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18-Membered-Ring Spherands Containing Five Anisyl Groups[1]

Roger C. Helgeson, Beverly J. Selle, Israel Goldberg, Carolyn B. Knobler, and Donald J. Cram*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1596

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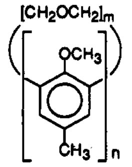
Abstract: The syntheses, characterization, and binding properties of four new spherands are reported, each of which contains five meta-linked anisyl binding sites incorporated in an 18-membered macrocyclic ring. A sixth binding site was $(CH_2)_2O$, $(CH_2)_2S$, $(CH_2)_2C(CO_2Et)_2$, or $(CH_2)_2CH(CO_2Et)$. A crystal structure of the first of the above compounds contains two independent and slightly different molecules per unit cell. In both molecules the five anisyl CH_3O groups and one CH_2OCH_2 group possess an up-down-up-down-up-down conformation in proceeding clockwise around the ring, and all six oxygens' unshared electron pairs line an elongated spherical cavity preorganized to bind the smaller alkali metal cations. The free energies for this system binding Li^+, Na^+, and K^+ picrates at 25 °C in $CDCl_3$ saturated with D_2O were respectively 12.8, 14.4, and 10.4 kcal mol^{-1} ($-\Delta G°$ values). Its sulfur analog was less selective in its binding, which still peaked with the Na^+ picrate ($-\Delta G° = 12.2$ kcal mol^{-1}). A crystal structure of this sulfur-containing spherand showed the six binding sites were preorganized similar to those of its oxygen analog. The two ester-containing systems failed to extract Li^+ and Na^+ picrate rapidly on the human time scale but were shown by other equilibration experiments to strongly bind $LiClO_4$ and $NaClO_4$ in $CDCl_3$ solution.

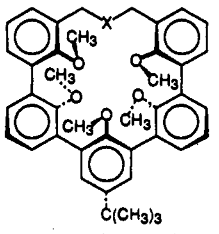
Previous papers in this series reported the synthesis, crystal structure, and alkali metal cation binding properties of a series of 18-membered-ring macrocycles which contained varying numbers of 2,6-disubstituted anisyl and CH_2OCH_2 units whose structures conformed to **1–6** in which $m + n = 6$. At one extreme is the parent corand, 18-crown-6 or **1**, which in solution is conformationally flexible, and which in the crystalline state exists with two CH_2 groups turned inward to fill its own cavity. At the other extreme is found the parent spherand **2**, which in both solution and the crystalline state contains an enforced cavity complementary to Na^+ and Li^+, fully preorganized for binding during its synthesis, rather than during the complexing act. Hosts **3**, containing one anisyl, and **4**, containing two anisyl groups, are poorer binders than **1**, because nonpreorganized anisyl oxygens are intrinsically poorer ligands than aliphatic ether oxygens.[2] However, when three contiguous anisyl groups are present as in hemispherand **5**, the three anisyl groups preorganize one another for binding, whereas the $(CH_2OCH_2)_3$ groups are conformationally mobile. Accordingly, **5** is a stronger ion binder than **1**, **3**, or **4** because of this preorganization.[2] The four anisyl groups of **6** are nicely preorganized, making it a stronger specific complexer than **5** but a weaker general complexer because of its lack of conformational adaptability.[3]

Missing in this series is **7**, composed of five anisyls and one CH_2OCH_2 group. Unlike CPK models of **1–6**, that of **7** appears to be as completely preorganized as is that of **2**, but unlike **2**, **7** has enough steric exposure of its cavity to potential guests to provide high equilibration rates in extractions from water into organic media.

We report here the syntheses, characterization, crystal structures, and binding properties of spherands **7** and **8**, and less thoroughly studied spherands **9** and **10**, which contain preorganized ester groups as ligating sites. In CPK models of **9**, the enforced cavity is much less accessible to potential guests and to solvent than in models of **7** and **8**. Macrocycle **10** was obtained as a byproduct of the synthesis of **9**.



1, m = 6, n = 0; **2**, m = 0, n = 6;
3, m = 5, n = 1; **4**, m = 4, n = 2;
5, m = n = 3; **6**, m = 2, n = 4



7, X = O; **8**, X = S;
9, X = $C(CO_2Et)_2$;
10, X = $CHCO_2Et$

Results

Syntheses. Known phenol **11**[4] was converted in THF with $NaH-(CH_3)_2SO_4$ to anisole **12** (82%) which was submitted to a Kumada[5] aryl–aryl twofold coupling reaction with 2 equiv of 4-dibenzofuranylmagnesium bromide[6] to give **13** (80%). This compound was dimetalated with *n*-BuLi, and the dilithio derivative formed was treated with CH_3O_2CCl to produce diester **14** (91%). The two dibenzofuran units and diester functional groups were cleaved with molten KOH–NaOH at 300 °C, and the polyphenolic diacid product was permethylated with $(CH_3)_2SO_4-K_2CO_3$ to give diester–pentaanisole compound **15** (82% overall) This diester was hydrolyzed to its diacid which was reduced with $BH_3-O(CH_2)_4$ to diol **16** (83%). The diol was chlorinated with Ph_3P–N–chlorosuccinimide (NCS) to produce the dibenzyl dichloride **17** (68%), used in most of the macroring closures. The use of less chlorinating agent gave a 26% yield of chloro alcohol **18**, 20% of dichloride **17**, and 15% of recovered diol **16**.

