Syntheses and Metal Ion Complexation of Novel 8-Hydroxyquinoline-Containing Diaza-18-Crown-6 Ligands and Analogues

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Ten new 8-hydroxyquinoline-containing diaza-18-crown-6 ligands and analogues were synthesized via a one-pot or stepwise Mannich reaction, reductive amination, or by reacting diaza-18-crown-6 with 5,7-dichloro-2-iodomethyl-8-quinolinol in the presence of *N*,*N*-diisopropylethylamine. The Mannich reaction of *N*,*N*′-bis(methoxymethyl)diaza-18-crown-6 with 4-chloro-2-(1*H*-pyrazol-3-yl)-phenol gave the NCH_2N-linked bis(3-(5-chloro-2-hydroxy)pyrazol-1-ylmethyl)-substituted diazacrown ether (**14**) in a 98% yield. The reaction of bis(*N*,*N*′-methoxymethyldiaza)-18-crown-6 with 2.2 equiv of 10-hydroxybenzoquinoline gave only the monosubstituted diazacrown ether ligand (**8**). Interaction of some of the ligands with various metal ions was evaluated by a calorimetric titration technique at 25 °C in MeOH. Bis(8-hydroxyquinoline-2-ylmethyl)-substituted ligand **13** forms a very strong complex with Ba^{2+} (log $K = 11.6$ in MeOH) and is highly selective for Ba^{2+} over Na^+, K^+, Zn^{2+}, and Cu^{2+} (selectivity factor $> 10^6$). The ^1H NMR spectral studies of the Ba^{2+} complexes with bis(8-hydroxyquinoline-2-ylmethyl)- and bis(5,7-dichloro-8-hydroxyquinoline-2-ylmethyl)-substituted diaza-18-crown-6 ligands (**13** and **10**) suggest that these complexes are cryptate-like structures with the two overlapping hydroxyquinoline rings forming a pseudo second macroring. UV−visible spectra of the metal ion complexes with selected ligands suggest that these ligands might be used as chromophoric or fluorophoric sensors.

Introduction

Metal ion complexing abilities and selectivities of crown ethers can be greatly improved when ligating, proton-ionizable groups are attached to the crown ethers. Phenolic sidearms have been extensively used to enhance the stability of the macrocyclic ligand for selected metal ions.[1] The sidearms are often composed of UV-active or fluorophoric proton-ionizable materials that allow an analytical determination of certain cations by spectrophotometric methods.[1a,b,d] Certain crown ethers contatining two bifunctional proton-ionizable groups such as catechol[2] or 2-aminophenol[1g] have been studied as heteronuclear metal ion receptors for simultaneous binding of soft transition and hard alkali or alkaline-earth metal ions in one molecule. For example, two bis(3-amino-2-hydroxybenzyl)-substituted diaza-18-crown-6 ligands formed strong complexes with Cu^{2+} and the ligand−Cu^{2+} complex formed heterobinuclear complexes with Na^+.[1g]

Our research group is particularly interested in developing ion-selective sensors to accurately monitor certain metal ion concentrations in various aqueous solutions. A key element of this research is the incorporation of additional proton-ionizable ligating units with chromophoric and fluorophoric abilities onto ion-selective macrocycles to provide concomitant changes in the photophysical properties of the system upon metal ion binding while maintaining or improving the ion selectivities of the macrocycles.[3,4]

8-Hydroxyquinoline is an analytical reagent containing a phenol-like function wherein ligand fluorescence is moderated upon complexation with certain metal ions.[5] 5-Chloro-8-hydroxyquinoline (CHQ)-substituted diaza-18-crown-6 ligands (**1** and **2**, Figure 1) prepared in our

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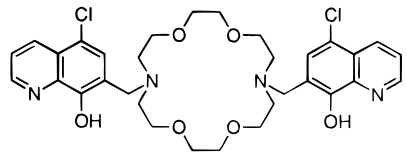

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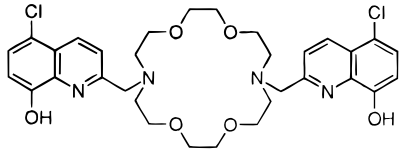

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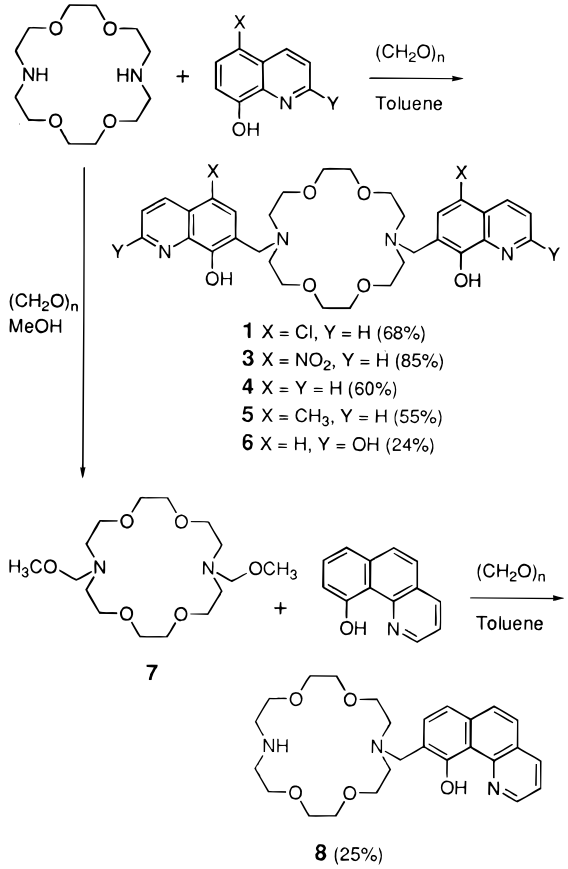
Figure 1. 5-Chloro-8-hydroxyquinoline (CHQ)-substituted diaza-18-crown-6 ligands **1** and **2**.

