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Evidence for Cryptand-like Behavior in Bibracchial Lariat Ether (BiBLE) Complexes Obtained from X-ray Crystallography and Solution Thermodynamic Studies

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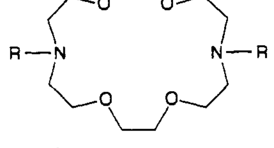
Abstract: Solution thermodynamic data (ΔH and $T\Delta S$ values), obtained using ion selective electrode techniques, have been determined and are presented for the Na^+ and K^+ complexes of three *N,N'*-disubstituted derivatives of 4,13-diaza-18-crown-6. They are the following: **1**, *N,N'*-bis(*n*-propyl); **2**, *N,N'*-bis(2-hydroxyethyl); and **3**, *N,N'*-bis(2-methoxyethyl). These data are correlated to X-ray crystal structure data for **2**·NaI, **2**·KI, **3**·NaI, and **3**·KI. The crystals of **3**·NaI·H_2O are triclinic space group $P\bar{1}$ with two molecules in the unit cell, dimensions: a = 9.5799 (12) Å, b = 10.3904 (13) Å, c = 12.7699 (13) Å, α = 90.362 (9)°, β = 97.090 (9)°, and γ = 94.489 (11)°. R = 0.033 for 3142 observed reflections.

The macrocyclic polyether compounds bearing one or more sidearms which we have called lariat ethers[1] were designed to be flexible and contain dynamic cation binders which would utilize the sidearm and macroring cooperatively. In previous studies of these systems, we have determined that they are, indeed, flexible structures which show enhanced binding (K_S) for cations like Na^+ and K^+ compared to simple, monocyclic crown ethers.[2] Solution binding studies,[3] C-13 NMR relaxation time studies,[4] and X-ray crystallographic[5] studies have all demonstrated that ring and side arm cooperate in cation binding when one or more donor groups are present as part of the latter. These flexible structures envelop cations in a three-dimensional sense and exhibit selectivities which are not directly correlated to the questionable "hole-size" concept.[2]

In order to assess the relative contribution of sidearm and macroring to overall binding strength, we have developed the method for measuring solution thermodynamic data which is presented in the preceding paper.[6] We have used this to study a carefully selected group of two-armed (bibracchial) lariat ethers (BiBLEs) based on the 4,13-diaza-18-crown-6 system;[7] and we compare those solution data directly to the solid-state crystal structures which are presented here. Cryptand-like behavior is exhibited by these BiBLE complexes in the solid state,[5] and a correlation of this structural information with solution thermodynamic data is presented.

Results and Discussion

BiBLEs based on the 4,13-diaza-18-crown-6 framework may be prepared by either single- or two-step approaches which we have outlined previously.[7] The compounds shown below and used in this study have been previously reported and fully characterized (see Experimental Section).[7]



1, R = $CH_2CH_2CH_3$
2, R = CH_2CH_2OH
3, R = $CH_2CH_2OCH_3$

The cation binding strengths, log K_S,[2,6] for the reaction

$$\text{ligand}_{(\text{solvated})} + \text{M}^+_{(\text{solvated})} = \text{complex}^+_{(\text{solvated})} \qquad (1)$$

were determined in anhydrous methanol solution at 25 °C and are shown in Table I along with the thermodynamic data. Lehn[8] has designated the values ΔH_C and ΔS_C as the enthalpies and entropies of complexation as characterized by the equation above. Note that in Table I, values designated ΔH_l and ΔS_l have also been included. Lehn refers to these as the enthalpies and entropies of ligation, that is, those for "transfer of the cation from the gas phase into the solvated ligand with formation of the differently hydrated (solvated) cryptate" complex (see eq 2).

$$\text{M}^+_{(\text{gas})} + \text{ligand}_{(\text{solvated})} = \text{complex}_{(\text{solvated})} \qquad (2)$$

Cation binding by either compound **2** or **3** is stronger than for **1**, which is expected because the former offer additional solvation in the form of sidearm donor groups which can afford the ring bound cation a three-dimensional array of binding sites. Such a situation is not possible with the *n*-propyl sidearms since no donor group is present in them. It seems likely that solvent or counteranion fills these apical voids. In any event, such an interpretation is largely enthalpic and parallels the reasoning commonly used in discussing cation binding affinities.

