A New Highly Selective Macrocycle for K$^+$ and Ba^{2+}: Effect of Formation of a Pseudo Second Macroring through Complexation

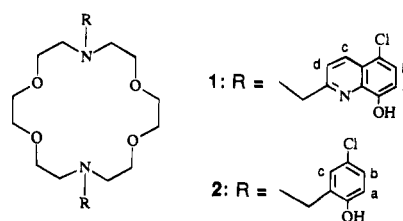**Xian Xin Zhang, Andrei V. Bordunov, Jerald S. Bradshaw, N. Kent Dalley, Xiaolan Kou, and Reed M. Izatt***

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Abstract: A new macrocyclic compound capable of forming a pseudo second macroring upon complexation has been characterized. The compound, 5-chloro-8-hydroxyquinoline (CHQ)-substituted diaza-18-crown-6 (**1**), exhibits unique complexing properties. log K values for the formation of K$^+$ and Ba^{2+} complexes with **1** in methanol are larger than those for the K$^+$ and Ba^{2+} complexes with all other lariat ethers. The log K value for the **1**-Ba^{2+} complex is the same magnitude as that of the cryptand [2.2.2]−Ba^{2+} complex. Selectivity factors for Ba^{2+} over other alkaline-earth cations and for K$^+$ over Na$^+$ in methanol are $> 10^7$ and $\sim 10^3$, respectively, which are the highest factors ever reported for lariat ethers. Moreover, the selectivity of **1** for Ba^{2+} over other alkaline-earth cations is larger than that of any other cryptand studied to date. UV−visible, ^{1}H NMR spectral, and X-ray crystallographic studies indicate that a pseudo second macroring is formed through $\pi−\pi$ interaction between the two CHQ rings upon complexation with K$^+$ and Ba^{2+}. This effect results in a cryptate-like structure and therefore highly stable complexes with high selectivity for these cations.

Although macrocyclic ligands bearing pendant arm(s) (lariat ethers) retain the highly dynamic properties of monocyclic crown ethers,[1–3] they display much weaker interaction with metal ions than do the macrobicyclic cryptands.[4,5] This is understandable since a lariat ether has only one macroring and usually does not form a second macroring upon complexation. In addition, the flexible lariat ethers can easily modify their conformation to accommodate different sizes of guest molecules resulting in lower selectivities than those found with cryptands.[5,6] If two pendant arms of a lariat ether interact with each other during complexation, a second macroring could form. The resulting complex would resemble a cryptate and should have the high stability of cryptate complexes. However, with one exception,[7] lariat ethers have not been shown to form an additional macroring when coordinated with a cation. The crystal structure of the K$^+$ complex of bis(phenanthridine)-substituted diaza-18-crown-6 revealed that the two phenanthridine rings were stacked together.[7] No quantitative evaluation was made for cation interaction with this lariat ether.

We now report the interaction of alkali and alkaline-earth metal ions with a new diaza-18-crown-6 ligand (**1**) bearing two 5-chloro-8-hydroxyquinoline (CHQ) side arms. Since 8-hydroxyquinoline forms a stable five-membered chelate ring with a metal cation,[8] **1** should display strong complexing ability. In addition, the two CHQ rings could interact through stacking to form a pseudo second macroring similar to the aforementioned two phenanthridine rings.[7] The results presented here show interaction between the two CHQ rings upon complexation. This effect results in not only K$^+$ and Ba^{2+} complexes with stabilities similar to those of their cryptate complexes but also unexpectedly high selectivities for these cations.

Experimental Section

Materials. Compound **1** was prepared by treating 1,10-diaza-18-crown-6 with 5-chloro-8-methoxy-2-(bromomethyl)quinoline followed by cleaving the methyl protecting group with LiCl in DMF at 130 °C.[9] Compound **2**, the bis(4-chlorophenol) analog of **1**, was prepared by treating *N,N′*-bis(methoxymethyl)diaza-18-crown-6 with 4-chlorophenol in refluxing benzene.[9] Reagent grade chemicals were obtained from the indicated sources and used without further purification: NaBr (J. T. Baker), KBr (Wasatch), CsCl (Fisher), Mg(ClO$_4$)$_2$ (Allied), CaCl$_2$· 2H$_2$O (Spectrum), SrBr$_2$ (Spectrum), and BaBr$_2$ (Johnson Matthey).