The key macroring-closing reactions appeared to be templated by Na^+ and proceeded in good yields at moderately high dilution to give NaCl complexes. Chloro alcohol **18** mixed with $NaH-O(CH_2)_4$ gave **7**·NaCl in 65% yield, and the NaCl decomplexed when a solution of **7**·NaCl in CH_2Cl_2 was repeatedly washed with deionized water (87%). Diol **16** also gave **7**·NaCl (29%) when treated with $p-CH_3C_6H_4SO_2Cl-NaH-O(CH_2)_4$ at reflux temperatures. Sulfide **8** was produced directly (47%) when

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[1] (a) Host-Guest Complexation 66. (b) The authors warmly thank the National Science Foundation and the Division of Basic Sciences of the Department of Energy for support of this research.

[2] Cram, D. J.; Trueblood, K. N., *Top. Curr. Chem.*, **1981**, *98*, 43–106.

[3] Artz, S. P.; Cram, D. J. *J. Am. Chem. Soc.*, **1984**, *106*, 2160–2171.

[4] Burger, A; Wilson, E. L.; Brindley, C. O.; Bernheim, F. *J. Am. Chem. Soc.* **1945**, *67*, 1416–1419.

[5] Tamao, K.; Minato, A.; Miyake, N.; Matsuda, T.; Koso, Y.; Kumada, M. *Chem. Lett.* **1975**, 133–136.

[6] Gilman, H.; Van Ess, P. R. *J. Am. Chem. Soc.* **1939**, *61*, 1365–1371.

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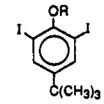
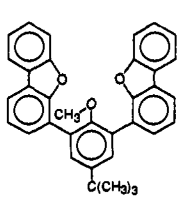


11, R = H; 12, R = CH$_3$



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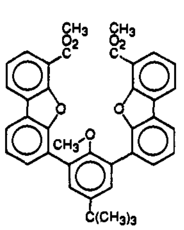

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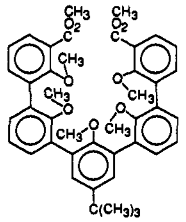

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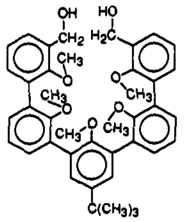

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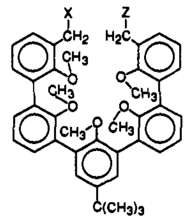
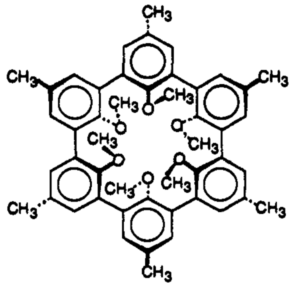


17, X = Z = Cl; 18, X = Cl, Z = OH

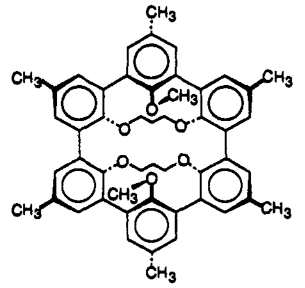
dichloride **17** was treated with $Na_2S{\cdot}9H_2O$–EtOH–C_6H_6 (70:1, v/v) at 80 °C. A separable mixture of diester complex **9**·NaCl (57%) and free **10** (15%) was obtained when dichloride **17** was treated under high dilution conditions in $O(CH_2)_4$ with NaH–$CH_2(CO_2Et)_2$ at reflux temperature. Repeated washing of a solution of **9**·NaCl in CH_2Cl_2 with deionized water gave **9** (90%).

Crystal Structures. Spherand **7** crystallized from CH_2Cl_2–EtOH gave crystals whose unit cell contained two molecules of **7** which differed slightly from one another in structure, face views of which are pictured in **7a** and **7b** of Chart I. In both **7a** and **7b**, the six oxygens possess an up-down-up-down-up-down arrangement in proceeding clockwise around the macroring from 2 o'clock to 12 o'clock with their unshared electron pairs all facing inward and their attached methyl or methylene groups facing outward. The average diameter of the resulting cavities were calculated by averaging the distances between the three sets of oxygen pairs most distant from one another (e.g., oxygens at 2 and 8, at 4 and 10, and at 6 and 12 o'clock, see Table I) and subtracting 2,8 Å, the diameter of a covalently bound oxygen atom. The resulting averaged diameter for the cavity of **7a** was 1.93 Å, and for **7b** was 1.94 Å, considerably larger than the diameter for the parent spherand **2** of 1.62 Å.[7]

Notice in Table I that **7a** and **7b** differ somewhat in the distances their heteroatoms are from the aryl carbon mean planes but that the average diameters of their cavities differ from one another by only 0.011 Å. In each structure, three methyls protrude from the near face of the macroring forming three umbrellas that in effect shield the oxygens from solvation on the near face. The two methyl groups that protrude from the far face leave an opening for solvation of the oxygens at 10, 12, and 2 o'clock by small molecules such as H_2O, NH_3, or NH_4^+. Clearly, **7a** and **7b** are preorganized for binding, but the ligating sites are more available for solvation than those of prototypical spherand **2**, fully drawn in **18**.