By using the ion-selective electrode-based method (see preceding paper)[6], we have obtained both enthalpies and entropies for these

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Table I. Thermodynamic Parameters for Macrocycles and Macrobicycles in Methanol

compd no.	ring size	sidearm	cation	log K_S	ΔH	$T\Delta S$	ΔH_1	$T\Delta S_1$	other[a]
1	18	$CH_2CH_2CH_3$	Na^+	2.86	-2.82 ± 0.05	1.08 ± 0.04	-113.8	-13.4	
1	18	$CH_2CH_2CH_3$	K^+	3.77	-6.28 ± 0.27	-1.14 ± 0.30	-96.6	-13.0	
2	18	CH_2CH_2OH	Na^+	4.83	-5.82 ± 0.12	0.76 ± 0.13	-116.8	-13.8	syn
3	18	CH_2CH_2OMe	Na^+	4.77	-7.24 ± 0.05	-0.73 ± 0.08	-118.2	-15.3	syn
2	18	CH_2CH_2OH	K^+	5.07	-8.80 ± 0.10	-1.89 ± 0.10	-99.1	-13.7	syn
3	18	CH_2CH_2OMe	K^+	5.52	-8.81 ± 0.03	-1.28 ± 0.02	-99.2	-13.1	anti
[2.2.2]	18, 18		Na^+	7.97[b]	-10.70	0.15	-120.7	-14.4	crypt
[2.2.2]	18, 18		K^+	10.61[b]	-17.06	-2.60	-107.4	-14.4	crypt

[a] Structure of cation complex. [b] The thermodynamic data were taken from Abraham, M. H.; de Namor, A. F. D.; Schulz, R. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, 869. log K_S values were calculated from the kinetic data in Shamsipur, M.; Popov, A. I. *J. Am. Chem. Soc.* **1979**, *101*, 4051.

various reactions. These values are presented in Table I along with data for [2.2.2]cryptand published previously.[9] Notice that for the Na^+ cation, ΔH_1 values for **2** and **3** are essentially the same. Likewise, ΔH_1 for K^+ is similar for these compounds. In general, ΔH_1 values for the Na^+ complexes are more negative than for the K^+ complexes. The average difference for $\Delta H_{1Na} - \Delta H_{1K}$ is −18.4 kcal/mol. This trend, which follows the values of the solvation enthalpies for these cations, is the same as that previously reported by Lehn for cryptate formation.[8] The negative ΔH_1 values clearly indicate that the ligands are sufficiently flexible to emulate solvent in its bulk behavior.

That enthalpies (ΔH_1) for sodium cation complexes are higher than for the corresponding potassium cation complexes seems incompatible with the observed equilibrium binding constants (log K_S values). Were it not for the effect of cation solvation during the complexation equilibrium, log K_S would be higher for Na^+ than for K^+.

In considering this problem, Lehn assessed ligand flexibility by plotting M^+–O bond distances in the complexes with the values expected from summing M^+ and O radii.[8] A completely flexible system is expected to exhibit a slope of 1, and Lehn's plot for [2.2.2]cryptand with Na^+, K^+, Rb^+, and Cs^+ showed a slope of "about 0.6". Unfortunately, we have crystal structure data only for Na^+ and K^+ complexes of **2** and **3** (see below), so our line will be both suspect and perfectly straight. Even so, it is interesting to note that ligands **2** and **3** with Na^+ and K^+ give "slopes" of 0.76. According to Lehn's interpretation, the BiBLEs must be more flexible than the crytands, a result confirmed by our previous C-13 NMR T_1 relaxation time studies.[4]

The $T\Delta S_1$ data for compounds **2**, **3**, and [2.2.2]cryptand range from −13.8 to −15.3. Of the six complexes for which data are available, five exist in the solid state as either a cryptate or pseudocryptate complex. The only exception is **3**·K^+ which exists in the anti conformation. It is the latter system which exhibits the lowest $T\Delta S_1$ value. The significance of this observation is currently unclear.

Lehn concludes that the cation binding by [2.2.2] to either Na^+ or K^+ is enthalpy driven. This is clear from the data in Table I wherein the highest log K_S values are for [2.2.2]·Na^+ and [2.2.2]·K^+. Our BiBLE complexes exhibit the same enthalpic driving force. Note that ΔH_1 for **2**·K^+ and **3**·K^+ are identical within experimental error, yet a substantial difference in the corresponding solution binding constants (log K_S) is observed. This difference is entropy driven. On the basis of the crystal structures observed for **2** and **3** with Na^+, one expects that the corresponding K^+ complexes will both assume the syn arrangement of sidearms. Instead, **2**·K^+ is syn and **3**·K^+ is anti.

X-ray Crystal Structure Data. The X-ray crystal structure of *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6·Na^+, **3**·Na^+, is shown in Figure 1. *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6, **2**, forms pseudocrypt complexes with both Na^+ and K^+ cations.[5] This is clear from the framework illustrations shown in Figures 3 and 4 (see below) in which only the cation and donor groups are drawn. The Na^+ and K^+ complexes of *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6, **3**, show different conformations in the solid state, as illustrated in Figure 2.

