Syntheses of Diaza-18-Crown-6 Ligands Containing Two Units Each of 4-Hydroxyazobenzene, Benzimidazole, Uracil, Anthraquinone, or Ferrocene Groups

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Six new diaza-18-crown-6 ligands each containing two aromatic side arms with responsive functions were prepared. Diaza-18-crown-6 containing two 4-hydroxyazobenzene (**3**) or two 4-hydroxy-4'-(dimethylamino)azobenzene (**4**) substituents were prepared *via* a one-pot Mannich reaction. Diaza-18-crown-6 containing two benzimidazole (**5**), two uracil (**6**) or two 9,10-anthraquinone (**7**) substituents were prepared by treating the diazacrown with the appropriate chloromethyl-containing compound. Reductive amination using sodium triacetoxyborohydride, diaza-18-crown-6 and ferrocenecarboxaldehyde was used to prepare bisferrocene-substituted diaza-18-crown-6 (**8**). Interactions of compounds **3**, **5**, and **6** with Na^+, K^+, Ba^{2+}, Ag^+, and Cu^{2+} were evaluated by a calorimetric titration technique at 25° in methanol. All three ligands form more stable complexes with Ag^+ and Cu^{2+} (**5** forms a precipitate with Ag^+) than with Na^+ and K^+. Ligand **5** also forms a highly stable complex with Ba^{2+}.

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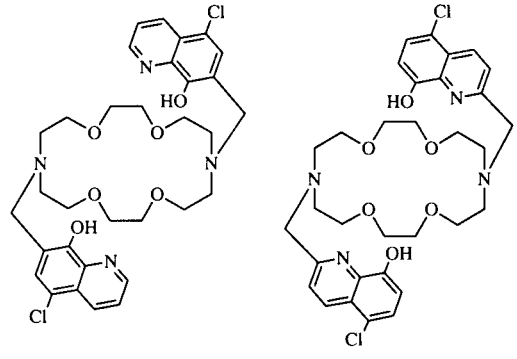
Introduction.

We are interested in developing ion-selective chemosensors to monitor metal ion concentrations in a variety of aqueous solutions. Chemosensors are small molecules that bind selectively the desired analyte with measurable concomitant changes in the physical properties of the system. Chemosensors have been studied in which complexation has been shown by changes in fluorescence [1,2], uv-vis absorption spectra [3,4] or redox potentials [5]. In an effort to develop new selective chemosensors for metal ions, we have prepared macrocycles appended with chelating fluorophores, chromophores or ferrocene units. The macrocyclic portions of the new compounds are expected to provide ion-selective binding while the appended groups offer measurable changes in photophysical or redox properties indicating ion complexation.

For example, 8-hydroxyquinoline-containing ligand **1** (Figure 1), with the 8-hydroxyquinoline attached through its position 7, is selective for Mg^{2+} over other alkali and alkaline earth cations [6]. Ligand **1** can serve as an effective chemosensor for Mg^{2+} as it has a very strong luminescence band at 540 nm even in the presence of higher concentrations of other alkali and alkaline earth cations [7]. Ligand **2**, on the other hand, with the 8-hydroxyquinoline attached through its position 2 forms only a weak complex with Mg^{2+} but it exhibits remarkable selectivity for K^+ and Ba^{2+} over other metal ions. Indeed, **2** formed a pseudocryptand when complexed with Ba^{2+} as shown by the ^1H nmr spectrum and an X-ray crystal structure [6].

The azacrown ethers containing various aromatic substituents are generally prepared by treating the azacrown with the halomethyl-substituted aromatic compound. The Mannich reaction has also been used to attach various phenolic compounds to the azacrown ethers [6b,8]. Aromatic substituents have also been attached to azacrown ethers by reductive amination using a suitable aromatic aldehyde [9].



1 **2**

Figure 1

In this paper, we describe the syntheses of diaza-18-crown-6 ligands containing two units each of 4-hydroxyazobenzene (**3** and **4**), benzimidazole (**5**), uracil (**6**), 9,10-anthraquinone (**7**) or ferrocene (**8**) groups (Scheme 1). Ligands **3** and **4** were prepared by the Mannich reaction, **5**-**7** by treating the diazacrown with the appropriate chloromethyl-containing compound and **8** by reductive amination using ferrocenecarboxaldehyde. Complexation studies showing that ligands **3**, **5**, and **6** form stable complexes with Ag^+ and Cu^{2+} are also included.

