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13. ABSTRACT (Maximum 200 words) Complexation of bis(8-hydroxyquinoline)-substituted tetraaza-15-crown-5 (1) (see our Technical Report No. 6) with Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , and Pb <sup>2+</sup> was evaluated potentiometrically in aqueous solution (0.10 M Me <sub>4</sub> NCl) 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-Cu <sup>2+</sup> complex provided a new absorption band at 258 nm.				
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**Preliminary Complexation Studies of Bis(8-hydroxyquinoline)-substituted  
Tetraaza-15-crown-5 with Various Metal Ions**

by

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PRELIMINARY COMPLEXATION STUDIES OF  
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15-CROWN-5 WITH VARIOUS METAL IONS

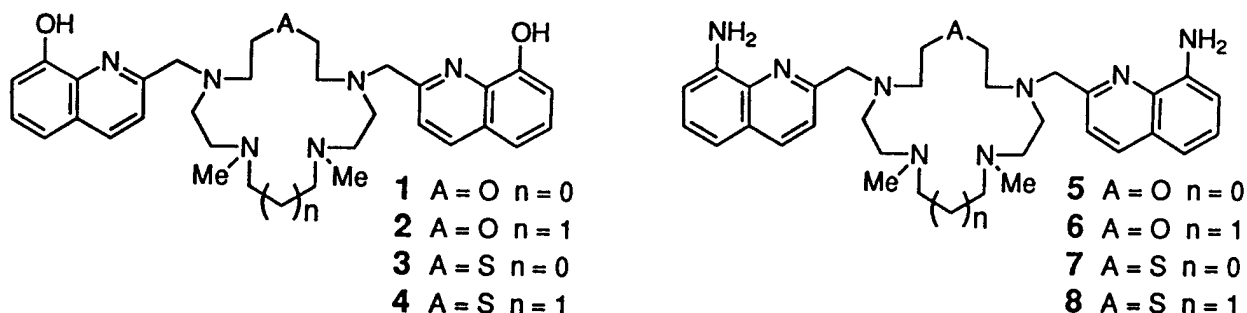
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## Results and Discussion

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.<sup>1</sup> 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  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were determined by a potentiometric titration technique<sup>2</sup> 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:



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

$$\beta_{pqr} = [\text{M}_p\text{H}_q\text{L}_r^{(2p+q-2r)}] / [\text{M}^{2+}]^p [\text{H}^+]^q [\text{L}^{2-}]^r \quad (2)$$

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 Macrocylic Ligand 1 in Aqueous Solution (0.10 M Me<sub>4</sub>NCl) at 25.0 °C

Reaction	log β
H <sup>+</sup> + L <sup>2-</sup> ⇌ HL <sup>-</sup>	9.55 ± 0.05
2H <sup>+</sup> + L <sup>2-</sup> ⇌ H <sub>2</sub> L	16.85 ± 0.08
3H <sup>+</sup> + L <sup>2-</sup> ⇌ H <sub>3</sub> L <sup>+</sup>	19.87 ± 0.09
4H <sup>+</sup> + L <sup>2-</sup> ⇌ H <sub>4</sub> L <sup>2+</sup>	21.31 ± 0.14

(log K<sub>3</sub> = 3.02 and log K<sub>4</sub> = 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 K<sub>1</sub> = 9.55) is hydroxyquinoline (9.65 at 25 °C, μ = 0.1),<sup>3</sup> 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.

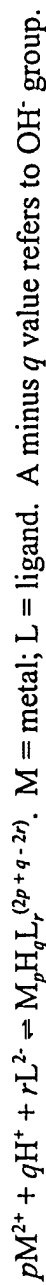
Data in Table 2 show that each metal ion studied forms several types of complexes with the ligand. The 1:1 complexes ML (*p* = 1, *q* = 0, *r* = 1 in eq. 1) and M(OH)L<sup>-</sup> (*p* = 1, *q* = -1, *r* = 1) are observed in each case. The complexes of ligand 1 with Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> are very stable in aqueous solution. The large stability constants (log β<sub>ML</sub> > 12 and log β<sub>MHL</sub> > 15) are shown in Table 2. The most stable complexes were observed for Cu<sup>2+</sup>. The values of log β<sub>CuL</sub> and log β<sub>CuHL</sub> are 15.5 and 18.6, respectively. Cd<sup>2+</sup> also forms very stable complexes with ligand 22 (log β<sub>CdL</sub> = 15.3 and log β<sub>CdHL</sub> = 17.5). Therefore, not only the fully deprotonated form of 22 (L<sup>2-</sup>) but also the monoprotonated ligand (HL<sup>-</sup>) forms very stable complexes with the metal ions studied (except for Co<sup>2+</sup>). In the case of Co<sup>2+</sup>, the complex CoHL<sup>+</sup> was not detected. However, Co<sup>2+</sup> forms a 1:2 (M:L) complex with 1 (log β<sub>CoL<sub>2</sub></sub> = 20.2). A dinuclear complex with Cu<sup>2+</sup>, Cu<sub>2</sub>L<sup>2+</sup>, was also observed. The equilibrium constants of the complexes containing hydrolysis products of the metal ions, M(OH)L<sup>-</sup>, range from 6.44 (log β<sub>Co(OH)L</sub>) to 9.62 (log