laboratory exhibit greatly improved ion-complexing ability and selectivity for certain metal ions compared to unsubstituted diaza-18-crown-6.[6−8] Ligands **1** and **2** have the CHQ sidearms attached through different CHQ positions to determine if the different attachments of CHQ would make a major difference in metal ion complexation by **1** and **2**. Ligand **1**, where CHQ is attached through its 7-position, formed very stable complexes in MeOH with Mg^{2+}, Ca^{2+}, Cu^{2+}, and Ni^{2+} (log K = 6.82, 5.31, 10.1, and 11.4, respectively). Indeed, **1** can serve as an effective chemosensor for Mg^{2+} as it has a very strong luminescence band at 540 nm when complexed with Mg^{2+} even in the presence of higher concentrations of other alkali and alkaline-earth cations.[8]

Ligand **2**, where CHQ is attached to the crown ether through its 2-position, exhibits remarkable selectivity for K^+ over Na^+ (selectivity factor: $\sim 10^3$) and Ba^{2+} over other alkaline-earth cations (selectivity factor: $>10^7$).[6] Values of log K for the formation of K^+ and Ba^{2+} complexes with **2** in MeOH (log K = 6.61 and 12.2, respectively) are larger than those for the K^+ and Ba^{2+} complexes with all other lariat ethers. The log K value for the **2**−Ba^{2+} complex is the same magnitude as that of the cryptand [2.2.2]−Ba^{2+} complex (log K = 12.9 in MeOH).[9] Indeed, **2** forms a pseudocryptand through $\pi-\pi$ interaction between the two CHQ rings when complexed with Ba^{2+} as shown by the ^{1}H NMR spectrum and the solid-state X-ray structure. All 10 donor atoms of **2** are involved in coordination with Ba^{2+}.[6]

The difference in metal ion affinities of **1** and **2**, as mentioned above, show that the position of attachment of phenol-like ligating chromophores is an important consideration in constructing chromophore-armed crown ethers. We now report the synthesis of several analogues of **1** (Scheme 1) and **2** (Scheme 2), which contain various substituents on the 8-hydroxyquinoline sidearms. These substituents include hydrogen rather than chlorine, nitro, and methyl groups in the 5-position, as well as an extra chlorine or a hydroxy group in the 2-position. Measurements of log K show that the metal ion selectivities of these analogues of **1** and **2** remain the same in that analogues of **1** form strong complexes with Mg^{2+} and analogues of **2** form a pseudocryptate with a large log K value for the interaction of bis(8-hydroxyquinoline-2-ylmethyl)-substituted ligand **13** with Ba^{2+}. The magnitudes of the log K values differ with different substituents on the 8-hydroxyquinoline sidearms.

Scheme 1. Syntheses of CHQ-7-ylmethyl-Substituted Analogues of 1 and a Related Ligand



Results and Discussion

Synthesis of Ligands. The Mannich reaction is one of the most useful synthetic methods for functionalizing azacrown ethers with proton-ionizable phenol groups. Many variations of this reaction have been developed.[10,11] Compound **1** was originally synthesized via a stepwise Mannich reaction.[6] First, intermediate *N*,*N*′-bis(methoxymethyl)diaza-18-crown-6 (**7**, Scheme 1) was prepared in a quantitative yield by stirring diaza-18-crown-6 with paraformaldehyde in absolute MeOH followed by evaporation of the solvent.[12] Second, **7** was treated with 5-chloro-8-hydroxyquinoline in refluxing benzene to give **1** in a 67% yield.[6] Compound **7** is an oil of low stability, but it is very reactive with various Mannich bases. Using

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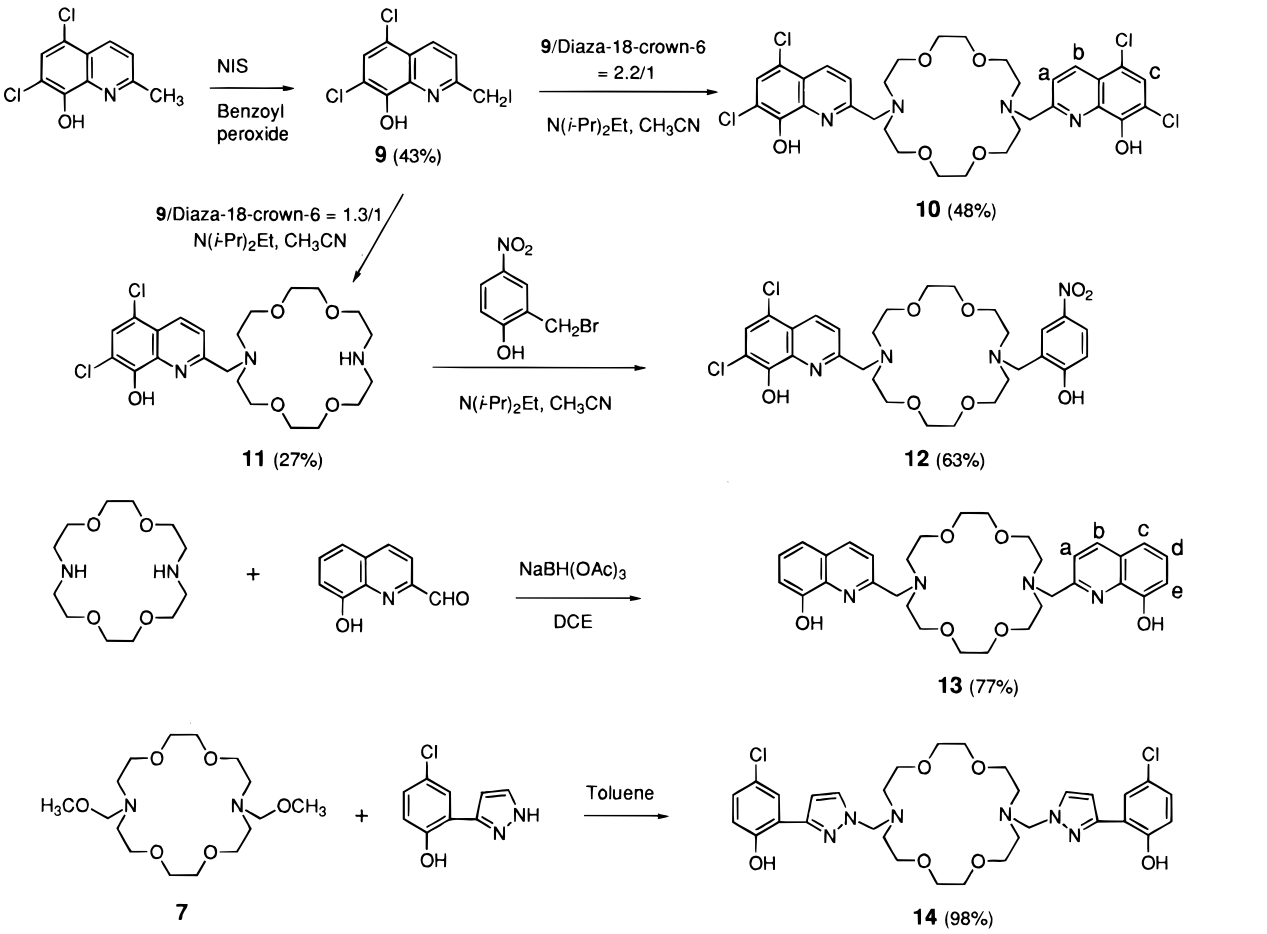
Scheme 2. Efficient Syntheses of Analogues of CHQ-2-ylmethyl-Substituted 2 and a Related Ligand