Results and Discussion.

Most chromoionophores designed to be selective for metal ions are of the proton-ionizable type [10]. Interaction of the proton-ionizable group with a complexed metal ion is reflected by changes in the optical properties of the chromoionophore. In addition, the deprotonated form can form

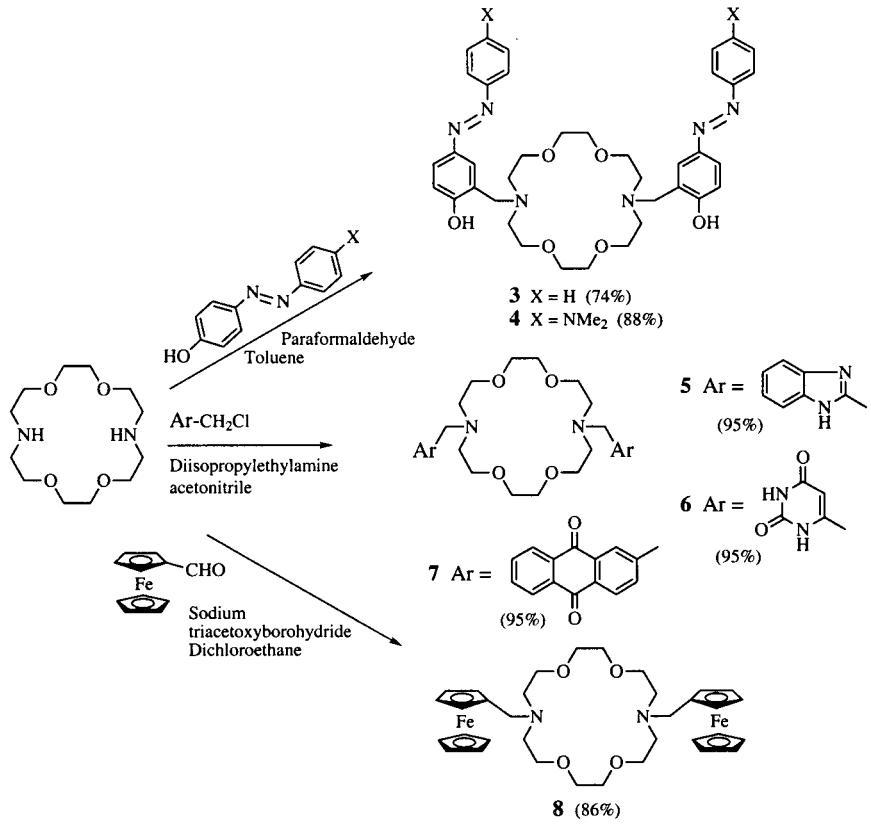
stronger complexes with metal ions than the neutral form. The azobenzene-type chromoionophores have often been used to signal interaction of metal ions with macrocycles [11]. Ligands **3** and **4** (Scheme 1) combine the complexation properties of proton- ionizable macrocyclic ligands with the signaling properties of the azobenzene chromoionophore. These types of compounds have been prepared by first attaching phenol derivatives onto the azacrown followed by reaction with the appropriate diazonium salt [12, 20a]. Performing a coupling reaction on two phenol groups attached to a diazacrown ether would be much less efficient than attaching an already formed azo compound. For this reason, we attached 4-phenylazophenol and 4-hydroxy-4'-(dimethylamino)azobenzene to diaza-18-crown-6 by means of a one-pot Mannich reaction [13] to give **3** and **4**, respectively (Scheme 1).

interesting intermolecular hydrogen bonding behavior [15]. The uracil units were attached by treating diaza-18-crown-6 with 6-(chloromethyl)uracil to form **6** as shown in Scheme 1.

9,10-Anthraquinone and ferrocene are well-known electroactive molecules. These molecules can serve as redox-switchable groups which may alter the complexing ability of the attached azacrown ligands [16]. Anthraquinone is a neutral to anionic redox switch while ferrocene is a neutral to cationic redox switch [17a]. Reduction of the anthraquinone moiety leads to excess negative charge and enhanced binding to metal ions [18]. Oxidation of ferrocene [Fe(II) → Fe(III)] causes a repulsive positive charge in proximity to the bound cation which would diminish the cation affinity of the macrocycles containing attached ferrocene units [17a].