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The methanol (MeOH) was of HPLC grade (Fisher) and had a water content of less than 0.05%.

Determination of Thermodynamic Quantities. log K, ΔH, and $T\Delta S$ values were determined as described earlier[10] in MeOH at 25.0 ± 0.1 °C by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20-mL reaction vessel. The metal ion solutions were titrated into the lariat ether solutions and the titrations were carried out to a 2-fold excess of the metal ions. Thermodynamic quantities for K^+ and Ba^{2+} interactions with **1** were determined by a cation competition technique.[11] ΔH values for these interactions were also evaluated from a direct titration. The results showed that the ΔH values obtained by direct and competitive titrations were in good agreement. The method used to process the calorimetric data and to calculate the log K and ΔH values has been described.[12]
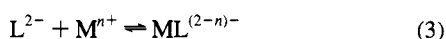
^{1}H NMR and UV–Visible Spectral Measurements. ^{1}H NMR spectra were recorded using a Varian Gemini 200 (200 MHz) spectrometer at 25.0 ± 0.1 °C in DMSO-d_6. Tetramethylsilane (TMS) was used as the internal standard. Deuterated DMSO was used since the OH proton signals could be observed in this solvent. **1** clearly showed an OH peak at δ = 9.80 ppm. However, a preliminary experiment showed that the ^{1}H NMR signal of the OH group of **2** overlapped the water signal in DMSO (δ = 3.35 ppm[13]). Therefore, the DMSO solvent was treated with 3A molecular sieves in order to remove the traces of water. The water content was monitored by taking the solvent ^{1}H NMR spectrum until the water peak was negligible.

UV–visible spectra were recorded at 25 ± 1 °C in a 1-cm quartz cell by using a Hewlett-Packard 8452A diode array spectrophotometer. Absolute MeOH was used as the solvent.

Complexation Equilibria. For interactions of metal ions with CHQ- and 4-chlorophenol-containing diaza-18-crown-6 ligands (**1** and **2**), two types of reactions may be considered due to the possibility of deprotonation of the phenol groups. If the phenol groups are not deprotonated, the complexation can be expressed as

$$H_2L + M^{n+} \rightleftharpoons H_2ML^{n+} \tag{1}$$
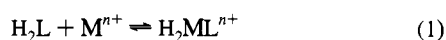
where H_2L represents **1** or **2** and M^{n+} a cation. On the other hand, if the phenol OH groups are deprotonated during complexation, two reactions should be considered:

$$H_2L \rightleftharpoons 2H^+ + L^{2-} \tag{2}$$

$$L^{2-} + M^{n+} \rightleftharpoons ML^{(2-n)-} \tag{3}$$

Thermodynamic, ^{1}H NMR and UV–visible spectral, and crystal structure data indicated that the complexation occurred according to eq 1, i.e., the phenol groups of **1** and **2** were not deprotonated. A calorimetric measurement showed that a change in ligand concentrations had no effect on thermodynamic quantities. log K, ΔH, and $T\Delta S$ values measured for the interaction of **1** with Na^+ in MeOH were identical at the different concentrations of **1** (from 1.6×10^{-3} to 3.5×10^{-3} M).[14,15] ^{1}H NMR spectra showed the OH proton signals of the CHQ of **1** and of the phenol of **2** in the vicinity of 10 ppm and 3.3 ppm in DMSO, respectively, for both free and complexed ligands (see Figures 1 and 2). These OH peaks were confirmed by D_2O exchange reactions.[13,16c]

Figure 1. ^{1}H NMR spectra of free **1** and its Na^+ and Ba^{2+} complexes in DMSO. Peak assignments are shown for aromatic and OH protons. The peaks labeled with an asterisk are attributed to the solvent.

Figure 2. ^{1}H NMR spectra of free **2** and its Na^+ and K^+ complexes in DMSO. Peak assignments are shown for aromatic and OH protons. The peaks labeled with an asterisk are attributed to the solvent.