Table 2. Overall Stability Constants<sup>a</sup> of Metal Ion Complexes with Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me<sub>4</sub>NCl) at

25.0 °C

P	q	r	log $\beta_{pqr}$					
			Cu <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>
1	0	1	15.52 ± 0.08	12.34 ± 0.04	13.46 ± 0.03	12.41 ± 0.03	15.33 ± 0.02	13.65 ± 0.03
1	1	1	18.55 ± 0.12		16.15 ± 0.18	15.55 ± 0.09	17.50 ± 0.05	16.93 ± 0.03
1	-1	1	8.53 ± 0.19	6.44 ± 0.06	7.49 ± 0.12	6.49 ± 0.05	9.62 ± 0.07	8.22 ± 0.08
2	0	1	18.92 ± 0.22					
1	0	2		20.19 ± 0.06				
1	-2	1						-3.59 ± 0.25

<sup>a</sup>The equilibria of the reactions are defined by the general equation:



$\beta_{\text{Cd(OH)L}}$ ). The  $\text{Ni}^{2+}$  forms a second type of hydrolysis complex,  $\text{Ni(OH)}_2\text{L}^{2-}$ , 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  $\text{Cu}^{2+}$ , a new peak develops at 258 nm (Figure 1). Other metal ions ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ) were also titrated with 1, but none produced a new peak or significantly interfered with the new 1- $\text{Cu}^{2+}$  complex peak at 258 nm (Figure 2). Thus, the 258 nm peak for the 1- $\text{Cu}^{2+}$  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  $\text{Me}_4\text{NCl}$  using an automatic microprocessor-controlled potentiometric titrator.<sup>4</sup> Temperature was controlled within  $\pm 0.1$  °C using a jacketed cell through which water from a constant-temperature bath was circulated. Potentials to within  $\pm 0.1$  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  $4.000 \pm 0.002$  and  $7.000 \pm 0.002$  at 25.0 °C (Cole-Parmer). Calculations were performed with the SUPERQUAD program<sup>5</sup> using an IBM computer. Compound 1 was used as its adduct with HCl ( $1 \cdot 6\text{HCl}$ ) which had good solubility in aqueous solution (0.01 M).