7 prevents the interaction of free formaldehyde with various other reacting functional groups on the phenols undergoing aminomethylation.

In this work, the convenient one-pot Mannich reaction[11] was used to synthesize compound **1** and its 5-nitro-(**3**), 5-hydro-(**4**), 5-methyl-(**5**), and 5-hydro-2-hydroxy-(**6**) analogues (Scheme 1). 5-Nitro-8-hydroxyquinoline, the starting material for **3**, is more electron-deficient than CHQ and should give **3** in a lower yield, as suggested by the yields of substituted bisphenol-armed diazacrown ethers produced when the diazacrown was treated with *p*-chlorophenol (77%) and *p*-nitrophenol (15%).[11] Unexpectedly, **3** was obtained in a higher yield (85%) than **1** (68%). Ligands **4** and **5** were likewise obtained in good yields via the one-pot Mannich reaction. Bis(dihydroxyquinoline)-substituted **6** was also obtained via the one-pot Mannich reaction from 2,8-quinolinediol.

It is expected that, if CHQ groups are attached to a macroring at the 7-position (as in **1**), CHQ chelation of a metal ion bound by the macroring can occur only from the phenolic oxygens and the quinoline nitrogen cannot participate in complex formation. The quinoline nitrogen cannot approach a metal ion bound by the macroring and the phenol group of CHQ. However, with 10-hydroxybenzoquinoline (HBQ) units attached to diaza-18-crown-6 through the HBQ 9-position, the nitrogen atom of the HBQ group could possibly take part in metal ion complexion in conjunction with the macroring. Thus, a bis-HBQ-substituted ligand might better chelate doubly charged cations because all of its 10 donor atoms could take part in the complexation. Unfortunately, when HBQ was treated with bis(methoxymethyl)diazacrown **7**, only mono-HBQ-substituted diaza-18-crown-6 **8** (Scheme 1) was formed even in the presence of 2.2 equiv of HBQ. No disubstituted ligand was observed by MS. It is possible that one attached HBQ prevents the second HBQ from reacting through steric hindrance or by intramolecular hydrogen bonding between the nitrogen atom of HBQ and the NH of the crown ether. Nevertheless, **8** proved to be a good candidate for use as a sensory molecule for Cu^{2+} (vide infra).

Compound **2** was originally synthesized in four steps: preparation of 5-chloro-8-methoxyquinaldine from 2-amino-4-chloroanisole,[13] NBS bromination of the methyl group, attachment of the bromomethyl-substituted quinoline to diaza-18-crown-6 in CH_3CN in the presence of Na_2CO_3, and demethylation of the methoxy functions using LiCl in DMF.[6] In this work, analogues of **2** were prepared in two simplified methods (Scheme 2). Treatment of commercially available 5,7-dichloro-8-hydroxyquinaldine (DCHQ) with NIS gave the more reactive 5,7-dichloro-2-iodomethyl-8-quinolinol **9**. In the presence of *N*,*N*-isopropylethylamine, 2.2 equiv of **9** were treated with diaza-18-crown-6 to form bis(5,7-dichloro-8-hydroxyquinolin-2-ylmethyl)-substituted **10** in a 48% yield without protecting the hydroxy groups. Using a lower amount of **9** gave mono-DCHQ-substituted diaza-18-crown-6 **11** in a lower yield. Compound **11** was further treated with α-bromo-4-nitro-*o*-cresol to give asymmetrically substituted diaza-18-crown-6 ligand **12** (Scheme 2).

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8-Hydroxyquinoline-2-ylmethyl-substituted diaza-18-crown-6 **13**, the 5-hydro analogue of **2**, was prepared by reductive amination in one step from 8-hydroxyquinoline-2-carboxaldehyde.[14] Sodium triacetoxyborohydride, $NaBH(OAc)_3$, proved to be an efficient reducing agent.[15] New ligands **10** and **13**, as compared to **2**, allow a study of the effect of the chlorine substituents on the complexation of metal ions by these 8-hydroxyquinoline-substituted ligands.

4-Chloro-2-(1*H*-pyrazol-3-yl)phenol-substituted diaza-18-crown-6 **14** (Scheme 2) was prepared to have a ligand with the potential to have an enlarged cavity when a pseudocryptate complex forms. *N*,*N*′-Bis(methoxymethyl) **7** was used as starting material because 4-chloro-2-(1*H*-pyrazol-3-yl)phenol contains an NH group capable of aminomethylation. Ligand **14** was obtained as a white solid in near quantitative yield after evaporation of the solvent, sonication of the residue in MeOH, filtration, and drying. Compared to **2**, **14** has an extra C−C bond between the aromatic nitrogen atom and phenol hydroxy group on the sidearms. In addition, the connections between the crown and ligating sidearms are $N-CH_2-N$ linkages. In this case, 10 of its 12 donor atoms may take part in complexion with metal ions.

Complexation Studies. Interactions of ligands **4**−**6**, **8**, **13**, and **14** with some or all of Na^+, K^+, Mg^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, and Co^{2+} were evaluated by a calorimetric titration technique[16] at 25.0 °C in an absolute MeOH solution. The values of equilibrium constants (log *K*) and enthalpy (ΔH) and entropy changes ($T\Delta S$) for these interactions are listed in Table 1. Also listed in Table 1 are like values for the interactions of **1** and **2** with these metal ions. Because of small reaction heat, thermodynamic quantities for the K^+-**6** interaction could not be calculated from the calorimetric titration data and those for Na^+-**8** have been roughly estimated by a competitive titration with Zn^{2+}. Compound **14** (1.5×10^{-3} M) forms a brown precipitate with Cu^{2+} in MeOH. In all other cases, the six new ligands form stable complexes with the metal ions studied (log $K \geq 3$).