18



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Spherand **8** was crystallized from CH_2Cl_2–EtOH to give material suitable for crystal structure determination. Chart I provides a stereo face view **8a** of sulfide **8** oriented similar to those of **7a** and **7b**, which **8a** resembles. In **8a**, the six heteroatoms possess an up-down-up-down-up-down arrangement in proceeding around the macrocycle from the oxygen at 2 o'clock through the oxygens at 4, 6, 8, and 10 and sulfur at 12 o'clock with their unshared electron pairs all facing inward, and their attached methyl or methylene groups facing outward. The distance between the sulfur at 12 o'clock and the oxygen at 6 o'clock was 5.96 Å, from which was subtracted the sum of the radii of a covalently bound oxygen (1.40 Å) and of a covalently bound sulfur (1.80 Å) to give 2.76 Å for the cavity dimension along the O-to-S axis. The distances between the other two sets of distant oxygens were 3.84 and 4.94 Å, from each of which was subtracted 2.80 Å, the diameter of a covalently bound oxygen, to give 1.04 and 2.14 Å, respectively, for the cavity dimensions along these two O-to-O axes. The average of the three cavity dimensions gives 1.98 Å, which is a rough estimate of the cavity diameter. Notice this diameter is only 0.04 Å larger than that of **7a** or **7b**; this difference is due to the greater length of the two S–CH_2 bonds as compared to that of the two O–CH_2 bonds.

Table I also includes the distances of the six heteroatoms from the aryl carbon mean planes. In **8a**, as in **7a** and **7b**, the three methyls which protrude from the near face of the macroring collectively shield the heteroatoms from solvation from the near face. The two methyl groups that protrude from the far face allow an opening for solvation of the sulfur at 12 o'clock and the oxygens at 10 and 2 o'clock by small hydrogen-bond donors. Overall, spherand **8a** is preorganized for binding.

Binding Properties of Spherands 7–11. Solutions of **7** and **8** in $CDCl_3$ were shaken at 25 °C with equal volumes of D_2O containing Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and $(CH_3)_3CNH_3^+$ picrates, and the amounts of picrate extracted and remaining were measured spectrophotometrically.[8] Equilibration of picrate between phases was complete in less than 3 min. From the values obtained, coupled with those observed in standard extractions in the absence of host in the $CDCl_3$ layer, the K_a (M-1) and $-\Delta G°$ (kcal mol^{-1}) were calculated[8] and are listed in Table II (average of two determinations).

Hosts **9** and **10** in $CDCl_3$ failed to extract any of the standard picrate salts from D_2O. However, the following results show that both hosts are strong, selective binders of Li^+ and Na^+ ions but that the complexation–decomplexation rates are slow on the ^1H NMR time scale.

The ^1H NMR spectra in 98:2 $CDCl_3$–$(CD_3)_2SO$ (v/v) of diester **9**, a mixture of **9** with 1 equiv of $LiClO_4$, or a mixture of **9** with 1 equiv of $NaClO_4$, resulted in three distinctly different spectra. The complexation rate was very fast on the human time scale. Similar homogeneous experiments with $KClO_4$ or $Ca(ClO_4)_2$ gave only the spectra of free **9**. Thus **9** is highly selective for binding Li^+ and Na^+ vs K^+, in harmony with predictions based on molecular model examination. Although Ca^{2+} has a diameter compatible with that of **9**, the very high hydration energy of this doubly charged species inhibits its ligation with a host which itself does not contain a negative charge.

In a second experiment, spheraplex **9**·NaCl dissolved in 98:2 $CDCl_3$–$(CD_3)_2SO$ (v/v) was equilibrated (12 h) at 25 °C with 1 equiv of **7**. The ^1H NMR spectrum of the mixture showed the presence of only **7**·Na^+ and free **9**, suggesting that the $-\Delta G°$ value for **9** binding Na^+ is <14.4 kcal mol^{-1}.

In further experiments, equivalent amounts of **19**·$NaClO_4$ and **9** were equilibrated (36 h) at 25 °C in 98:2 (v/v) $CDCl_3$–$(CD_3)_2SO$ to give a 70:30 ratio of **9**·$NaClO_4$: **9** (^1H NMR spectra). When the equilibration was approached by mixing equivalent amounts of **9**·$NaClO_4$ and **19**, a 60:40 ratio of **9**·$NaClO_4$:**9** was observed under the same conditions. Since **19** has a $-\Delta G°$ value of 13.3 kcal mol^{-1}, these results suggest that **9** has a $-\Delta G°$ of about 13.4 kcal mol^{-1}. Similar equilibration experiments at 60

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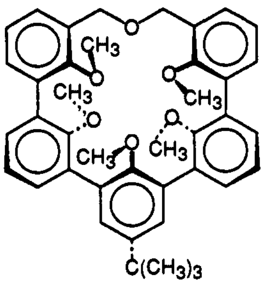
Chart I

Line drawings

Stereoviews of crystal structures



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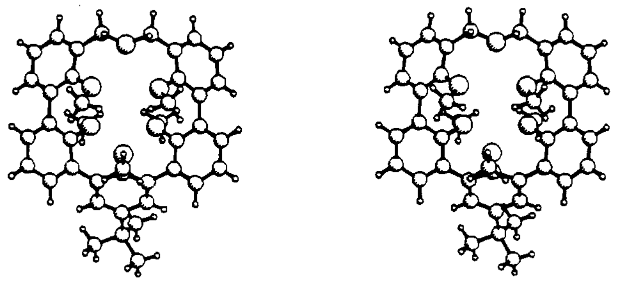
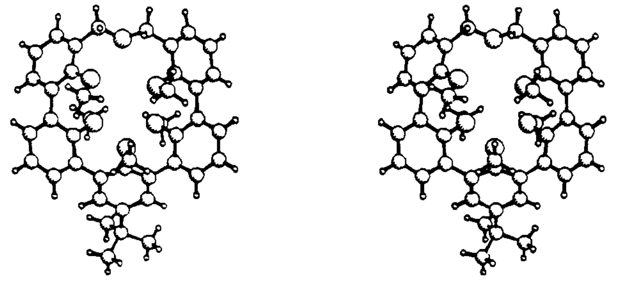
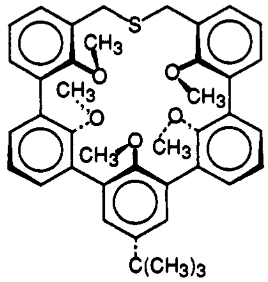