Ligand **7** containing two 9,10-anthraquinone units was synthesized by treating diaza-18- crown-6 with 2-(chloro-

Scheme 1. Synthesis of Diaza-18-crown-6 Containing Two Side Arms



Benzimidazole in the neutral form shows an emission band near 290 nm, whereas the protontated form emits a broad structureless band with a maximum near 360 nm [14]. We expect that interaction of a benzimidazole-linked macrocyclic ligand such as **5** (Scheme 1) with a cation would result in an alteration of the emission maximum. Ligand **5** was prepared by treating diaza-18-crown-6 with 2-(chloromethyl)-benzimidizole in acetonitrile in the presence of *N,N*-diisopropylethylamine. Uracil is a chromophore which also has

methyl)-9,10-anthraquinone in the presence of *N,N*-diisopropylethylamine in acetonitrile as shown in Scheme 1. Ligand **8** [17], on the other hand, was synthesized by an efficient reductive amination process [9]. Ferrocenecarboxaldehyde, diaza-18-crown-6, and sodium triacetoxyborohydride were stirred together for 12 hours to give **8** in an 86% yield. Pure **8** was isolated by sonicating the crude product in methanol followed by filtration. Separation by chromatography was not needed.

Interactions of ligands **3**, **5**, and **6** with Na^+, K^+, Ba^{2+}, Ag^+, and Cu^{2+} have been evaluated by a calorimetric titration technique [19] at 25° in absolute methanol 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. Because of the very low solubility of **4** and **7** in methanol, the thermodynamic quantities involving these two compounds were not evaluated. Ligand **6** has two uracil sidearms and shows weaker interaction with all metal ions studied than ligands **3** and **5**. All three ligands form more stable complexes with Ag^+ and Cu^{2+} (**5** and Ag^+ form a precipitate) than with Na^+ and K^+.

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

ligand	cation	log *K*	ΔH	$T\Delta S$
1 [a]	Na^+	2.89 Å 0.05	-14.1 Å 0.8	2.4
	K^+	3.39 Å 0.03	-24.4 Å 0.7	-5.0
	Ba^{2+}	3.60 Å 0.05	-11.6 Å 0.5	8.9
	Cu^{2+}	10.1 Å 0.1	-92.5 Å 0.6	-34.9
2 [a]	Na^+	3.74 Å 0.01	-26.4 Å 0.3	-5.1
	K^+	6.61 Å 0.03	-58.1 Å 0.1	-20.4
	Ba^{2+}	12.2 Å 0.4	-76.1 Å 0.7	-6.5
	Cu^{2+}	4.7 Å 0.2	-116 Å 4	-89
3	Na^+	2.44 Å 0.02	-16.3 Å 0.5	-2.4
	K^+	2.87 Å 0.06	-27.8 Å 0.8	-11.4
	Ba^{2+}	4.24 Å 0.07	-32.6 Å 0.8	-8.4
	Ag^+	6.60 Å 0.05 [c]	-62.3 Å 0.6 [c]	-24.6
	Cu^{2+}	5.27 Å 0.08	-66.8 Å 0.8	-36.7
5	Na^+	3.25 Å 0.03	-12.0 Å 0.7	6.55
	K^+	3.67 Å 0.02	-33.8 Å 0.6	-12.9
	Ba^{2+}	> 5.5	-26.3 Å 0.4	>5.1
	Ag^+	(Brown precipitate)		
	Cu^{2+}	> 5.5	-56.0 Å 0.7	>-24.6
6	Na^+	[b]		
	K^+	[b]		
	Ba^{2+}	[b]		
	Ag^+	4.96 Å 0.01	-51.8 Å 0.3	-23.5
	Cu^{2+}	4.18 Å 0.06	-55.0 Å 0.8	-31.1

[a] Reference 6b. [b] No measurable heat other than heat of dilution indicating that *H* or/and log *K* is small. [c] Quantities were determined by competitive calorimetric titration.

Hydroxyazobenzene-containing ligand **3** shows a high selectivity for Ag^+ (log $K = 6.60$) over Na^+, K^+, and Ba^{2+} and benzimidazole-containing ligand **5** shows high selectivities for Ba^{2+} (log $K > 5.5$) and Cu^{2+} (log $K > 5.5$) over Na^+ (log $K = 3.25$) and K^+ (log $K = 3.67$). The ^1H nmr spectrum of the **5**-Ba^{2+} complex suggests that the two benzimidazole rings and the macrocyclic ring are involved in complexation since nmr signals for one benzene hydrogen atom and various ring hydrogen atoms are shifted down field. Although the interactions of uracil-containing **6** with the metal ions are weaker than those of **3** and **5**, it still shows good selectivity for Ag^+ and Cu^{2+} over Na^+, K^+, and Ba^{2+}.