High selectivity of ligand **8** for Zn^{2+} and of ligand **13** for Ba^{2+} over the other metal ions studied are evident. Selectivity of **8** for Zn^{2+} could be due to a proper preorganization of the ligand for the Zn^{2+} ions. Strong coordination may occur between Zn^{2+} and three nitrogen atoms and a hydroxyl group, which could provide an approximate tetrahedral coordination array for Zn^{2+}. Ligand **13** shows a similar high selectivity for Ba^{2+}, as does CHQ-substituted ligand **2**[6] (see Table 1). Selectivity factors of **13** for Ba^{2+} over Na^+, K^+, and Zn^{2+} are $\geq 10^6$.

As in the case of Ba^{2+}-**2** complex,[6] a pseudocryptate structure presumably formed through a $\pi-\pi$ interaction of the two 8-hydroxyquinoline rings of **13** is the main reason for the highly stable Ba^{2+}-**13** complex. This supposition is supported by ^{1}H NMR spectral data in DMSO-d_6 (see Table 2). As compared with CHQ-substituted **2**, 8-hydroxyquinoline-substituted **13** exhibits a slightly lower binding constant with Ba^{2+} (log $K = 11.6 \pm 0.2$ for **13** and 12.2 for **2**).[6] 5,7-Dichloro-8-hydroxyquinoline-substituted ligand **10** may also selectively bind Ba^{2+} over other metal ions; however, the very low solubility of **10** in MeOH would not allow the determination of its binding constants with metal ions. However, the ^{1}H NMR spectral data in DMSO-d_6 (Table 2) show large upfield shifts for the 8-hydroxyquinoline protons of **10** in the presence of Ba^{2+}, suggesting that ligand **10** also forms a stable complex with Ba^{2+}.

Ligands **4** and **5**, like ligand **1**, form stable complexes with Mg^{2+} with log *K* values of 5.7 and 5.0, respectively (Table 1). The Mg^{2+} complexes with **4** and **5** are more

Table 1. Log *K*, ΔH (kJ/mol), and $T\Delta S$ (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0 °C

ligand	cation	log *K*	ΔH	$T\Delta S$
1[a]	Na^+	2.89	−14.1	2.4
	K^+	3.39	−24.4	−5.0
	Mg^{2+}	6.82	−2.5	36.4
	Ba^{2+}	3.60	−11.6	8.9
	Zn^{2+}	5.12	−114	−85
	Cu^{2+}	10.1	−92.5	−34.9
	Co^{2+}	5.14	−91.1	−61.8
2[a]	Na^+	3.74	−26.4	−5.1
	K^+	6.61	−58.1	−20.4
	Mg^{2+}	*b*		
	Ca^{2+}	4.71	−25.2	1.7
	Sr^{2+}	4.67	−24.6	2.1
	Ba^{2+}	12.2	−76.1	−6.5
4	Mg^{2+}	5.7 ± 0.2	10.7 ± 0.9	43.2
	Co^{2+}	3.91 ± 0.08	−91.2 ± 0.5	−68.9
5	Mg^{2+}	5.02 ± 0.08	13.9 ± 0.9	42.6
	Co^{2+}	3.96 ± 0.06	−84.5 ± 0.5	−61.9
6	K^+	*b*		
	Ba^{2+}	3.57 ± 0.06	−29.4 ± 0.7	−9.0
	Zn^{2+}	4.80 ± 0.08	−64.8 ± 0.6	−37.4
	Cu^{2+}	5.01 ± 0.07	−57.6 ± 0.6	−29.0
8	Na^+	∼3[c]	∼ −5[c]	
	K^+	3.52 ± 0.03	−31.2 ± 0.4	−11.1
	Ba^{2+}	4.22 ± 0.05	−19.2 ± 0.8	4.9
	Zn^{2+}	>5.5	−19.0 ± 0.5	>12.4
	Cu^{2+}	4.28 ± 0.09	−55.3 ± 0.7	−30.9
13	Na^+	3.65 ± 0.01	−25.3 ± 0.2	−4.5
	K^+	5.88 ± 0.04[d]	−55.6 ± 0.7[d]	−22.0
	Ba^{2+}	11.6 ± 0.2[d]	−73.0 ± 0.5[d]	−6.8
	Zn^{2+}	4.92 ± 0.07[e]	−95.7 ± 0.6	−67.6
	Cu^{2+}	4.39 ± 0.09	−100 ± 1	−74.9
14	Na^+	3.02 ± 0.05	−20.0 ± 0.6	−2.8
	K^+	3.82 ± 0.02	−47.8 ± 0.3	−26.0
	Ba^{2+}	4.87 ± 0.04	−26.4 ± 0.4	1.4
	Zn^{2+}	4.80 ± 0.08	−64.8 ± 0.6	−37.4
	Cu^{2+}	(brown ppt)		

[a] Data from ref 6. [b] No measurable heat other than heat of dilution, indicating that ΔH or/and log *K* is small. [c] Estimated by a competitive calorimetric titration with Zn^{2+}. [d] Determined by a competitive calorimetric titration. [e] When $[Zn^{2+}]$/**13** ≥ 2, a white precipitate formed.

Table 2. Proton Chemical Shifts (δ, ppm)[a] of 8-Hydroxyquinoline Substituents of Free and Complexed Ligands 10 and 13 and Cation-Induced Shifts (CIS, Hz)[b] in DMSO-d_6 at 20 °C

	10			**13**				
cation	H_a	H_b	H_c	H_a	H_b	H_c	H_d	H_e
none	7.914	8.306	7.691	7.712	8.221	7.355	7.359	7.061
Ba^{2+}	7.301	7.904	7.094	7.334	7.913	6.805	6.816	6.594
	(184)	(121)	(179)	(113)	(92)	(165)	(163)	(140)

[a] Concentrations of the ligands were 0.01 M and those of the Ba^{2+} were 0.04 M. Tetramethylsilane (TMS) was used as the internal standard. [b] CIS (Hz) = $300 \times [\delta_{lig}$ (ppm) − δ_{compl} (ppm)]. The CIS values (in Hz) are in parentheses.