7a



7b



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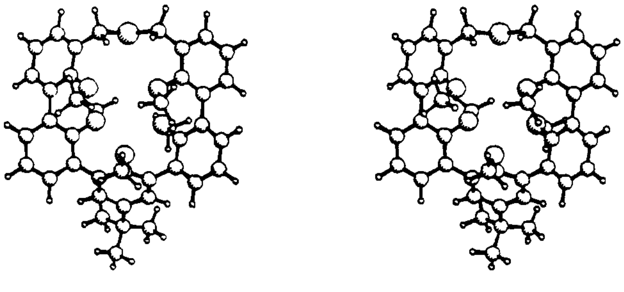


8a

Table I. Distances in Crystal Structures of Spherands

distances (Å)	spherand 7a	7b	8
average hole diameter	1.932	1.943	1.980
between heteroatoms			
at 4 and 10 o'clock	4.432	4.697	4.939
at 6 and 12 o'clock	5.396	5.447	5.958
at 8 and 2 o'clock	4.369	4.084	3.843
heteroatoms and mean plane[a]			
at 2 o'clock	−1.233	−1.234	−0.791
at 4 o'clock	0.932	1.117	1.246
at 6 o'clock	−1.170	−1.176	−1.247
at 8 o'clock	0.944	0.825	0.668
at 10 o'clock	−1.343	−1.350	−1.345
at 12 o'clock	0.281	0.204	0.942

[a] Defined by 10 aryl carbons at 2,6-positions of five anisyl units. The minus and plus signs indicate atoms above or below the mean plane.

°C with **9**, **19**, and $LiClO_4$ in the same medium indicated **9** binds Li^+ about the same as **19**, whose $-\Delta G°$ value is ~16.8 kcal mol^{-1}.

Mixing equivalent amounts of monoester **10** with $NaClO_4$ in 98:2 (v/v) $CDCl_3$–$(CD_3)_2SO$ at 25 °C gave an ^1H NMR spectrum of only **10**·$NaClO_4$ at a rate rapid on the human time scale. The same was true for **10** mixed with $LiClO_4$ under the same conditions. The ^1H NMR spectra of **10**, **10**·$NaClO_4$, and **10**·$LiClO_4$ were clearly different from one another. When 1 equivof $KClO_4$ was mixed with **10** under the same conditions, no complexation was detected. Equilibration experiments involving **10**, $NaClO_4$, and $LiClO_4$ in 98:2 (v/v) $CDCl_3$–$(CD_3)_2SO$ indicated that **10** binds Li^+ by at least a power of 10 greater in K_a value than **10** binds Na^+.

Table II. Values of K_a (M^{-1}) and $-\Delta G°$ (kcal mol^{-1}) for Spherands[a] 7 and 8 Binding Alkali Metal and Ammonium Picrates at 25 °C in $CDCl_3$ Saturated with D_2O

picrates	7: K_a (M^{-1})	7: $-\Delta G°$ (kcal mol^{-1})	8: K_a (M^{-1})	8: $-\Delta G°$ (kcal mol^{-1})
Li^+	2.5×10^9	12.8	9.2×10^7	10.8
Na^+	3.6×10^{10}	14.4	8.9×10^8	12.2
K^+	5.2×10^7	10.4	1.4×10^7	9.9
Rb^+	6.7×10^5	7.9	8.2×10^6	9.4
Cs^+	3.3×10^5	6.7	1.4×10^7	9.8
$NH4^+$	2.9×10^6	8.7	1.5×10^7	9.8
$CH_3NH_3^+$	9.7×10^4	6.9	6.6×10^6	9.3
$(CH_3)_3CNH_3^+$		<5	1.4×10^5	7.0

[a] All concentrations of host and guest were 0.001 M for **8** and for the first three entries for **7**, but those for the remainder for **7** were 0.015 M.

Discussion

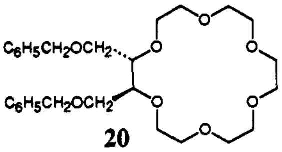
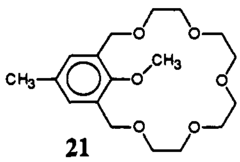
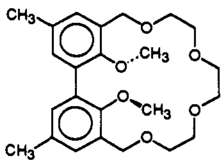
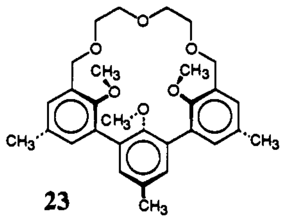
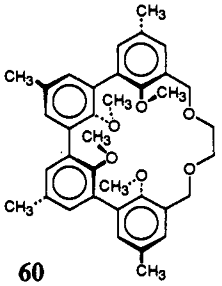
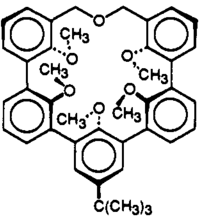
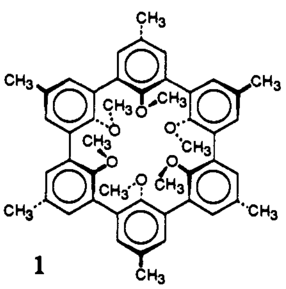
Correlation of Binding Free Energies with Structure. The diameter of the cavity of **18** in spheraplex **18**·Na^+ was 1.75 Å, and in **18**·Li^+ was 1.48 Å, compared to the diameter of the cavity of free **18** of 1.62 Å. Thus, **18** stretched to accommodate Na^+