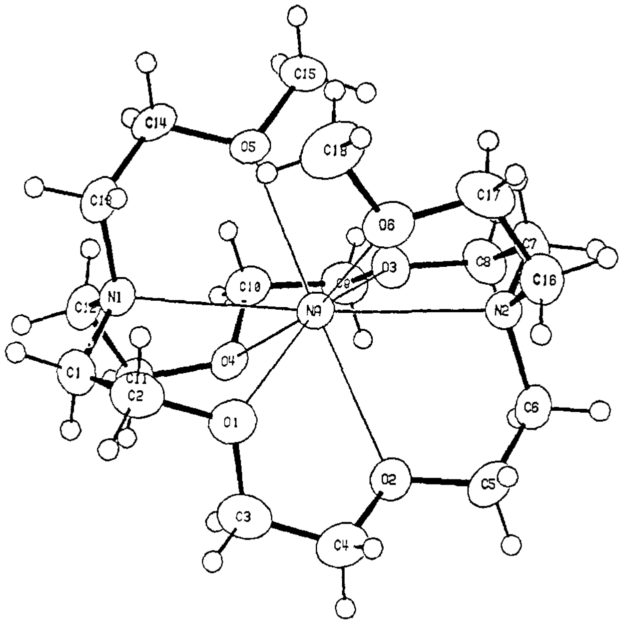

Figure 1. Perspective drawing of *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6, **3**, complexing sodium cation.

In Table II are presented the atomic positional parameters for sodium *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6 iodide monohydrate, (**3**·NaI·H_2O). Figure 1 presents the full structure of the complex while Figure 3b shows a skeletal drawing of its donor atoms and the metal ion. The skeletal drawing reveals that the macroring donor atoms adopt a "twist-boat" conformation. The oxygen atom in each sidearm occupies a "flagpole" position. The sodium ion lies on the line connecting the two nitrogens. The arrangement of all the donor atoms is reminiscent of a [2.2.2]-cryptate complex. Because the iodide ion is not coordinated to the metal ion, Na^+ is octacoordinated. The water molecule present in the crystal forms a hydrogen bond bridge between two iodide anions and is not in the coordination sphere of the cation. It is therefore not pictured in the figures.

Structural Comparison of BiBLE and Cryptate Complexes. When two sidearms are attached to a macroring, complexation may be augmented by ligation from the same or opposite sides of the macroring. When complexation occurs from the same side, the structures resemble macrobicyclic complexes. When complexation occurs from the opposite side, the structures resemble macrotricyclic complexes. The donor group arrangements in the sodium cation complexes of **2**, **3**, [2.2.2], and [2.2.1] are shown in Figure 3, and potassium cation complexes are illustrated in Figure 4. With the exception of **3**·KI, all the complexes have the syn conformation.

Both sodium cation complexes of **2** and **3** have the syn arrangement of the sidearms, and the macroring donors are in the twist-boat conformation. This conformation, seen for the macroring of simple crowns as well, better encapsulates the sodium cation, which is smaller than the potassium cation. The sidearm

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Table II. Coordinates for **3**·NaI·H_2O

atom	*x*	*y*	*z*
I	0.15594 (3)	0.34713 (3)	0.17665 (2)
Na	0.7084 (1)	0.8398 (1)	0.29437 (9)
O1	0.6752 (3)	0.8109 (3)	0.4899 (2)
O2	0.8084 (3)	1.0299 (2)	0.4198 (2)
O3	0.8282 (2)	0.8983 (2)	0.1374 (2)
O4	0.9583 (2)	0.7446 (2)	0.2890 (2)
O5	0.5918 (2)	0.6626 (2)	0.1748 (2)
O6	0.4441 (2)	0.8919 (3)	0.2779 (2)
N1	0.7314 (3)	0.5853 (3)	0.3703 (2)
N2	0.6619 (3)	1.0739 (3)	0.2176 (2)
C1	0.7297 (4)	0.5877 (4)	0.4855 (3)
C2	0.6387 (4)	0.6854 (4)	0.5218 (3)
C3	0.7884 (6)	0.8757 (5)	0.5492 (3)
C4	0.8025 (5)	1.0105 (4)	0.5279 (3)
C5	0.7755 (5)	1.1560 (4)	0.3901 (4)
C6	0.7671 (5)	1.1666 (4)	0.2746 (3)
C7	0.6814 (4)	1.0694 (4)	0.1054 (3)
C8	0.8165 (4)	1.0172 (4)	0.0851 (3)
C9	0.9556 (3)	0.8417 (4)	0.1226 (3)
C10	0.9587 (4)	0.7181 (4)	0.1797 (3)
C11	0.9838 (4)	0.6349 (3)	0.3522 (3)
C12	0.8600 (4)	0.5341 (3)	0.3422 (3)
C13	0.6031 (4)	0.5151 (3)	0.3172 (3)
C14	0.5816 (4)	0.5293 (3)	0.1993 (3)
C15	0.5601 (4)	0.6819 (4)	0.0645 (3)
C16	0.5184 (4)	1.1046 (4)	0.2305 (4)
C17	0.4111 (4)	0.9919 (5)	0.2086 (3)
C18	0.3379 (4)	0.7896 (5)	0.2693 (4)
O1W	0.1823 (3)	0.6089 (3)	0.9773 (3)