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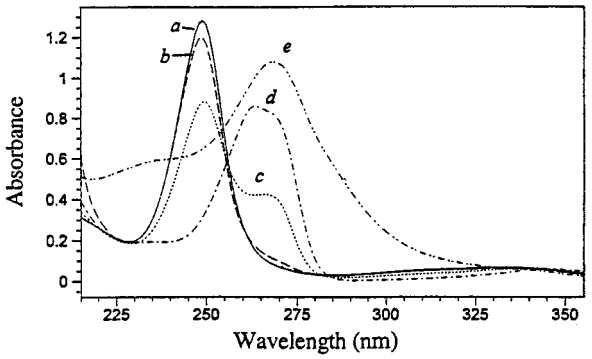

Figure 2. UV spectra of free and complexed **4** in MeOH. (a) 1.1×10^{-5} M **4**; (b) solution a + 1.0×10^{-3} M Ba^{2+}; (c) solution a + 1.0×10^{-3} M Mg^{2+}; (d) solution a + 1.0×10^{-3} M Zn^{2+}; and (e) 3.4×10^{-6} M **4** + 2.9×10^{-4} M Cu^{2+}.

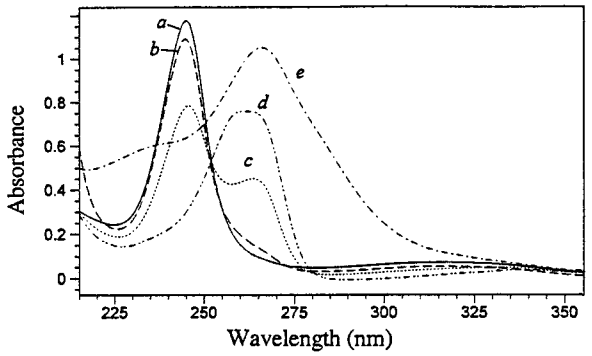

Figure 3. UV spectra of free and complexed **5** in MeOH. (a) 1.1×10^{-5} M **5**; (b) solution a + 1.0×10^{-3} M Ba^{2+}; (c) solution a + 1.0×10^{-3} M Mg^{2+}; (d) solution a + 1.0×10^{-3} M Zn^{2+}; and (e) 3.4×10^{-6} M **5** + 2.9×10^{-4} M Cu^{2+}.

stable than the corresponding Co^{2+} complexes. The same effect was observed previously for ligand **1**.[6]

UV−Visible Spectra. Selected UV−visible spectra of free and metal-ion complexed ligands **4**, **5**, **8**, and **13** in MeOH are shown in Figures 2−5, respectively. In general, complexation with transition and post-transition metal ions (Cu^{2+} and Zn^{2+}) results in a large change in ligand absorption spectra, but alkali and alkaline-earth metal ions (Na^+, K^+, and Ba^{2+}) cause small or no changes. Ligand **8** shows four UV−visible absorption bands at 214 (not shown), 242, 275 (a shoulder), and 372 nm. As shown in Figure 4, K^+ and Ba^{2+} cause no significant changes in the absorption bands. However, Zn^{2+} and Cu^{2+} cause changes to the absorption spectrum of **8**. In the presence of Zn^{2+}, the absorption maxima of the ligand at 242 and 372 nm shift to 250 and 400 nm, respectively. The absorption peak of the Zn^{2+}-**8** complex at 400 nm may be used to monitor Zn^{2+} concentrations in solution because the other metal ions studied do not have absorptions at that wavelength. Cu^{2+} causes not only a large increase in absorption intensity for the peaks of **8** at 242 and 275 nm but also some shifts to the absorption maxima. The shoulder of free **8** at 275 nm is developed into a very strong band with the absorption maximum at 272 nm (see Figure 4). Note that the concentration of **8** in Figure 4 is decreased from 1.3×10^{-5} to 5.0×10^{-6} M in the case of Cu^{2+}. Increased absorptions in the vicinity of 270 nm in the presence of Cu^{2+} have also been observed for ligands **4**, **5**, and **13** (see Figures 2, 3, and 5).

Absorption maxima of free ligands **4**, **5**, and **13** in the vicinity of 245 nm are shifted by Zn^{2+} to 262 nm and by Cu^{2+} to 267 nm (Figures 2, 3, and 5). It is shown in Figure 5 that K^+ and Ba^{2+} cause a significant decrease in absorption intensity at 245 nm of free ligand **13**, providing additional evidence for overlapping of the two 8-hydroxyquinoline rings through $\pi-\pi$ interaction.[7] We previously observed a new absorption peak at 265 nm in the Mg^{2+}-**1** complex.[6] Ligands **4** and **5** show a similar spectral property. The new absorption peaks appear for the Mg^{2+}-**4** and Mg^{2+}-**5** complexes at 265 nm (see Figures 2c and 3c). The unique spectral properties of **4** and **5** may make them useful fluorescent sensors for Mg^{2+}.[8]

Experimental Section

The ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in DMSO-d_6 or $CDCl_3$. FAB ionization was used to record the high-resolution mass spectra. Solvents and starting materials were purchased from commercial sources where available. Compound **7** was synthesized as described.[12]

7,16-Bis(5-chloro-8-hydroxyquinoline-7-ylmethyl)-1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane (1). (Scheme 1)-An anhydrous toluene solution (180 mL) of 4,13-diaza-18-crown-6 (1.00 g, 3.82 mmol), paraformaldehyde (280 mg, 9.30 mmol), and 5-chloro-8-hydroxyquinoline (1.63 g, 9.10 mmol) was refluxed for 20 h. The solvent was evaporated under reduced pressure, and a small amount of MeOH was added. The mixture was ultrasonicated for 20−30 min. The resulting solid was collected by filtration and dried to give 1.68 g (68%) of **1** as a yellow solid. The mp and NMR spectral data were identical to those reported.[6]