and contracted to complex Li^+ but could not stretch enough to complex K^+ whose diameter is about 2.7 Å (nor any of the larger alkaline earth metal cations). Spherand **18** complexed Li^+ with $-\Delta G^\circ > 23$ kcal mol^{-1}, which is greater by ~4 kcal than the 19.2 kcal mol^{-1} by which **18** complexed Na^+. The cavity diameters in free **7** and **8** were 1.94 and 1.98, respectively, compared to that of Na^+ (~1.90 Å) and the 1.48 Å diameter of Li^+ in **18**·Li^+. Thus spherand **7** and **8** appear beautifully preorganized to bind Na^+, so it is not surprising that binding free energies peak at 14.4 kcal mol^{-1} for **7** and at 12.2 kcal mol^{-1} for **8**. Model examination suggests that only the five CH_3O oxygens can simultaneously contact Li^+ in **7**·Li^+ and **8**·Li^+, which correlates with the lower binding for these two spheraplexes of 12.8 and 10.8 kcal mol^{-1}, respectively. The much lower binding energy with **7** and **8** compared to **18** is attributed to the fact that the former two systems are easily solvated by a molecule of water from the face shielded by only two methyl groups, whereas the oxygens in **18** are completely shielded from solvation.

The presence of the respective CH_2OCH_2 and CH_2SCH_2 units in **7** and **8** not only expands the cavity and exposes it to solvation but also introduces a flexibility into the 18-membered macroring which provides measurable binding for K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and $(CH_3)_3CNH_3^+$ picrates. The respective values for **7** and **8** complexing these ions are as follows (kcal mol^{-1}): K^+, 10.4 and 9.9; Rb^+, 7.9 and 9.4; Cs^+, 6.7 and 9.8; NH_4^+, 8.7 and 9.8; $CH_3NH_3^+$, 6.9 and 9.3; $(CH_3)_3CNH_3^+$, <5 and 7.0. Thus **7** binds K^+ better than **8**, but the larger ions are more strongly complexed by the sulfide than the oxide cycle by $-\Delta\Delta G^\circ$ values that range from a low of 1.1 for NH_4^+ to a high of 3.1 kcal mol^{-1} for Cs^+. Not only is the macroring of **8** larger than that of **7** due to the longer bonds in CH_2–S–CH_2 as compared to CH_2–O–CH_2, but also the softer character of S compared to O means bond angle deformations involving S are less costly than those that involve O.

Molecular model examination of **9** indicates that one C=O group's oxygen must line the cavity, that the cavity is badly deformed, and is inaccessible to solvation, is less accessible to small ions than that of **18**, and that its cavity should be smaller than the cavity of **7**. All of these structural features are in harmony with the $-\Delta G^\circ$ estimates for **9** binding Li^+ with ~16.8 and Na^+ with ~13.4 kcal mol^{-1} and with the slow complexation-decomplexation rates. Model examination of **10** shows the same kind of effects as **9**, but the spherand is less compressed.

Table III. Changes in Free Energies of Complexation ($-\Delta G^\circ$, kcal mol^{-1}, at 25 °C in $CDCl_3$ Saturated with D_2O) by Increasingly Preorganized Hosts of Alkali Metal and Ammonium Picrates

	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
 **20**	6.3	8.4	11.4	9.9	8.5	10.1
 **21**	5.5	6.4	8.5	7.5	6.9	7.6
 **22**	6.5	8.7	9.8	8.6	7.8	7.9
 **23**	7.2	12.2	11.7	10.5	9.0	9.8
 **60**	7.2	13.5	10.7	8.4	7.1	8.7
 **57**	12.8	14.4	10.4	7.9	6.7	8.7
 **1**	>23	19.2				

Preorganization as a Dominant Determinant of Binding Strength and Specificity. Table III lists the structures and $-\Delta G^\circ$ values for seven 18-membered macrocycles binding Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+ picrates at 25 °C in $CDCl_3$ saturated with D_2O, all of which possess six potential oxygen ligating sites for the six listed guests.[2,3,9] In proceeding from corand **20** at the top of Table III to spherand **18** at the bottom, the trends suggest the following conclusions. (1) Introduction of one or two anisyl groups in place of the CH_2OCH_2 groups, as in **21** and **22**, depresses the binding and specificity by lowering the degree of preorganization intrinsic in corand **20** without disturbing the rank of K^+ as the most strongly bound guest. (2) By the time three anisyl groups are introduced, as in **23**, their degree of preorganization of ligands and inhibition of solvation increases the general binding of almost all ions but now favors Na^+ binding over that of the other ions. (3) In passing from **24** to **7** containing respectively four and five self-organizing anisyl groups, the systems grow more specific for Na^+ over K^+, but less specific for Na^+ over Li^+. The $-\Delta G^\circ$ values for Na^+ and Li^+ increase, particularly that for Li^+, whose $-\Delta G^\circ$ value is 5.6 kcal mol-1 larger for **7** than for **24**. (4) In **18**, which is fully preorganized for Li^+ and Na^+ binding and for completely inhibiting solvation, Li^+ is preferred over Na^+ binding by >4 kcal mol^{-1} and no other ions besides these two are bound. The $-\Delta G^\circ$ of binding of Li^+ by **18** is >10 kcal mol-1 larger than by **7**, and for Na^+ the difference is 4.8 kcal mol^{-1}. The results *taken as a whole* show that as the number of anisyl units increases, the cavity becomes smaller and more preorganized, binding and specificity increases for the small ions, and the rates of equilibration among spherand, guest, and spheraplex decrease. (5) Clearly, preorganization overcomes the poorer intrinsic ligating ability of anisyl as compared to aliphatic ethers once three adjacent anisyls are incorporated into the host.

