu(OH)C}} \). The Ni\(^{2+} \) forms a second type of hydrolysis complex, Ni(OH)\(_2\)L\(^2\), which has a very low equilibrium constant (Table 2).

**UV-Visible spectra.** The UV spectra of free and complexed ligand 1 are shown in Figures 1 and 2. The free 1 has an absorption maximum at 244 nm. Upon addition of Cu\(^{2+} \), a new peak develops at 258 nm (Figure 1). Other metal ions (Zn\(^{2+} \), Pb\(^{2+} \), Cd\(^{2+} \), Ag\(^{+} \), Hg\(^{2+} \), Co\(^{3+} \), and Ni\(^{2+} \)) were also titrated with 1, but none produced a new peak or significantly interfered with the new 1-Cu\(^{2+} \) complex peak at 258 nm (Figure 2). Thus, the 258 nm peak for the 1-Cu\(^{2+} \) complex could be used for sensing purposes.

**Experimental Section**

**Determination of Protonation and Stability Constants.** The protonation and stability constants were determined by potentiometric titration in aqueous solution at 25 °C. The titrations were carried out at a constant ionic strength of 0.10 \( M \) \( \text{Me}_2\text{NCl} \) using an automatic microprocessor-controlled potentiometric titrator.\(^4 \) Temperature was controlled within ± 0.1 °C using a jacketed cell through which water from a constant-temperature bath was circulated. Potentials to within ± 0.1 mV were measured using an Orion Model 701A Digital Ion Analyzer in conjunction with a Cole-Parmer combination electrode (Ag/AgCl reference cell). The electrode was calibrated by two precision buffer solutions, pH 4.000 ± 0.002 and 7.000 ± 0.002 at 25.0 °C (Cole-Parmer). Calculations were performed with the SUPERQUAD program\(^5 \) using an IBM computer. Compound 1 was used as its adduct with HCl (1•6HCl) which had good solubility in aqueous solution (0.01 \( M \)).
Figure 1. UV-visible spectra of free 1 and its Cu$^{2+}$ complexes in an aqueous buffered solution. [1] = $0.977 \times 10^{-5} \, M$, [buffer] = $5.0 \times 10^{-2} \, M$ acetic acid (pH = 4.7).

The labels a - e indicate 1 - 5 equivalents of Cu$^{2+}$ added to the ligand successively.

Figure 2. UV-visible spectra of free and complexed 1 in acetic acid buffer solution (pH = 4.7). (a and b) Cu$^{2+}$ (1 and 2 equivalents, respectively), (c) Zn$^{2+}$, (d) Pb$^{2+}$, and (e) Cd$^{2+}$ (2 equivalents each). [1] = $0.977 \times 10^{-5} \, M$ and [buffer] = $5.0 \times 10^{-2} \, M$ acetic acid.
UV-visible Spectral Measurements. UV-visible spectra were recorded at 23 ± 1 °C in a 1-cM quartz cell using a Hewlett-Packard 8452A Diode Array spectrophotometer. Both ligand and metal ions were prepared in aqueous acetic acid buffer (pH = 4.7). Concentrations of acetic and sodium acetate were 5.00 x 10⁻² M and 5.00 x 10⁻² M, respectively, and concentration of ligand 1 was 1.00 x 10⁻⁵ M. The metal ion concentrations were 1-5 times the ligand concentration.

REFERENCES