As compared with 8-hydroxyquinoline-containing ligand **2** [6], **5** likewise forms a highly stable complex with Ba^{2+} but the stability of the **5**-Cu^{2+} complex is higher than that of the **2**-Cu^{2+} one. Stability of Cu^{2+} complexes with **3** and **6** are much lower than that with 8-hydroxyquinoline-containing ligand **1** [6]. The K^+/Na^+ selectivity demonstrated by **3** and **5** is close to that by **1** but much less than that by **2**.

EXPERIMENTAL

The ^1H nmr spectra (300 MHz) and ^{13}C nmr spectra (75 MHz) were recorded in deutereochloroform or perdeutereodimethyl sulfoxide. Ionization (FAB) was used to record the high resolution mass spectra. Solvents and starting materials were purchased from commercial sources where available.

General Procedure A for the Syntheses of Compounds **3** and **4** Using the One-pot Mannich Reaction [13].

An anhydrous toluene solution (180 ml) of 4,13-diaza-18-crown-6 (1.0 g, 3.8 mmoles), paraformaldehyde (280 mg, 9.3 mmoles), and the appropriate phenol (9.1 mmoles) was refluxed for 20 hours. The solvent was evaporated under reduced pressure and a small amount of methanol was added. The mixture was sonicated for 20 to 30 minutes and the resulting solid was filtered and dried.

General Procedure B for the Synthesis of Compounds **5-7** [20].

4,13-Diaza-18-crown-6 (1.0 g, 3.8 mmoles), *N,N*-diisopropylethylamine (2.7 ml, 15.3 mmoles), and the appropriate compounds containing chloromethyl groups (8.4 mmoles) in 200 ml of acetonitrile were refluxed for 12 hours and cooled to room temperature. After standing overnight, the precipitate was filtered and dried. The product was further purified by sonication in a small amount of methanol followed by filtration and drying.

7,16-Bis(2-hydroxy-5-(phenylazo)benzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**3**).

Compound **3** was prepared by general procedure A from 4-phenylazophenol to give a light yellow solid, mp 111-113°; yield 74%; ^1H nmr: δ 2.92 (t, J = 5.2 Hz, 8H), 3.63 (s, 8H), 3.70 (t, J = 5.2 Hz, 8H), 3.93 (s, 4H), 6.94 (d, J = 8.5 Hz, 2H), 7.47 (m, 6H), 7.65 (d, J = 2.0 Hz, 2H), 7.84 (m, 6H); ^{13}C nmr: δ 54.0, 58.6, 69.1, 71.0, 117.1, 122.6, 123.0, 123.1, 125.5, 129.2, 130.3, 146.0, 153.0, 161.7; hrms Calcd. for $C_{38}H_{46}N_6O_6$ $(M+Na)^+$ 705.3357. Found: 705.3386.

Anal. Calcd for $C_{38}H_{46}N_6O_6$: C, 66.84; H, 6.79. Found: C, 67.09; H, 6.75.

7,16-Bis(2-hydroxy-5-(4'-dimethylaminophenylazo)benzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**4**).

Compound **4** was prepared by general procedure A from 4-hydroxy-4'-(dimethylamino)azobenzene to give a yellow solid, mp 185-186°, yield 88%; ^1H nmr: δ 2.90 (t, J = 5.2 Hz, 8H), 3.06 (s, 12 H), 3.63 (s, 8H), 3.56 (d, J = 5.2 Hz, 8H), 3.91 (s, 4H), 6.75 (d, J = 9.0 Hz, 4H), 6.91 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 2.2 Hz, 2H), 7.74 (dd, J = 2.2, 8.5 Hz, 2H), 7.81 (d, J = 9.0 Hz, 4H); ^{13}C nmr: δ 40.6, 54.0, 58.8, 69.2, 71.0, 111.8, 116.9, 122.3, 122.9, 124.5, 124.5, 143.9, 146.4, 152.1, 160.3; hrms Calcd. for $C_{42}H_{56}N_8O_6$ $(M+Na)^+$: 791.4221. Found: 791.4204.