When two drops of D_2O were added, the OH peaks disappeared. The crystal structures of the $1-Ba^{2+}$ and $2-Ba^{2+}$ complexes showed the presence of two bromide ions for each complex which indicated conclusively that the phenol groups were not deprotonated.[9] UV–visible spectra also provided evidence for this point (see UV–visible section below).

The pK values of the OH groups of 4-chlorophenol and 5-chloro-8-hydroxyquinoline have been reported as 9.2[16] and 9.28,[17] respectively, in aqueous solution at 25 °C. These pK values indicate that the compounds are very weak acids in aqueous solution. This is probably the main reason that the OH groups of the chlorophenol and CHQ substituents of **1** and **2** do not deprotonate in MeOH during complexation with the metal ions studied here.

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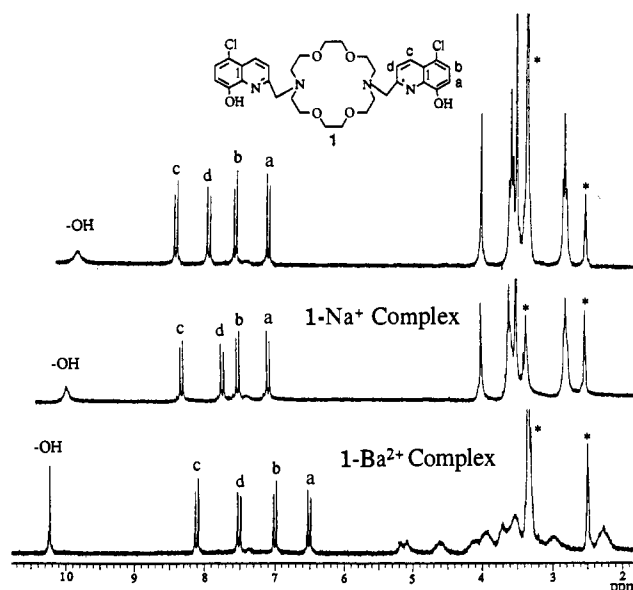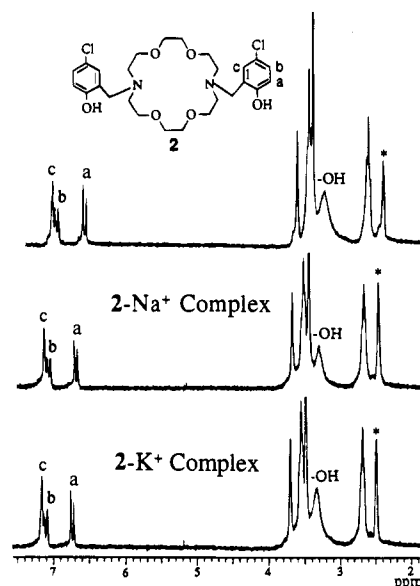
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Table 1. log K, ΔH (kJ·mol⁻¹), and $T\Delta S$ (kJ·mol⁻¹) Values[a] for Interactions of Quinoline- and Phenol-Substituted Diaza-18-crown-6 Ligands with Cations in Methanol at 25.0 °C

	1			**2**		
cation	log K	ΔH	$T\Delta S$	log K	ΔH	$T\Delta S$
Na⁺	3.74 ± 0.01	−26.4 ± 0.3	−5.1	2.85 ± 0.03	−16.0 ± 0.6	0.3
K⁺	6.61 ± 0.03[b]	−58.1 ± 0.1	−20.4	2.76 ± 0.04	−24.1 ± 0.5	−8.4
Cs⁺	2.70 ± 0.08	−36.9 ± 0.8	−21.5	c		
Mg²⁺	c			c		
Ca²⁺	4.71 ± 0.05	−25.2 ± 0.7	1.7	4.48 ± 0.07	−3.3 ± 0.5[b]	22.3
Sr²⁺	4.67 ± 0.04	−24.6 ± 0.3	2.1	<2		
Ba²⁺	12.2 ± 0.4[b]	−76.1 ± 0.7	−6.5	3.52 ± 0.06	−32.2 ± 0.5	−12.2

[a] Values are the averages taken from two to four determinations. Uncertainties are given as standard deviations. [b] Quantities were determined by competitive calorimetric titration. [c] No measurable heat other than heat of dilution indicating that ΔH and/or log K is small.