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(9) Cram, D. J.; Lein, G. M. *J. Am. Chem. Soc.* **1985**, *107*, 3657–3668.

Experimental Section

General Procedures. All chemicals were reagent grade. All reactions were conducted in an atmosphere of dry argon or nitrogen. Tetrahydrofuran (THF) and Et_2O were freshly distilled from sodium benzophenone ketyl prior to use. All other solvents were reagent grade. Diethyl malonate and *p*-toluenesulfonyl (tosyl) chloride were purified before use.

Flash chromatography was performed with silica gel 60 (E.M. Merck, particle size 0.040–0.063 mm, 230–400 mesh, ASTM). Gravity columns were packed with silica gel 60 (E.M. Merck, particle size 0.063–0.200 mm) or aluminum oxide (E.M. Merck, neutral grade, particle size 0.063–0.200 mm, 70–230 mesh, ASTM). Thin layer chromatography was conducted on precoated silica gel plates (E.M. Merck, F_{254}, thickness 0.2 mm). All melting points were measured on a Mel-Temp apparatus and are uncorrected. Mass spectra were recorded on an AE-1 Model MS-9 double-focusing spectrometer interfaced by the Kratos Co. to a Data General Nova 3. Mass spectra are reported (70 eV) by listing the observed mass number followed by its percent of the base peak in parentheses. Proton NMR spectroscopy was performed at 200.1 MHz on a Bruker WP-200 spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane in $CDCl_3$ as solvent unless indicated otherwise. Coupling constants in hertz (Hz) are expressed with splitting patterns designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Association constants were obtained at 0.015 or 0.001 M host in $CDCl_3$ and guest in D_2O (initial concentrations) by a standard colorimetric procedure.[8]

4-(1,1-Dimethylethyl)-2,6-diiodoanisole (12). A standard methylation procedure was applied to 75 g (0.19 mol) of phenol **11**,[4] 18 g of NaH, 40 g of Me_2SO_4, and 1 L of THF to give, after chromatography on 600 g of alumina–hexane–CH_2Cl_2 (2%, v/v), 64 g (82%) of **12**: mp 47–48 °C; MS (200 °C) *m/e* 416 (M^+, 60); ^1H NMR δ 1.27 (s, CCH_3, 9H), 3.83 (s, OCH_3, 3H), 7.73 (s, Ar*H*, 2H). Anal. Calcd for $C_{11}H_{14}I_2O$: C, 31.76; H, 3.39. Found: C, 31.79; H, 3.36.

4,4′-[5-(1,1-Dimethylethyl)-2-methoxy-1,3-phenylene]bis(dibenzofuran (13). To a suspension of 11.4 g (0.47 mol) of Mg and 0.2 mL of $BrCH_2CH_2Br$ in 50 mL of Et_2O was added (75 min) a solution of 94 g (0.38 mol) of 4-bromodibenzofuran[6] (*CAUTION: Halodibenzofurans are Toxic*) in 350 mL of Et_2O. The mixture was gently refluxed for 12 h, cooled to 25 °C, and cannulated into an addition funnel. This Grignard reagent was added over 2.5 h to a solution of 70 g (0.17 mol) of **12** and 1.6 g (2.4 mmol) of $NiCl_2 2PPh_3$[5] in 125 mL of Et_2O. The suspension was refluxed for 48 h, cooled to 25 °C, and poured into ice–aqueous HCl. The resulting ether layer was dried ($MgSO_4$) and evaporated under reduced pressure, after which the residue was dissolved in C_6H_6 and added to a 600 g silica gel column made up in 1:9 C_6H_6–$(CH_2)_6$ (v/v). With 1:2 and 1:1 respective solvent mixtures as the mobile phase, 66.6 g (80%) of **13** was eluted: mp 172–174 °C, after recrystallization from CH_2Cl_2–EtOH: MS (220 °C) *m/e* 496 (M^+, 60); ^1H NMR δ 1.44 (s, CCH_3, 9H), 3.18 (s, OCH_3, 3H), 7.30–8.00 (m, ArH, 16H). Anal. Calcd for $C_{35}H_{28}O_3$: C, 84.65; H, 5.68. Found: C, 84.71; H, 5.68.

Dimethyl 4,4′-[5-(1,1-Dimethylethyl)-2-methoxy-1,3-phenylene]bis-(dibenzofurandicarboxylate) (14). A solution of 43 g (87 mmol) of **13** in 1.4 L of THF was cooled to −78 °C, and 120 mL of 2.1 M *n*-BuLi-hexane was added. The mixture was warmed to 25 °C and stirred at 25 °C for 7 h. The solution was cooled to −78 °C, and 146 g (1.5 mol) of CH_3O_2CCl was added in one portion. The solution was slowly warmed to 25 °C and concentrated under reduced pressure, and the residue was partitioned between 600 mL of $CHCl_3$ and 1 L of H_2O. The organic layer was dried ($MgSO_4$) and evaporated in vacuo. The residue was dissolved in CH_2Cl_2 and flash chromatographed (SiO_2, 300 g in 1:1 CH_2Cl_2–hexane, v/v) with CH_2Cl_2 as the eluting phase to give 48 g (91%) of **14**: mp 196–198 °C; MS (200 °C) *m/e* 612 (M^+, 100); ^1H NMR δ 1.49 (s, CCH_3, 9H), 3.24 (s, $ArOCH_3$, 3H), 3.95 (s, CO_2CH_3, 6H), 7.40–8.22 (m, Ar*H*, 14H). Anal. Calcd for $C_{39}H_{32}O_7$: C, 76.45; H, 5.26. Found: C, 76.35; H, 5.26.