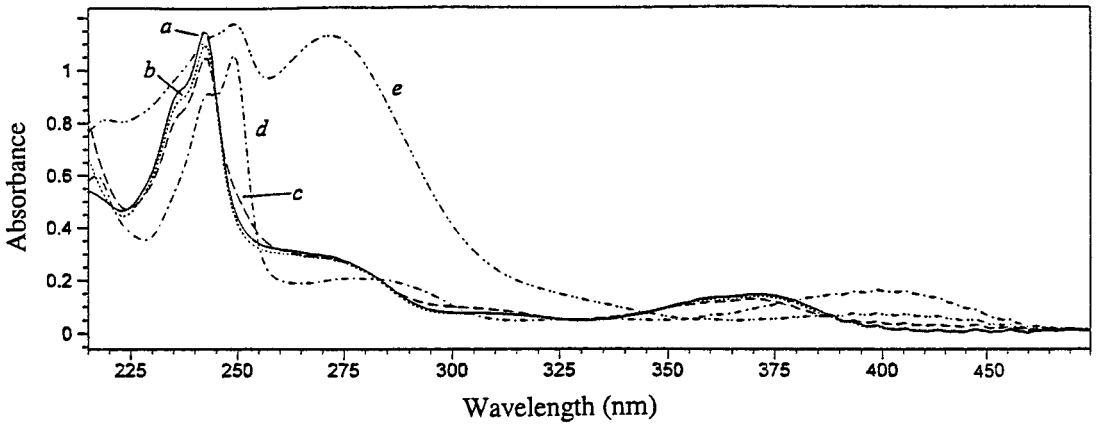

Figure 4. UV-visible spectra of free and complexed **8** in MeOH. (a) 1.3×10^{-5} M **8**; (b) solution a + 1.0×10^{-3} M K^+; (c) solution a + 1.0×10^{-3} M Ba^{2+}; (d) solution a + 1.0×10^{-3} M Zn^{2+}; and (e) 5.0×10^{-6} M **8** + 3.8×10^{-4} M Cu^{2+}.

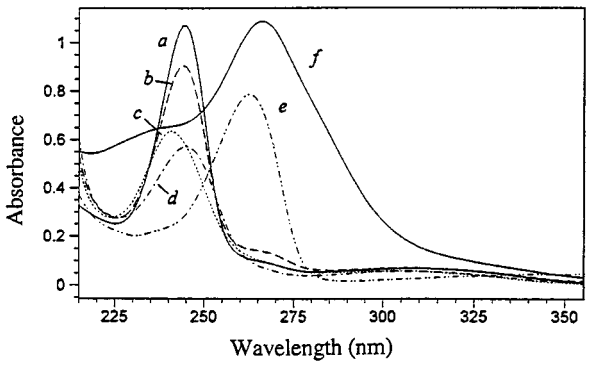

Figure 5. UV spectra of free and complexed **13** in MeOH. (a) 1.3×10^{-5} M **13**; (b) solution a + 1.0×10^{-3} M Na^+; (c) solution a + 1.1×10^{-3} M K^+; (d) solution a + 1.0×10^{-3} M Ba^{2+}; (e) solution a + 1.0×10^{-3} M Zn^{2+}; and (f) 3.1×10^{-6} M **13** + 3.0×10^{-4} M Cu^{2+}.

7,16-Bis(5-nitro-8-hydroxyquinoline-7-ylmethyl)-1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane (3). (Scheme 1) An anhydrous toluene solution (180 mL) of 4,13-diaza-18-crown-6 (1.00 g, 3.82 mmol), paraformaldehyde (280 mg, 9.30 mmol), and 5-nitro-8-hydroxyquinoline (1.73 g, 9.10 mmol) was refluxed for 20 h. A light yellow precipitate was formed during the reflux and was collected by filtration of the hot toluene solution. The product was further purified by refluxing in MeOH followed by filtration and drying to give 2.16 g (85%) of **3** as a light yellow solid: mp 163−164 °C; ^{1}H NMR (DMSO-d_6) δ 3.39 (t, J = 4.8 Hz, 8H), 3.53 (s, 8H), 3.84 (t, J = 4.8 Hz, 8H), 4.50 (s, 4H), 7.63 (dd, J = 4.2, 8.8 Hz, 2H), 8.65 (s, 2H), 8.75 (dd, J = 1.7, 4.2 Hz, 2H), 9.34 (dd, J = 1.5, 8.8 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 53.1, 55.8, 65.4, 69.9, 114.1, 123.7, 124.7, 126.0, 132.2, 133.7, 141.4, 146.4, 174.7; HRMS calcd for $C_{32}H_{39}N_6O_{10}$ (M + H)$^+$ 667.2728, found 667.2714. Anal. Calcd for $C_{32}H_{38}N_6O_{10}$: C, 57.65; H, 5.75. Found: C, 57.73; H, 5.67.

7,16-Bis(8-hydroxyquinoline-7-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (4). (Scheme 1) A solution of anhydrous toluene (45 mL), 4,13-diaza-18-crown-6 (0.52 g, 2.0 mmol), 8-hydroxyquinoline (0.61 g, 4.2 mmol), and paraformaldehyde (0.14 g, 4.5 mmol) was refluxed for 15 h. The solvent was evaporated under reduced pressure, and residue was separated by chromatography on silica gel using CH_2Cl_2/MeOH/NH_4OH (30/5/1) as eluant to give 0.69 g (60%) of **4**: mp 114.5−116.0 °C; ^{1}H NMR δ 2.97 (t, J = 5.6 Hz, 8H), 3.69 (s, 8H), 3.74 (t, J = 5.4 Hz, 8H), 4.03 (s, 4H), 7.23 (s, 4H), 7.35 (dd, J = 4.2, 4.4 Hz, 2H), 8.09 (dd, J = 1.6, 1.8 Hz, 2H), 8.89 (d, J = 4.2 Hz, 2H); ^{13}C NMR δ 53.8, 58.4, 69.5, 70.9, 117.5, 119.2, 121.3, 127.9, 128.7, 135.9, 139.7, 149.2, 153.7; HRMS calcd for $C_{32}H_{41}N_4O_6$ (M + H)$^+$ 577.3028, found 577.3029. Anal. Calcd for $C_{32}H_{40}N_4O_6$; C, 66.65; H, 6.99. Found: C, 66.63; H, 7.09.