Table 2. Chemical Shifts δ (ppm)[a] of 5-Chloro-8-hydroxyquinoline and 4-Chlorophenol Groups of Free and Complexed Macrocycles **1** and **2** and Cation-Induced Shifts (CIS)[b] in DMSO at 25.0 °C

	1					**2**			
cation	H_a	H_b	H_c	H_d	H_{OH}	H_a	H_b	H_c	H_{OH}
none	7.055	7.521	8.376	7.896	9.798	6.719	7.117	7.171	3.325
Na⁺	7.076	7.506	8.313	7.724	9.985	6.732	7.115	7.175	3.338
	(−4.20)	(3.0)	(12.6)	(34.4)	(−37.4)	(−2.59)	(−0.42)	(−0.82)	(−2.60)
K⁺	6.407	6.992	7.929	7.285	9.308	6.744	7.121	7.174	3.335
	(129.6)	(105.9)	(89.4)	(122.3)	(98.0)	(−5.07)	(−0.86)	(−0.54)	(−2.00)
Ba²⁺	6.497	7.001	8.105	7.512	10.206	6.741	7.121	7.177	3.353
	(111.6)	(104.0)	(54.2)	(76.9)	(−81.6)	(−4.40)	(−0.86)	(−1.20)	(−5.60)

[a] Concentrations of the ligands were 0.01 M and those of the metal ions were 0.04~0.08 M. [b] CIS (Hz) = 200 [δ_{lig} (ppm) − δ_{compl} (ppm)]. The CIS values (in Hz) are in parentheses. A minus value indicates a downfield shift while a positive value indicates an upfield shift.

Results and Discussion

Thermodynamic Quantities. log K, ΔH, and $T\Delta S$ values for interactions of **1** and **2** with metal cations in MeOH at 25.0 °C are listed in Table 1. Comparing **1** with its phenol-substituted analog, **2**, two apparent differences in the cation-binding behavior are observed. First, **1** forms more stable complexes with alkali and alkaline-earth metal ions than does **2**. Weaker interactions in the case of **2** are a result of smaller enthalpy contributions. Second, **1** shows high selectivities for Ba²⁺ over all other cations studied and for K⁺ over Na⁺ and Cs⁺, while **2** shows no special selectivity among the metal cations. These facts show the importance of pendant arms on cation binding and selectivity. The CHQ arms of **1** have a larger π electron area than the phenols of **2** and the CHQs have nitrogen donor atoms. This allows **1** to exhibit better complexation properties. In fact, log K values for the formation of K⁺ and Ba²⁺ complexes with **1** are larger than those for K⁺ and Ba²⁺ complexes with all other lariat ethers.[4-6] The log K value for the **1**-Ba²⁺ complex (12.2 in MeOH) is the same magnitude as that of the cryptand [2.2.2]−Ba²⁺ complex (12.9 in MeOH[18,19]). Also, selectivity factors for Ba²⁺ over other alkaline-earth cations and for K⁺ over Na⁺ are >10⁷ and ~10³, respectively (Table 1) which are the highest factors ever reported for lariat ethers.[4-6] Moreover, the selectivity of **1** for Ba²⁺ is larger than that of any cryptand studied to date.[4,20]

The unique complexing properties of **1** are related to its peculiar molecular structure. Burton and Davis calculated the charge distributions for 8-hydroxyquinoline and its derivatives.[21] Their study showed that the phenol ring of CHQ is electron-rich and the pyridine ring electron-deficient. Therefore, π−π

interaction could occur between the two CHQ rings if the two rings approach each other in such a way that the pyridine part of the one CHQ overlaps the phenol part of the other CHQ. A possible way to bring the two CHQ rings together is through coordination with a cation that provides the correct template effect. The current study shows that K⁺ and Ba²⁺ provide this effect. Since **1** bears two CHQ rings, by complexation with K⁺ and Ba²⁺ the two CHQ substituents of **1** may overlap each other through π−π interaction so that a pseudo second macroring is formed. This effect results in a cryptate-like structure and, therefore, highly stable complexes. ¹H NMR and UV−visible spectral and X-ray crystallographic data support this conclusion.