Dimethyl 5″-(1,1-Dimethylethyl)-2,2′,2″,2‴,2⁗-pentamethoxy[1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl]-3,3⁗-dicarboxylate (15). Approximately half of a mixture of 113 g (2.8 mol) of NaOH and 188 g (2.8 mol) of 85% KOH was heated in a steel crucible to 200 °C. To the molten base was added 27.5 g (45 mmol) of **14** followed by the remainder of the NaOH–KOH mixture in such a way that **14** was covered by the base. The temperature was raised to 300 °C, and the material was kept at that temperature for 1 h. The paste-like material was poured onto a metal tray, cooled to 25 °C, and dissolved in H_2O. The solution was filtered and acidified to pH 1 with concentrated hydrochloric acid, and the precipitate that formed was filtered and dried over P_2O_5 under vacuum. The solid was added to a mixture of 66 g (0.53 mol) of $(CH_3)_2SO_4$ and 100 g (0.72 mol) of K_2CO_3 in 1 L of acetone. The mixture was refluxed for 48 h, cooled to 25 °C and filtered, and the solvent was removed under reduced pressure. The residue was partitioned between $CHCl_3$ (500 mL) and 1 L of 10% aqueous NH_4OH. The organic layer was dried ($MgSO_4$), concentrated to 80 mL, and flash-chromatographed (SiO_2, 300 g) with acetone–CH_2Cl_2 (1:49, v/v) to give 26 g (82%) of **15** as a colorless foam: MS (250 °C) *m/e* (M^+, 100); ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (s, CCH_3, 9H), 3.28 (s, $ArOCH_3$, 6H), 3.31 (s, $ArOCH_3$, 3H), 3.60 (s, $ArOCH_3$, 6H), 3.93 (s, CO_2CH_3, 6H), 7.20–7.81 (m, Ar*H*, 14H). Anal. Calcd for $C_{43}H_{44}O_9$: C, 73.28; H, 6.29. Found: C, 73.19; H, 6.36.

5″-(1,1-Dimethylethyl)-2,2′,2″, 2‴, 2⁗-pentamethoxy[1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl]-3,3⁗-dimethanol (16). To a solution of 7.5 g (10.6 mmol) of **15** in 300 mL of EtOH was added a solution of 20 g (0.5 mol) of NaOH in 25 mL of H_2O. The mixture was refluxed for 3 h, cooled to 25 °C, and concentrated to 50 mL under reduced pressure. The resulting solution was diluted with 500 mL of H_2O, acidified to pH 1 with concentrated hydrochloric acid, and filtered. The crude diacid was dried and dissolved in 500 mL of THF, and 45 mL (45 mmol) of 1 M BH_3·THF was added by syringe. The mixture was refluxed for 3 h and cooled to 25 °C, and excess BH_3 was cautiously decomposed with H_2O. Saturated aqueous K_2CO_3 solution (200 mL) was added, and the resulting mixture was stirred at 25 °C for 12 h. The organic solvent was evaporated under reduced pressure, and the residue was partitioned between $CHCl_3$ and H_2O. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure, and the resulting oil was dissolved in CH_2Cl_2 and chromatographed on 250 g of silica gel made up in CH_2Cl_2. Elution of the product with acetone–CH_2Cl_2 mixtures (1:9 and 1:4, v/v) gave 5.75 g (83%) of **16** as a colorless foam: MS (250 °C) *m/e* 648 (M^+, 100); ^1H NMR δ 1.34 (s, CCH_3, 9H), 3.30 (s, OCH_3, 9H), 3.51 (s, OCH_3, 6H), 4.77 (s, $ArCH_2$, 4H), 7.12–7.45 (m, ArH, 14H). Anal. Calcd for $C_{41}H_{44}O_7$: C, 75.90; H, 6.84. Found: C, 75.92; H, 6.54.

[1,1′:3′,1″:3″,1‴:3‴,1⁗-Quinquephenyl], 3,3⁗-Bis(chloromethyl)-5″-(1,1-dimethylethyl)-2,2′,2″,2‴,2⁗-pentamethoxy- (17). Procedure A. A mixture of 8.4 g (31.7 mmol) of Ph_3P, 4.1 g (30.8 mmol) of *N*-chlorosuccinimide, and 600 mL of THF under N_2 at 25 °C was stirred for 15 min. To this suspension was added 8 g (12.3 mmol) of **16**, and the mixture was stirred for 6 h. The suspension was diluted with $CHCl_3$ (1 L) and 10% aqueous NaCl (800 mL), and the layers were separated. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in benzene and added to a silica gel column (300 g) made up in C_6H_6. Elution of the column with 3 L of benzene gave 5.7 g (68%) of **7** as a white foam after drying under vacuum: MS *m/e* M^+ (^{35}Cl) 684; ^1H NMR δ 1.34 (s, CCH_3, 9H), 3.30 (s, OCH_3, 6H), 3.31 (s, OCH_3, 3H), 3.54 (s, OCH_3, 6H), 4.73 (s, CH_2Cl, 4H), 7.16–7.45 (m, Ar*H*, 14H). Anal. Calcd for $C_{41}H_{42}Cl_2O_5$: C, 71.81; H, 6.17. Found: C, 71.88, H, 6.07.