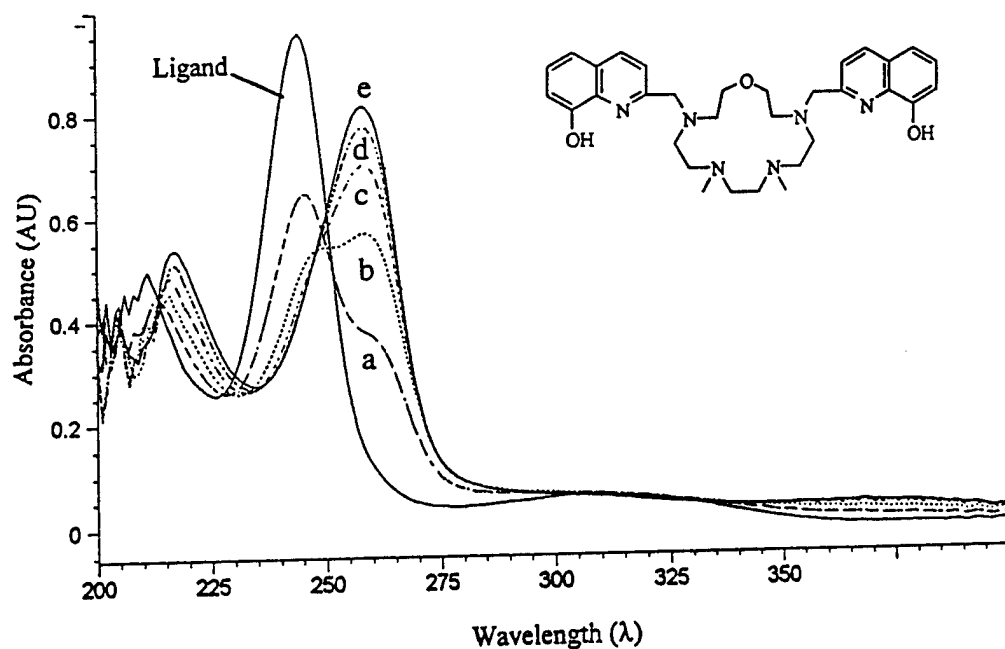


Figure 1. UV-visible spectra of free 1 and its  $\text{Cu}^{2+}$  complexes in an aqueous buffered solution.  $[1] = 0.977 \times 10^{-5} \text{ M}$ ,  $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$  acetic acid ( $\text{pH} = 4.7$ ). The labels a - e indicate 1 - 5 equivalents of  $\text{Cu}^{2+}$  added to the ligand successively.

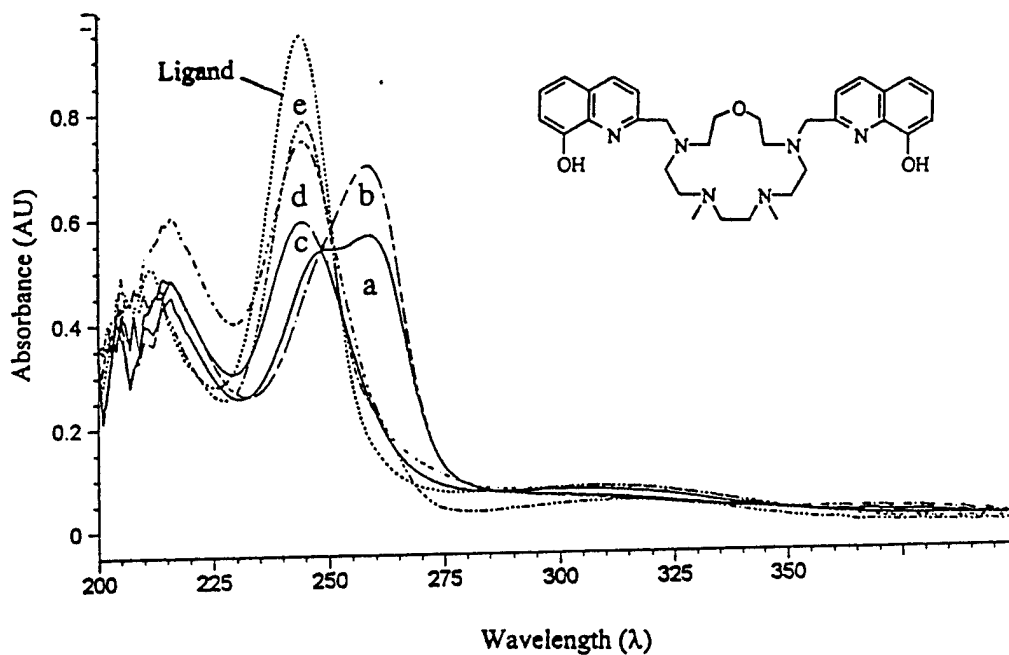


Figure 2. UV-visible spectra of free and complexed 1 in acetic acid buffer solution ( $\text{pH} = 4.7$ ). (a and b)  $\text{Cu}^{2+}$  (1 and 2 equivalents, respectively), (c)  $\text{Zn}^{2+}$ , (d)  $\text{Pb}^{2+}$ , and (e)  $\text{Cd}^{2+}$  (2 equivalents each).  $[1] = 0.977 \times 10^{-5} \text{ M}$  and  $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$  acetic acid.



**UV-visible Spectral Measurements.** UV-visible spectra were recorded at  $23 \pm 1$  °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  $5.00 \times 10^{-2}$  M and  $5.00 \times 10^{-2}$  M, respectively, and concentration of ligand 1 was  $1.00 \times 10^{-5}$  M. The metal ion concentrations were 1-5 times the ligand concentration.

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