¹H NMR Spectra. Chemical shifts of the CHQ and chlorophenol protons of free and complexed ligands **1** and **2** are listed in Table 2. The cations induce a change in chemical shifts of the aromatic protons. The amounts of cation-induced shifts (CIS) are different for the two macrocyclic ligands. In most cases, **1** shows large upfield while **2** shows small downfield or almost no shifts of the aromatic proton signals (Figures 1 and 2). The downfield shifts of the protons of **2** are a result of the electron-donating interaction of the phenol hydroxy group with the cations, which results in a magnetic deshielding effect.

Upfield shifts of aromatic proton signals can be caused by overlapping of the two aromatic rings. This results in a magnetic shielding effect.[22] Large upfield shifts of aromatic proton signals were observed in the K⁺ complex with the bis(phenanthridine)-substituted diaza-18-crown-6[7] and for pyridine[23] and bipyridine[24,25] protons when they overlap other aromatic units. Thus, the large upfield shifts of CHQ proton signals for the **1**-K⁺ and **1**-Ba²⁺ complexes are a result of π-stacking between the two CHQ rings when binding the cations

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from the same side of the diaza-crown ring. The complexes of this quasi cryptand are much like cryptate complexes.

Smaller CIS values of the 1-Na⁺ complex, as compared with the 1-K⁺ and 1-Ba²⁺ complexes (Table 2 and Figure 1), indicate that the effect of the CHQ ring overlapping is not significant for the 1-Na⁺ complex in DMSO. This observation is in agreement with the small log K value for 1-Na⁺ interaction. In addition, the CIS values of the 1-Na⁺ and all 2 complexes studied in DMSO are smaller than those in 2:8 CDCl₃/CD₃OD[9] probably due to weaker host−guest interactions in DMSO.[4] However, the K⁺ and Ba²⁺ complexes of 1 display large upfield shifts (>100 Hz) in DMSO as they do in 2:8 CDCl₃/CD₃OD,[9] which suggests again the $\pi-\pi$ overlapping between the two CHQ rings in the 1-K⁺ and 1-Ba²⁺ complexes.

Crystal Structures. Crystal structures of the complexes of 1-Ba²⁺ and 2-Ba²⁺ have been determined[26] and a detailed description of the structures will be reported elsewhere.[9] Several key structural features of the complexes are presented here. In the solid state structure of 1-Ba²⁺, the cation is coordinated by all oxygen and nitrogen atoms of the ligand (Figure 3a). This supports the observation of Fronczek and Gandour[27] that lariat ethers enforce a high coordination number for the cation. The eleventh coordination site of the Ba²⁺ is occupied by a water oxygen atom. The coordination of the Ba²⁺ by both CHQ arms brings the two aromatic bidentate groups close together so that $\pi-\pi$ interactions are possible. In both CHQ groups, the N and O donor atoms are involved in coordination of the cation forming stable five-membered rings. The two CHQ rings are nearly parallel. The dihedral angle between the least-squares planes of the aromatic groups is 13° with the electron-rich phenol rings overlapping the electron-deficient pyridine rings (see Figure 3a). The distance between the centers of the CHQ rings is 3.6 Å. These features of the solid state structure of the 1-Ba²⁺ complex are consistent with those of the solution structure of the complex as indicated by ¹H NMR studies.

The solid state structure of the 2-Ba²⁺ complex differs significantly from that of the 1-Ba²⁺ complex. The two phenol rings are far from each other (Figure 3b) and one of the phenol groups does not interact with the Ba²⁺. The Ba²⁺ is coordinated by the six donor atoms of the macroring of the ligand, a phenol oxygen atom of one lariat arm, a water oxygen atom, and an oxygen atom of DMF (one of the solvents used in crystallization). Interaction between the two phenol groups of 2 in the complex is unlikely because of geometric and electronic features. Each aromatic arm has only one donor atom and both arm aromatic groups are electron rich. The lack of interaction between the two phenol rings is also established in the solution state by the small downfield shifts of the ¹H NMR signals in DMSO and in 2:8 CDCl₃/CD₃OD.[9]