7,16-Bis(5-methyl-8-hydroxyquinoline-7-ylmethyl)-1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane (5). (Scheme 1) Ligand **5** was prepared as above for **4** to give 0.69 g (55%) of **5** from 0.52 g (2.0 mmol) of 4,13-diaza-18-crown-6, 0.67 g (4.2 mmol) of 5-methyl-8-hydroxyquinoline, and 0.14 g (4.5 mmol) of paraformaldehyde: mp 151.5−153.0 °C; ^{1}H NMR δ 2.57 (s, 6H), 2.98 (t, J = 5.2 Hz, 8H), 3.65 (s, 8H), 3.75 (t, J = 5.2 Hz, 8H), 4.00 (s, 4H), 5.31 (s, 0.25H, CH_2Cl_2), 7.07 (s, 2H), 7.42 (dd, J = 3.4, 3.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 8.91 (d, J = 4.0 Hz, 2H); ^{13}C NMR δ 18.0, 53.8, 58.1, 69.6, 70.9, 118.6, 120.9, 123.8, 127.6, 128.2, 132.6, 139.9, 148.6, 151.7; HRMS calcd for $C_{34}H_{45}N_4O_6$ (M + H)$^+$ 605.3341, found 605.3344. Anal. Calcd for $C_{34}H_{44}N_4O_6 \cdot {}^1/_4CH_2Cl_2$: C, 65.72, H, 7.17. Found: C, 65.74; H, 6.83.

7,16-Bis(2,8-quinolinediol-7-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (6). (Scheme 1) 4,13-Diaza-18-crown-6 (0.739 g, 2.82 mmol), paraformaldehyde (207 mg, 6.87 mmol), and 2,8-quinolinediol (1.00 g, 6.21 mmol) were refluxed in anhydrous toluene (150 mL) for 20 h. The solvent was evaporated under reduced pressure. Compound **6** (white solid, mp 191−192 °C, 420 mg, 24%) was purified by column chromotography on silica gel (60−200 mesh) using CH_2Cl_2/MeOH/NH_4OH (30/5/1) as eluent: ^{1}H NMR ($CDCl_3$) δ 2.88 (t, J = 5.1 Hz, 8H), 3.62 (s, 8H), 3.71 (t, J = 5.1 Hz, 8H), 3.94 (s, 4H), 6.61 (d, J = 9.5 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 9.5 Hz, 2H), 9.23 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 54.3, 58.6, 68.9, 71.1, 117.7, 119.8, 122.2, 122.4, 128.0, 140.6, 144.1, 162.3; HRMS calcd for $C_{32}H_{41}N_4O_8$ (M + H)$^+$ 609.2924, found 609.2911.

7-(10-Hydroxybenzoquinoline-9-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (8). (Scheme 1) *N*,*N*′-Bis(methoxymethyl)diaza-18-crown-6 (**7**) (1.00 g, 2.85 mmol) and 10-hydroxybenzoquinoline (1.22 g, 6.27 mmol) were refluxed in 50 mL of toluene for 20 h. The solvent was evaporated under reduced pressure. The slightly yellow oil residue was purified by column chromotography on silica gel (60−200 mesh) using CH_2Cl_2/MeOH/Et_3N (3/2/1) as eluent. Compound **8** (334 mg, 25%) was isolated as an oil: ^{1}H NMR ($CDCl_3$) δ 2.83 (t, J = 4.8 Hz, 4H), 2.94 (t, J = 5.7 Hz, 4H), 3.63 (m, 12H), 3.73 (t, J = 5.7 Hz, 4H), 4.04 (s, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.57 (m, 2H), 7.82 (dd, J = 8.1, 14.7 Hz, 2H), 8.25 (dd, J = 1.5, 7.8 Hz, 1H), 8.80 (dd, J = 1.7, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 49.6, 52.8, 54.2, 70.3, 70.5, 71.1, 115.6, 117.7, 120.8, 124.2, 126.6, 129.4, 131.7, 134.2, 136.4, 144.8, 148.7, 157.4; HRMS calcd for $C_{26}H_{35}N_3O_5$ (M + Na)$^+$ 492.2474, found 492.2470. Anal. Calcd for $C_{26}H_{35}N_3O_5$: C, 66.50; H, 7.51. Found: C, 66.41; H, 7.39.

5,7-Dichloro-2-iodomethyl-8-quinolinol (9). (Scheme 2) In the presence of benzoyl peroxide (0.5 g), a solution of 5,7-dichloro-8-hydroxyquinaldine (11.4 g, 50.0 mmol) in 130 mL of CCl_4 was refluxed with *N*-iodosuccinimide (NIS) (15.0 g, 66.6 mmol) for 3 days. The hot solution was filtered. The brown filtrate was evaporated to 50 mL and put in the refrigerator. The resulting brown precipitate was filtered and washed with cold CH_3CN to give a yellow solid. The product was recrystalized from a mixture of benzene/hexane (3/1) to give 7.43 g (43%) of **9** as a yellow solid: mp 161−162 °C; ^{1}H NMR ($CDCl_3$) δ 4.67 (s, 2H), 7.56 (s, 1H), 7.62 (d, J = 8.5 Hz, 1H), 8.27 (br s, 1H), 8.43 (d, J = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 4.9, 116.1, 121.0, 122.7, 124.0, 128.7, 135.0, 138.0, 147.5, 158.4; HRMS calcd for $C_{10}H_6Cl_2INO$ (M + H)$^+$ 353.8948, found 353.8947. Anal. Calcd for $C_{10}H_6Cl_2INO$: C, 33.93; H, 1.71. Found: C, 34.14; H, 1.43.

7,16-Bis(5,7-Dichloro-8-hydroxyquinoline-2-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (10). (Scheme 2) Diaza-18-crown-6 (1.00 g, 3.82 mmol), **9** (2.96 g, 8.40 mmol), and *N*,*N*-diisopropylethylamine (2.00 mL, 21.9 mmol) were refluxed in 80 mL of CH_3CN for 12 h. The solvent was evaporated in reduced pressure. The residue was dissolved in 50 mL of CH_2Cl_2, washed with water, and dried (Na_2SO_4). After evaporation of CH_2Cl_2, the residue was purified by column chromotography on silica gel (60−200 mesh) using CH_2Cl_2/MeOH/NH_4OH (40/5/1) as eluent. Compound **10** (1.31 g, 48%) was isolated as a red oil: ^{1}H NMR ($CDCl_3$) δ 2.91 (t, J = 5.4 Hz, 8H), 3.64 (s, 8H), 3.68 (t, J = 5.4 Hz, 8H), 4.06 (s, 4H), 7.48 (s, 2H), 7.78 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.1, 61.7, 70.0, 70.9, 115.5, 120.5, 122.6, 124.1, 127.7, 133.7, 138.1, 148.0, 160.5; HRMS calcd for $C_{32}H_{36}Cl_4N_4O_6$ (M + H)$^+$ 713.1467, found 713.1457. Anal. Calcd for $C_{32}H_{36}Cl_4N_4O_6$: C, 53.79; H, 5.08. Found: C, 54.00; H, 4.96.