Table III. Comparison of Selected Structural and Binding Parameters of Sodium Complexes of BiBLEs and Cryptands

interaction	[2.2.2][a]	**3**	**2**[b]	[2.2.1][c]
M–O, Å	2.582	2.572	2.611	2.491
ring	2.582	2.582	2.437	2.499
	2.582	2.486	2.590	2.451
	2.566	2.669	2.564	2.519
	2.566			2.446
	2.566			
sidearm		2.488	2.426	
		2.614	2.588	
M–N, Å	2.782	2.838	2.630	2.703
	2.722	2.677	2.637	2.591
R, Å	1.19	1.19	1.14	1.10
N–M–N, deg	180	174.8	159.5	138.1
N–N, Å	5.504	5.509	5.183	4.944
coordn no.	8	8	8	7
log K_S	7.98[d]	4.75[e]	4.87[e]	9.65[d]

[a] Reference 12. [b] Reference 15. [c] Reference 13. [d] Reference 14. [e] Reference 7a.

Table IV. Comparison of Selected Structural and Binding Parameters of Potassium Complexes of BiBLEs and Cryptands

interaction	[2.2.2][a]	**3**[b]	**2**[b]	[2.2.1][c]
M–O, Å	2.776	2.848	2.834	2.871
ring	2.776	2.848	2.834	2.759
	2.789	2.803	2.848	2.818
	2.789	2.803	2.848	2.702
	2.790			2.850
	2.790			
sidearm		2.860	2.721	
		2.860	2.721	
M–N, Å	2.874	2.941	3.128	2.916
	2.874	2.941	3.128	2.897
R, Å	1.38	1.438	1.46	1.40
N–M–N, deg	180	180	176.4	124.4
N–N, Å	5.748	5.882	6.253	5.143
coordn no.	8	8	8	8
log K_S	10.41[d]	5.46[e]	5.08[e]	8.54[d]

[a] Reference 15. [b] Reference 5c. [c] Reference 13. [d] Reference 14. [e] Reference 7a.

donors in the **2**·Na$^+$ complex are slightly closer to the metal ion than in the **3**·Na$^+$ complex.

Structural data for Na$^+$ complexes of BiBLEs and cryptands are presented in Table III. The structural parameters (N–N distances, N–M–N angles, and *R* value) for **3** are quite similar to [2.2.2] while those of **2** fall between those observed for the [2.2.2] and [2.2.2] complexes. The effective ionic radii[10] for sodium cation are 1.12 Å when heptacoordinated and 1.18 Å when octacoordinated. These values correspond nicely to the *R* values for the two cryptate complexes and the sodium cation complex of **3**, but the corresponding complex of **2** has an intermediate value.

Structural data for K$^+$ complexes of BiBLEs and cryptands are presented in Table IV. The BiBLEs have longer N–N distances as well as larger *R* values. In [2.2.2] and both BiBLEs the N–M–N angle is approximately 180°. For the **2**·K$^+$ complex the *R* value is 1.46 Å, but if the K–N distances, which are substantially longer than in any other complex, are excluded, *R* is 1.40 Å. Excluding the two N atoms makes K$^+$ formally hexacoordinated.

The *R* values are 1.380–1.40 and 1.438–1.46 Å for the cryptates and the BiBLE complexes, respectively. These *R* values coincide nicely with Shannon's effective ionic radii[10] of potassium cation for six (1.38 Å) and seven (1.46 Å) donors. These donor numbers are invariably one lower than the coordination number observed in complexes of BiBLEs and two lower for cryptands. Shannon's computations are based on oxides and fluorides. These macrocycles with neutral donor atoms differ, because for a given distance more softer donors are required to neutralize the charge.

The difference in the conformation of the two K$^+$–BiBLE complexes is fascinating. The expected macroring conformation for potassium complexes of 18-membered crowns is the chair of D_{3d} conformation. In fact, **2**·KI is the only example to date of an unsubstituted (on carbon) macroring whose donor atoms are in a boatlike arrangement. In this complex the sidearm donor atoms are hydroxyl oxygens, which are somewhat more polar donors than ethereal oxygens. The former side-arm oxygens can get closer to the metal ion when the macroring is in the boat conformation than when it is in the chair. To accommodate this shorter oxygen–metal distance, the two nitrogen atoms in the **2** complex are displaced from the metal ion so that their contribution to binding is minimal. In the **3** complex in which all the oxygens are ethereal, the complex is formed with oxygen–metal distances quite similar for all the oxygens. This is best accommodated with a D_{3d} conformation for the macroring.