The presence of the bromide ions in the solid states of both 1-Ba²⁺ and 2-Ba²⁺ complexes indicates that the O−H protons are not ionized in the complexation process, which has also
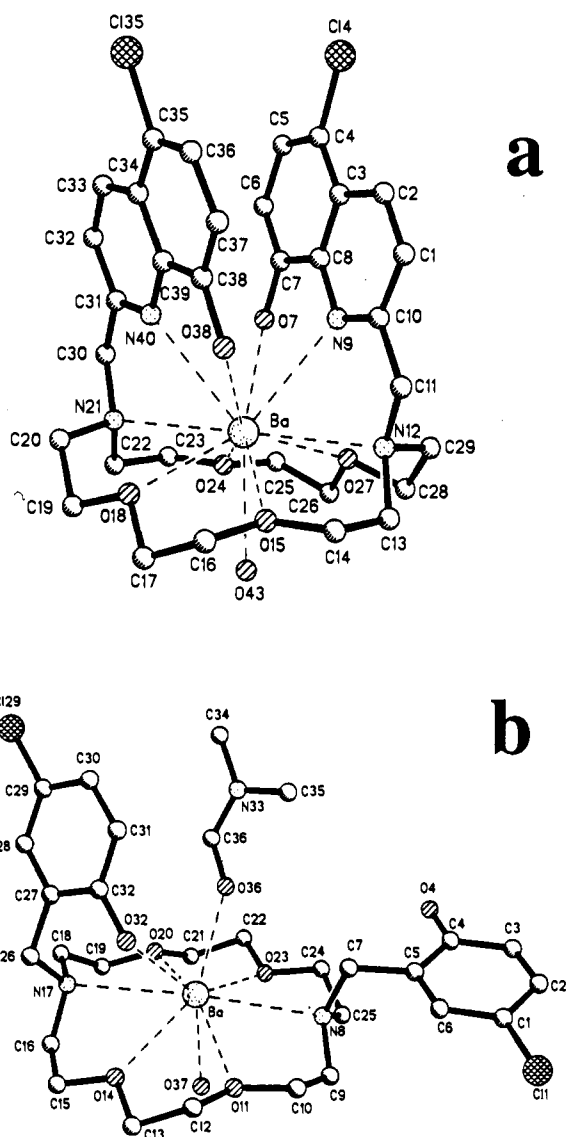
(26) Crystal data for 1-Ba²⁺: Ba[(C₃₂H₃₈N₄O₆Cl₂)(H₂O)]Br₂(2CHCl₃)·(disordered solvent molecule) [because the disordered solvent molecule could not be identified, it was not possible to calculate a formula weight or a density of 1-Ba²⁺]: triclinic, space group $P\bar{1}$ (No. 2); a = 10.655(4) Å, b = 11.907(5) Å, c = 19.789(9) Å, α = 84.74(3)°, β = 80.70(3)°, γ = 81.13(3)°; V = 2454 Å³; Z = 2; $R(F)$ = 0.054, $R_w(F)$ = 0.069. Crystal data for 2-Ba²⁺: Ba[(C₂₆H₃₆N₂O₆Cl₂)(C₃H₇NO)(H₂O)]Br₂; M = 931.7, monoclinic, space group $P2_1/c$ (No. 14); a = 11.664(6) Å, b = 9.717(5) Å, c = 33.064(11) Å, β = 91.06(3)°; V = 3747 Å³; D_{calcd} = 1.652 g cm⁻³; Z = 4; $R(F)$ = 0.060, $R_w(F)$ = 0.082. Experimental and structural data, positional and thermal parameters, bond lengths and angles and anisotropic thermal parameters will be deposited at Cambridge Crystallographic Data Center with data for related compounds all included in ref 9.