Anal. Calcd. for $C_{42}H_{56}N_8O_6 \cdot 0.5H_2O$: C, 64.84; H, 7.38. Found: C, 64.80; H, 7.26.

7,16-Bis(benzimidazol-2-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**5**).

Compound **5** was prepared by general procedure B from 2-(chloromethyl)benzimidazole to give a light yellow solid, mp 213-215°, yield 95%; ^{1}H nmr: δ 2.82 (bs, 8H), 3.52 (m, 16H), 4.08 (s, 4H), 7.15 (s, 4H), 7.36 (s, 2H), 7.68 (s, 2H), 11.64 (s, 2H); ^{13}C nmr: δ 54.3, 56.4, 69.3, 70.5, 111.3, 119.0, 121.9, 122.0, 134.3, 143.8, 154.5; hrms Calcd. for $C_{28}H_{38}N_6O_4$ $(M+Na)^+$ 545.2833. Found: 545.2860.

Anal. Calcd. for $C_{28}H_{38}N_6O_4$: C, 64.35; H, 7.33. Found: C, 64.41; H, 7.22.

7,16-Bis(uracil-6-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**6**).

Compound **6** was prepared by general procedure B from 6-(chloromethyl)uracil (dissolved in a small amount of dimethylformamide) to give a light yellow solid, mp 233-235°, yield 95%; ^{1}H nmr: δ 2.72 (m, 8H), 3.42 (s, 2H), 3.52 (m, 16H), 5.52 (s, 4H), 10.26 (s, 2H), 10.89 (s, 2H); ^{13}C nmr: δ 53.9, 54.8, 68.9, 69.7, 97.5, 151.4, 155.2, 164.2; hrms Calcd. for $C_{22}H_{34}N_2O_6$ $(M+H)^+$ 511.2518. Found: 511.2520.

Anal. Calcd. for $C_{22}H_{34}N_6O_8$: C, 51.76; H, 6.71. Found: C, 52.00; H, 6.66.

7,17-Bis(9,10-anthraquinon-2-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**7**).

Compound **7** was prepared by general procedure B from 2-(chloromethyl)-9,10-anthraquinone to give a light yellow solid, mp 174-175°, yield 95%; ^{1}H nmr: δ 2.87 (t, J = 5.6 Hz, 8H), 3.64 (s, 8H), 3.68 (t, J = 5.6 Hz, 8H), 3.88 (s, 4H), 7.79 (m, 6H), 8.24 (m, 8H); ^{13}C nmr: δ 54.2, 59.6, 70.0, 70.9, 126.9, 127.1, 127.3, 132.3, 133.3, 133.5, 133.5, 133.9, 134.0, 134.3, 147.7, 182.9, 193.2; hrms Calcd. for $C_{42}H_{42}N_2O_8$ $(M+Na)^+$ 725.2818. Found: 725.2839.

Anal. Calcd. for $C_{42}H_{42}N_2O_8$: C, 71.78; H, 6.02. Found: C, 72.00; H, 6.42.

7,16-Bisferrocenylmethyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**8**).

4,13-Diaza-18-crown-6 (1.0 g, 3.8 mmoles) and ferrocenecarboxaldehyde (1.72 g, 8.02 mmoles) were mixed in 1,2-dichloroethane (30 ml) and then treated with sodium triacetoxyborohydride (2.45 g, 11.5 mmoles) [9]. The mixture was stirred at room temperature under a nitrogen atmosphere for 12 hours. The reaction was quenched by adding aqueous saturated sodium bicarbonate and the product was extracted with chloroform. The chloroform extract was dried and the solvent was evaporated. A small amount of methanol was added to the crude product and the mixture was sonicated for 30 minutes. The deposit was filtered, washed with cold methanol, and dried to give pure compound **8**, a dark yellow solid, in an 86% yield. The mp and nmr spectra data were identical with those reported [17a].

Determination of Thermodynamic Quantities.

Values of log *K*, Δ*H*, and TΔ*S* were determined as described earlier [19] in absolute methanol solutions at 25.0 ± 0.1° by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20-ml reaction vessel. The metal ion solutions were titrated into the macrocyclic ligand solutions and the titrations were carried out to a 2-fold excess of the metal ions. The titration experiments showed that all interactions studied had a 1:1 cation-ligand ratio. The methods used to process the calorimetric data and to calculate the log *K* and *H* values have been described [21].

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