From an examination of molecular models and a consideration of previously reported X-ray studies,[11] one can rationalize either the syn or anti structure. It is clear that the cryptand-like (syn) arrangement of donor groups is especially favorable for cation solvation. On the other hand, the near perfect fit of K$^+$ into the 18-membered ring hole is an alluring possibility. It seems reasonable that a structure in which K$^+$ is in the hole and the two sidearms provide apical solution is, at the least, a local minimum on the energy surface. In fact, to our knowledge, all K$^+$ complexes of 18-membered ring crown ethers reported to date form a complex in which K$^+$ is centrally located in or near the macroring's donor atom plane.

Apparently, the most favorable situation is for either Na$^+$ or K$^+$ to form a cryptate-like complex, if this is possible. This is the observed structure of **2**·K$^+$. In **3**·K$^+$, steric hindrance between the two methyl groups makes the cryptand-like structure less favorable than the anti arrangement, and it is the latter which

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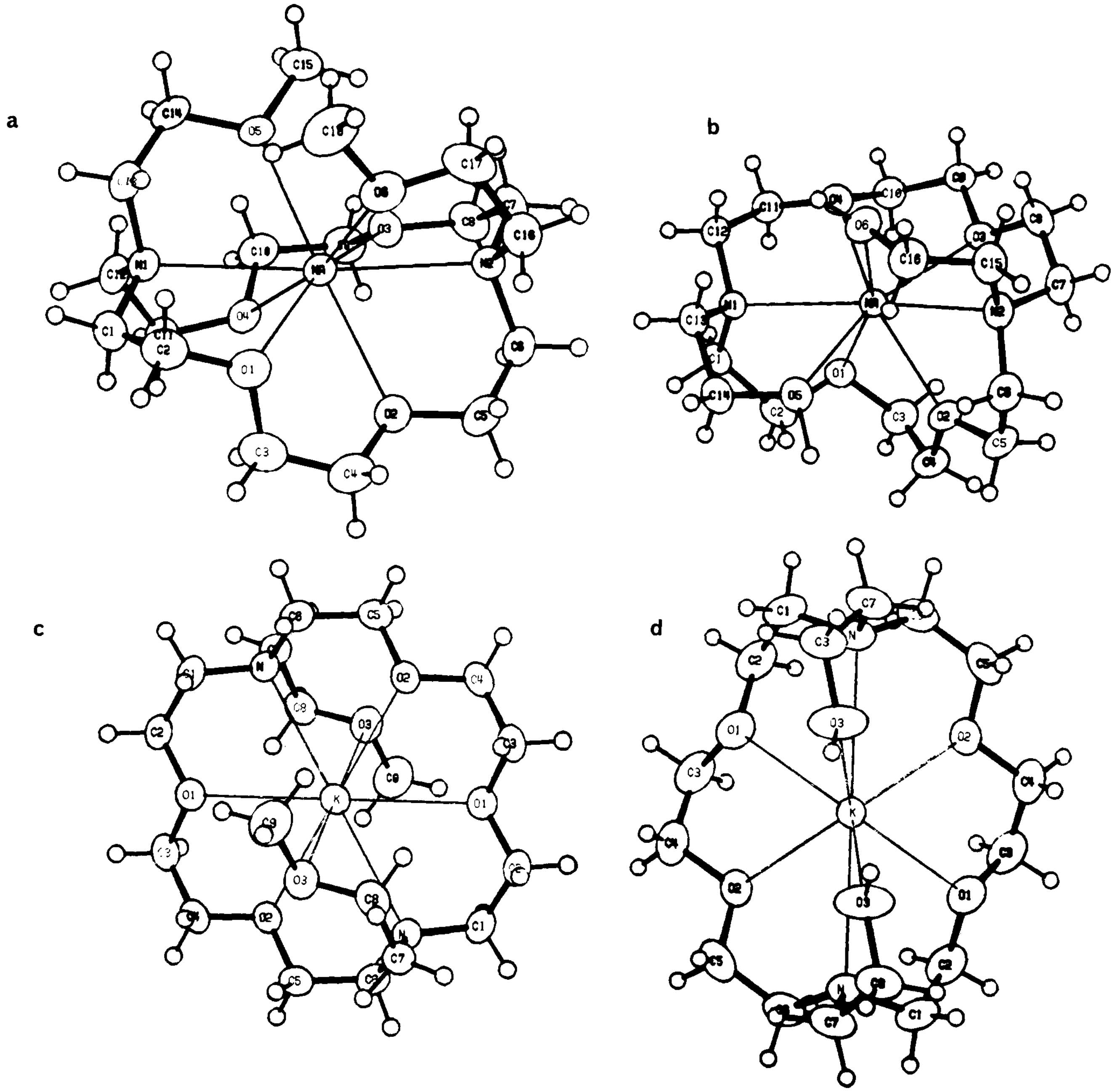

Figure 2. Solid-state structural drawings for the (a) Na$^+$ and (c) K$^+$ complexes of *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6, **2**, and the (b) Na$^+$ and (d) K$^+$ complexes of *N,N'bis*(2-methoxyethyl)-4,13-diaza-18-crown-6, **3**.

is observed in the crystal. It is possible, of course, that packing forces also contribute significantly making the global minima in solution and in the solid state different.