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Figure 3. Crystal structures of the 1-Ba²⁺ (a) and 2-Ba²⁺ (b) complexes. The hydrogen atoms, the two anions (Br⁻), and in the case of 1-Ba²⁺ the solvent molecules not involved in the coordination are omitted for clarity.

been verified by spectral data for the complexes in solution. The smaller log K value for the formation of the 2-Ba²⁺ complex in MeOH compared to that of 1-Ba²⁺ is due to fewer donor atoms of 2 and the lack of interaction between the two phenol rings. 2 has a maximum of eight donor atoms compared to the ten donor atoms of 1. It is not possible to extrapolate the role of the uncomplexed phenol oxygen atom in the solid state to the solution state. In the absence of solvent molecules containing a strong donor atom such as found in DMF, both phenol oxygen atoms could be involved in the coordination of the cation. In any case, however, the interaction of the phenol groups with the cation in the 2-Ba²⁺ complex is much weaker than that of the CHQ groups with the cation in the 1-Ba²⁺ complex because 2 has only one donor atom for each aromatic group and so the formation of stable five-atom chelate rings is not possible.
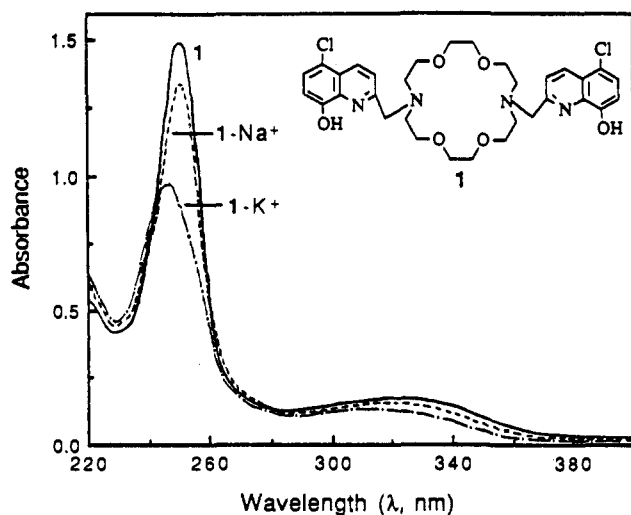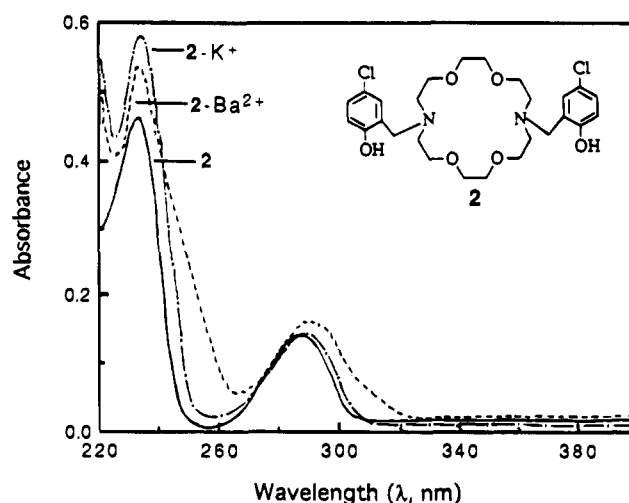
UV−Visible Spectra. UV−visible spectral data are listed in Table 3. Comparisons of absorption spectra of free and complexed ligands are shown in Figures 4 and 5. Kimura and co-workers observed an increase in UV absorption intensity for the bromophenol group of bromophenol-containing macrocycles as the ligands interacted with cations.[28] In our case, 2 shows

Table 3. UV–Visible Absorbance Peaks and Molar Absorptivity Values for Free and Complexed Macrocycles **1** and **2** in Methanol

compd	λ_{max} $(10^{-4}\epsilon,\ M^{-1}\ cm^{-1})$	λ_{max} $(10^{-4}\epsilon,\ M^{-1}\ cm^{-1})$	λ_{max} $(10^{-3}\epsilon,\ M^{-1}\ cm^{-1})$
1	204 (5.98)	249 (7.41)	319 (6.56)
1-Na⁺	207 (8.89)	248 (6.65)	318 (6.34)
1-K⁺	207 (9.21)	245 (4.42)	315 (4.96)
1-Ba²⁺	207 (9.37)	250 (3.90)	316 (4.87)
2	204 (3.66)	231 (1.57)	286 (4.21)
2-Na⁺	206 (6.37)	231 (1.72)	286 (4.32)
2-K⁺	206 (6.69)	231 (1.91)	286 (4.38)
2-Ba²⁺	207 (6.85)	231 (1.80)	290 (4.97)
In 0.01 M (CH₃)₄N⁺OH⁻ MeOH Solution:			
1-Na⁺	207 (9.82)	263 (5.79)	349 (6.51)
1-K⁺	207 (9.59)	262 (4.48)	346 (5.47)
2-Na⁺	206 (7.20)	247 (1.75)	305 (5.99)
2-K⁺	207 (7.18)	245 (2.08)	298 (5.83)