7-(5,7-Dichloro-8-hydroxyquinoline-2-ylmethyl)-1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane (11). (Scheme 2) Compound **11** (red oil, 252 mg, 27%) was prepared as for **10** from diaza-18-crown-6 (0.50 g, 1.91 mmol), **9** (0.875 g, 2.48 mmol), and *N*,*N*-diisopropylethylamine (1.00 mL, 11.0 mmol): ^{1}H NMR ($CDCl_3$) δ 2.96 (m, 8H), 3.53 (m, 8H), 3.65 (m, 8H), 4.40 (s, 2H), 7.51 (s, 1H), 7.66 (d, J = 8.8 Hz, 2H), 8.39 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 47.8, 53.9, 60.1, 68.9, 69.8, 69.9, 70.6, 115.9, 118.4, 121.1, 124.3, 127.3, 133.2, 139.5, 150.8, 161.3; HRMS calcd for $C_{22}H_{31}Cl_2N_3O_5$ (M + H)$^+$ 488.1719, found 488.1727. Anal. Calcd for $C_{22}H_{31}Cl_2N_3O_5$: C, 54.10; H, 6.40. Found: C, 53.86; H, 6.46.

7-(5,7-Dichloro-8-hydroxyquinoline-2-ylmethyl)-16-(2-hydroxy-5-nitrobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (12). (Scheme 2) Compound **12** (red oil, 165 mg, 63%) was prepared as for **10** from **11** (200 mg, 0.41 mmol), α-bromo-4-nitro-*o*-cresol (0.114 g, 0.49 mmol), and *N*,*N*-diisopropylethylamine (1.00 mL, 11.0 mmol): ^{1}H NMR ($CDCl_3$) δ 2.68 (m, 4H), 2.99−3.87 (m, 20H), 3.95 (brs, 2H), 4.30 (brs, 2H), 6.36 (d, J = 8.5 Hz, 1H), 7.24 (m, 1H), 7.50 (s, 1H), 8.00 (m, 2H), 8.34 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 53.2, 56.0, 57.8, 58.6, 67.4, 68.2, 68.8, 69.3, 107.8, 116.7, 118.2, 119.4, 125.6, 125.7, 127.5, 129.6, 129.7, 132.7, 135.3, 144.2, 155.2. Anal. Calcd for $C_{29}H_{36}Cl_2N_4O_8$: C, 54.46; H, 5.67. Found: C, 54.34; H, 5.45.

7,16-Bis(8-hydroxyquinoline-2-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (13). (Scheme 2) Diaza-18-crown-6 (1.00 g, 3.82 mmol), 8-hydroxyquinoline-2-carboxaldehyde (1.45 g, 8.40 mmol), and sodium triacetoxyborohydride ($NaBH(OAc)_3$, 2.45 g, 11.5 mmol)) in 80 mL of 1,2-dichloroethane (DCE) were stirred at room temperature under an N_2 atmosphere for 12 h. The reaction was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with $CHCl_3$. The $CHCl_3$ extract was dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (60−200 mesh) using CH_2Cl_2/MeOH/NH_4OH (40/5/1) as eluent. Compound **13** (1.70 g, 77%) was isolated as an yellow solid: mp 118−120 °C; ^{1}H NMR ($CDCl_3$) δ 2.94 (t, J = 5.6 Hz, 8H), 3.62 (s, 8H), 3.67 (t, J = 5.6 Hz, 8H), 4.02 (s, 4H), 7.14 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 54.7, 62.0, 70.1, 71.0, 110.2, 117.8, 122.1, 127.3, 127.7, 136.5, 137.6, 152.3, 158.8; HRMS calcd for $C_{32}H_{40}N_4O_6$ $(M + Na)^+$ 599.2846, found 599.2853. Anal. Calcd for $C_{32}H_{40}N_4O_6$: C, 66.65; H, 6.99. Found: C, 66.46; H, 7.03.

7,16-Bis(3-(5-chloro-2-hydroxyphenyl)pyrazol-1-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (14). (Scheme 2) *N*,*N*′-Bis(methoxymethyl)diaza-18-crown-6 (**7**) (1.00 g, 2.85 mmol) and 4-chloro-2-(1*H*-pyrazol-3-yl)phenol (1.22 g, 6.27 mmol) were refluxed in 50 mL of toluene for 20 h. The solvent was evaporated under reduced pressure, and a small amount of MeOH was added. The mixture was sonicated for 20−30 min. The resulting solid was collected by filtration and dried to give 1.93 g (98%) of **14** as a white solid: mp 117−118 °C; ^{1}H NMR ($CDCl_3$) δ 2.89 (t, J = 5.0 Hz, 8H), 3.67 (m, 16H), 5.20 (s, 4H), 6.58 (d, J = 2.4 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 7.13 (dd, J = 2.6, 8.8 Hz, 2H), 7.49 (d, J = 2.4 Hz, 2H), 7.61 (d, J = 2.4 Hz, 2H), 10.95 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 52.4, 70.2, 70.3, 70.7, 102.1, 118.3, 118.5, 124.1, 125.9, 128.8, 131.7, 150.3, 154.6; HRMS calcd for $C_{32}H_{40}Cl_2N_6O_6$ $(M + Na)^+$ 697.2284, found 697.2277. Anal. Calcd for $C_{32}H_{40}Cl_2N_6O_6$: C, 56.89; H, 5.97. Found: C, 57.06; H, 5.92.

Determination of Thermodynamic Quantities. Values of log K, ΔH, and $T\Delta S$ were determined as described earlier[16] in absolute MeOH solutions at 25.0 ± 0.1 °C by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20-mL reaction vessel. The method used to process the calorimetric data and to calculate the log K and ΔH values has been described.[17]

UV−Visible Spectral Measurements. UV−visible spectra were recorded at 23 ± 1 °C in a 1-cm quartz cell by using a Hewlett-Packard 8453 spectrophotometer. Absolute MeOH was used as the solvent.

Acknowledgment. This research was supported by the Office of Naval Research.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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