In considering the structures **2**·Na$^+$, **2**·K$^+$, **3**·Na$^+$, **3**·K$^+$, one might designate the unusual structure to be **3**·K$^+$ since it is the only one in the anti arrangement. In fact, the odd structure is **2**·K$^+$, even though it is similar in appearance to the other structures. If our reasoning is correct, then we predict that other 18-membered ring BiBLE complexes of Na$^+$ will be in the syn arrangement, but no other K$^+$ complex can be. This is because hydrogen is the smallest substituent possible on oxygen.

Summary

Solution thermodynamic data have been determined for Na$^+$ and K$^+$ complexes of N,N'-disubstituted 4,13-diaza-18-crown-6 derivatives having *n*-propyl **1**, 2-hydroxyethyl **2**, and 2-methoxyethyl **3** sidearms. The data are complicated, but the complexation process can be described as enthalpy driven. Solid-state structures have been obtained for the complexes **2**·Na$^+$, **2**·K$^+$, **3**·Na$^+$, and **3**·K$^+$. Although three of the four complexes have the syn or cryptand-like arrangement of donor groups, **2**·K$^+$ is shown to be the odd structure rather than *anti*-**3**·K$^+$.

Experimental Section

Thermodynamic Measurements. Solution thermodynamic measurements were conducted by using ion selective electrodes in anhydrous methanol solution at 25 °C as described in the accompanying paper. Calibration of the method using known complexation reactions was conducted and is described therein.[6]

Preparation in Ligands. The substituted bibracchial lariat ethers used in this study were prepared as described previously.[7]

Crystallization of 3·NaI. Crystals of the title compound were obtained by recrystallization from tetrahydrofuran. The colorless solid had mp 216 °C. [Anal. Calcd for $C_{18}H_{38}N_2O_6NaI$: C, 40.91; H, 7.26; N, 5.30. Found: C, 40.61; H, 7.30; N, 5.24]. All spectral and analytical data for this compound confirm its formation as a nonhydrated species. The compound was sent for combustion analysis (Atlantic Microlabs, Atlanta, GA) and apparently survived without hydration. The sample sent for X-ray analysis was somewhat amorphous, and the crystal selected was the best in the sample. This may have been a crystal of hydrate in the midst of predominantly anhydrous material or the entire sample may have hydrated in transit and handling.

X-ray Experimental. Intensity data were obtained from a colorless crystal of dimensions 0.32 × 0.36 × 0.44 mm, sealed in a thin-walled