Figure 4. UV spectra of free and complexed **1** in MeOH: [**1**] = 2.04 × 10⁻⁵ M; [Na⁺] = 1.35 × 10⁻³ M; [K⁺] = 1.80 × 10⁻³ M.

Figure 5. UV spectra of free and complexed **2** in MeOH: [**2**] = 3.09 × 10⁻⁵ M; [K⁺] = 2.30 × 10⁻³ M; [Ba²⁺] = 2.16 × 10⁻³ M.

increased UV absorption intensity upon complexation with Na⁺, K⁺, and Ba²⁺ (Table 3 and Figure 5) indicating an interaction between the phenol substituent of the ligand and the cations. On the other hand, **1** exhibits a different UV behavior from that of **2** due to $\pi-\pi$ interaction between the two CHQ rings. The absorption intensity of the CHQ of free **1** at 249 and 319 nm decreases in its complexes with Na⁺, K⁺, and Ba²⁺ (Table 3 and Figure 4). Since $\pi-\pi$ overlapping can result in a decrease in UV absorption intensity of aromatic rings,[25] the UV spectra of the complexes of **1** provide an evidence for CHQ ring stacking.

In an alkaline solution ((CH₃)₄N⁺OH⁻), the chlorophenol and CHQ bands experience large bathochromic shifts (Table 3). For example, the absorption maxima of **1** at 249 and 319 nm shift to 263 and 349 nm, respectively, in the **1**-Na⁺ complex, and the absorption maxima of **2** at 231 and 286 nm shift to 247 and 305 nm, respectively, in the **2**-Na⁺ complex. The significant bathochromic shifts of these absorption bands are due to deprotonation of the phenol groups of **1** and **2** in the strong base medium. The resulting phenolate and oxinate ions cause an increase in electron density of the aromatic rings, which

results in the large bathochromic shifts of the UV bands and an enhancement in absorption intensity.[13] Because the absorption maxima of complexed **1** and **2** in the neutral MeOH exhibit small or no shifts from those of the free ligands (Table 3), the UV–visible spectral data demonstrate that the complexation with the cations in neutral MeOH solution does not deprotonate the phenols of **1** and **2**.

The absorption peak of phenols in the vicinity of 286 nm may be used as a criterion for complex formation.[28] Strong complexation usually results in a large change for this band in both absorption position and intensity. Compared with the **2**-Na⁺ and **2**-K⁺ complexes in neutral MeOH, the **2**-Ba²⁺ complex exhibits both increased absorption intensity at 290 nm and a bathochromic shift of the band (from 286 to 290 nm, the **2**-Na⁺ and **2**-K⁺ complexes have no shifts). Thus, the spectral data suggest a stronger interaction of **2** with Ba²⁺ than that of **2** with either Na⁺ or K⁺, which is consistent with the results of the thermodynamic studies.

Conclusion

$\pi-\pi$ interaction occurs between the two CHQ rings of the lariat ether **1** during the complexation with K⁺ and Ba²⁺. The resulting quasi cryptate complexes are very stable and K⁺ and Ba²⁺ are uniquely selected by the macrocycle. We believe that coordination of **1** with a cation whose size matches the pseudo three-dimensional cavity of the lariat ether induces the two CHQ rings to stack together to form a second macroring. Neither a large nor a small cation could form this quasi cryptate due to an unfavorable size relationship between the cation and the ligand. Thus, the CHQ-substituted macrocycle not only forms highly stable complexes with size-matched cations but also shows high selectivity for those cations.

(28) Kimura, E.; Kimura, Y.; Yatsunami, T.; Shionoya, M.; Koike, T. *J. Am. Chem. Soc.* **1987**, *109*, 6212−6213.

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