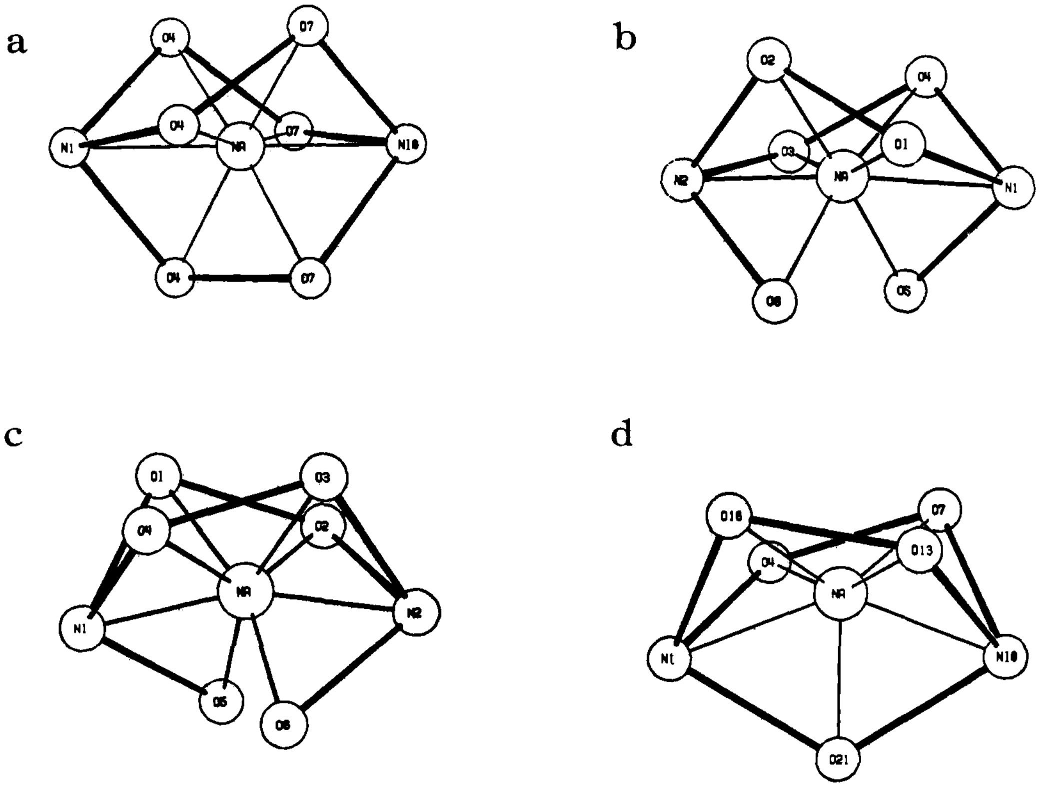

Figure 3. Skeletal or framework drawings illustrating only donor atoms, connectivities, and complexed sodium cations for the following: (a) [2.2.2]cryptand; (b) *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6, **3**; (c) *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6, **2**; and (d) [2.2.1]cryptand.

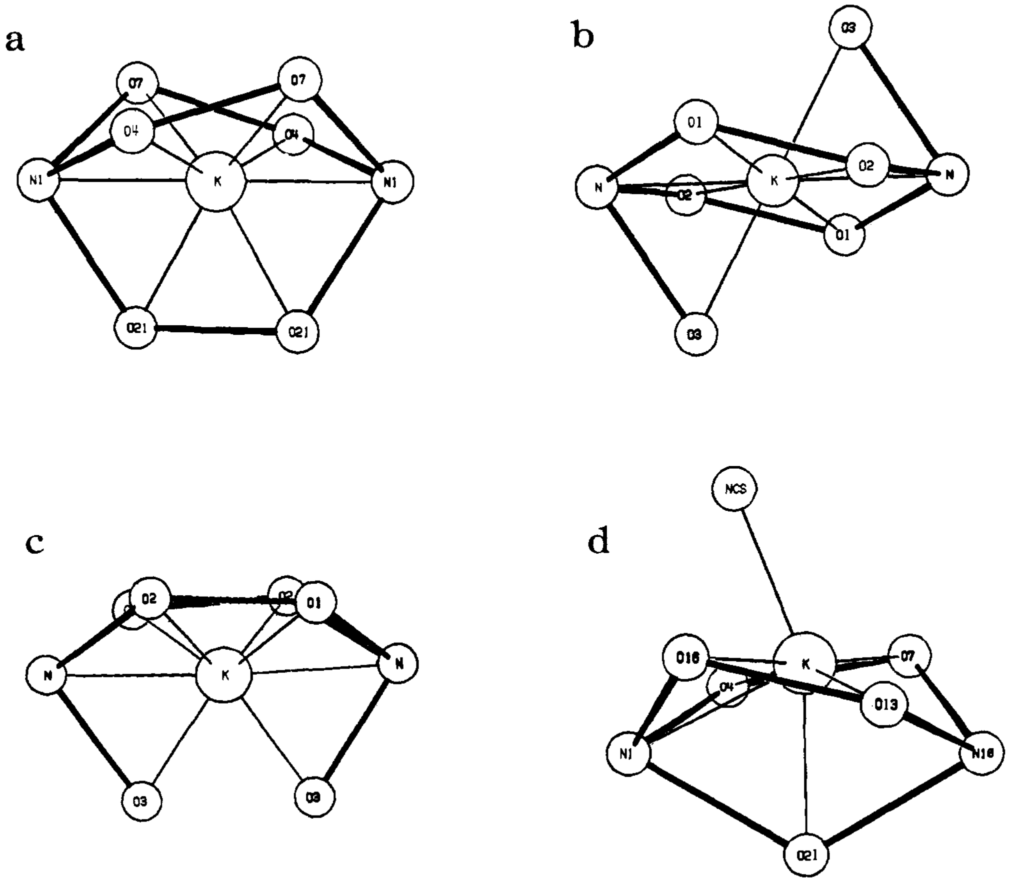

Figure 4. Skeletal or framework drawings illustrating only donor atoms, connectivities, and complexed potassium cations for the following: (a) [2.2.2]cryptand: (b) *N,N'*-bis(2-methoxyethyl)-4,13-diaza-18-crown-6, **3**; (c) *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6, **2**; and (d) [2.2.1]cryptand.

glass capillary for protection from humidity, on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator. Crystal data are as follows: $C_{18}H_{38}N_2O_6NaI{\cdot}H_2O$, fw = 564.4, triclinic space group $P\bar{1}$, a = 9.5799 (12) Å, b = 10.3904 (13) Å, c = 12.7699 (13) Å, α = 90.362 (9)°, β = 97.090 (9)°, γ = 94.489 (11)°, V = 1257.4 (5) Å^3, Z = 2, D_{calcd} = 1.443 g cm^3, T = 26 °C, γ = 0.71073 Å, μ(Mo Kα) = 13.1 cm^{-1}. One hemisphere of data having 1° < θ < 25° was collected by ω-2θ scans of variable rate 1.8–4.0 deg min^{-1}. Data reduction included corrections for background, Lorentz polarization, and absorption effects. The latter were based on ψ scans of reflections near $\chi = 90°$, and the minimum relative transmission coefficient was 95.38%. Of 4419 unique data, 3142 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by heavy atom methods and refined by full-matrix least squares based upon F with weights $\omega = \sigma^{-2}(F_o)$, by using the Enraf-Nonius SDP programs. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference maps and were included as fixed contributions with isotropic $B = 6.0$ Å^2. A secondary extinction coefficient refined to a value of $2.8\ (4) \times 10^{-7}$. Convergence was achieved with maximum shift/esd = 0.10, $R = 0.033$, $R_w = 0.056$, error of fit = 1.684 for 263 variables, and the maximum residual density was 0.37 e Å^{-3}. Coordinates are listed in Table II.

Acknowledgment. We warmly thank the National Institutes of Health for support of this work.

Supplementary Material Available: Complete tables of bond distances and bond angles, coordinates for hydrogen atoms, and anisotropic thermal parameters (6 pages); listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

π-Electron Properties of Large Condensed Polyaromatic Hydrocarbons

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Abstract: Hückel molecular orbital (HMO) theory has been used to calculate energy level densities, bond orders, electron distributions, free valence, resonance energies, and heats of formation for several homologous series of large, hexagonally symmetric benzenoid polyaromatic molecules with well-defined edge structures containing up to 2300 carbon atoms. When extrapolated to the infinite limit, values for all properties converge to reasonable values. This is in contrast to several other π-electron theories that do not yield correct graphite limits. Carbon atoms at the edge of such large molecules are predicted to behave like those in small polynuclear aromatic molecules, with properties strongly dependent on local structure. Regardless of edge structure, interior carbons several bond lengths from an edge have properties similar to those in an infinite graphite sheet. Edge structure has a larger influence on heats of formation than that predicted by group additivity methods. Only a weak correlation was found between the energy of the highest occupied molecular orbital and the reactivity of the most reactive position.

1. Introduction

Graphite and many carbonaceous substances consist primarily of large polyaromatic molecules of varying size, shape, and edge composition. An understanding of the chemistry of graphite is hampered by the inability to isolate these large molecules for individual study. As a result, the chemistry of graphite is often treated phenomenologically. Reactivity is thought to involve edges, defects, and other "active" sites, although the chemical nature of these is a matter of speculation.

The molecules in graphite belong to a class of compounds whose electronic properties are characterized primarily by their networks of mobile π-electrons. The chemical behavior of molecules of this type has been studied both experimentally and theoretically for many years and is thoroughly understood. A number of semiempirical theories have been developed and successfully applied to a large number of relatively small π-electron molecules[1-5], and to graphite itself considered as an infinite π-electron array.[6] Presumably, these theories should also apply to the large chemical structures present in graphitic substances.[7] If so, they could be used to develop structure-reactivity relations that in turn would aid in devising reaction mechanisms for these materials. In view of this, we have been using several of these theories to predict properties of some very large polyaromatic compounds.[8-10] Our initial goals have been to compare theories and to examine their convergence behavior. This latter consideration is important since any reliable theory should extrapolate to the correct graphite limits. Early in our work we noticed that the edge structure and overall size of such compounds were critically important factors in determining their reactivity. Our efforts have since focused on separating and studying these two variables individually.

We have been examining two types of theories. The simplest are based on Kekulē structure counts. One of these, structure-resonance theory (SRT)[5] was applied to molecules containing as many as 16 000 carbon atoms. Most properties predicted by SRT are consistent and reasonable. Local properties such as bond orders and aromaticity indices converge properly to graphite limits and appear to be qualitatively correct. Unfortunately, some overall molecular properties such as ionization potentials diverge with increasing size, and others such as resonance energies per electron converge to different values depending on edge structure. Another method that is mathematically related to SRT is perturbation molecular orbital (PMO) theory.[2,3] It predicts electron localization energies. These have been used as reactivity indices for substitution reactions. This method, however, makes the implausible prediction that localization energies are zero for all positions in a sufficiently large graphite-like layer.[10]

Molecular orbital techniques were the second of the theoretical types we tested. These are more versatile in that they yield orbital energies and wave functions for π-electrons from which a variety of electronic properties can be calculated. The oldest and simplest

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