[1,1′:3′,1″:3″,1‴:3‴,1⁗-Quinquephenyl], 5″-(1,1-Dimethylethyl)-3-(chloromethyl)-3⁗-(hydroxymethyl)-2,2′,2″,2‴,2⁗-pentamethoxy- (18). Procedure A was applied to 5.2 g (8 mmol) of **16**, 1.3 g (9.8 mmol) of *N*-chlorosuccinimide, and 2.62 g (10 mmol) of Ph_3P in 350 mL of THF. The crude product was chromatographed on 350 g of silica gel made up in CH_2Cl_2. Elution of the column with CH_2Cl_2 gave 1.1 g (20%) of dichloride **17**. Elution with 5% Et_2O–95% CH_2Cl_2 gave 1.4 g (26%) of chloro alcohol **18** as a white foam: MS *m/e* M^+ (^{35}Cl) 666; ^1H NMR δ 1.34 (s, CCH_3, 9H), 3.30–3.54 (m, OCH_3, 15H), 4.73 (s, CH_2Cl, 2H), 4.77 (s, CH_2OH, 2H), 7.16–7.46 (m, Ar*H*, 14H). Anal. Calcd for $C_{41}H_{43}ClO_6$: C, 73.80; H, 6.50. Found: C, 73.82; H, 6.54. Further elution of the column with 4:1 CH_2Cl_2–Et_2O (v/v) gave 0.8 g (15%) of recovered diol **16**.

23-Oxahexacyclo[23.3.1.$1^{2,6}$.$1^{7,11}$.$1^{12,16}$.$1^{17,21}$]tritritiaconta-1(29),2,4,6-(33),7,9,11(32),12,14,16(31),17,19,21(30),25,27-pentadecaene, 9-(1,1-Dimethylethyl)-29,30,31,32,33-pentamethoxy- (7). Procedure B. To a refluxing suspension of 2.0 g (41.7 mmol) of NaH (50% mineral oil dispersion) in 1 L of THF under Ar was added a solution of 2.0 g (3 mmol) of **18** in 600 mL of THF (30 h). The mixture was refluxed an additional 12 h and cooled to 0 °C, and H_2O was added to decompose excess NaH. The solution was evaporated under reduced pressure and the residue partitioned between CH_2Cl_2 (300 mL) and 4 M aqueous NaCl solution. After the mixture had stirred for 4 h, the layers were separated, and the organic phase was dried ($MgSO_4$), concentrated to 10 mL, and diluted with 150 mL of petroleum ether. Filtration gave 1.35 g (65%) of **7**·NaCl as a white solid: mp >300 °C; ^1H NMR δ 1.39 (s, CCH_3, 9H), 2.78 (s, OCH_3, 6H), 3.07 (s, OCH_3, 3H), 3.54 (s, OCH_3, 6H), 4.51 (d, $J = 9.5$ Hz, $ArCH_2$, 2H), 5.05 (d, $J = 9.5$ Hz, $ArCH_2$, 2H), 7.28–7.59 (m, Ar*H*, 14H). Anal. Calcd for $C_{41}H_{42}O_6$·NaCl: C, 71.45; H, 6.14. Found: C, 71.26; H, 6.25.

A 250-mg (0.36 mmol) sample of **7**·NaCl in 50 mL of CH_2Cl_2 was washed with five 150-mL portions of deionized H_2O to give 200 mg

(87%) of **7**: mp 264-266 °C, after recrystallization from CH_2Cl_2–EtOH; MS *m/e* 630 (M^+, 100); ^1H NMR δ 1.34 (s, $C(CH_3)_3$, 9H), 2.54 (s, OCH_3, 6H), 3.00 (s, OCH_3, 3H), 3.38 (s, OCH_3, 6H), 4.43 (d, $J = 8.5$ Hz, $ArCH_2$, 2H), 4.82 (d, $J = 8.5$ Hz, $ArCH_2$, 2H), 6.95–7.49 (m, ArH, 14H). Anal. Calcd for $C_{41}H_{42}O_6$: C, 78.07; H, 6.71. Found: C, 78.17; H, 6.82.

In an alternative synthesis of **7**·NaCl, a modified Procedure B was applied to diol **16** and tosyl chloride. A solution of 1.25 g (1.9 mmol) of **16** and 360 mg (1.9 mmol) of tosyl chloride in 600 mL of THF was added over 16 h to a refluxing suspension of 2.0 g (41.7 mmol) of NaH (50% mineral oil dispersion) in 1 L of THF under argon. The mixture was refluxed for 12 h and the product isolated to give 355 mg (29%) of **7**·NaCl with identical properties to authentic material.

23-Thiahexacyclo[23.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}]tritritiaconta-1(29),2,4,6-(33),7,9,11(32),12,14,16(31),17,19,21(30),25,27-pentadecaene, 9-(1,1-Dimethylethyl)-29,30,31,32,33-pentamethoxy- (8). To a vigorously stirred suspension of 0.89 g (3.7 mmol) of $Na_2S{\cdot}9H_2O$ in 300 mL of EtOH at 25 °C under Ar was added a solution of 0.71 g (1.04 mmol) of dichloride **17** in 40 mL of 7:1 EtOH–C_6H_6 (v/v) over a 9-h period. The mixture was stirred for 10 h at 25 °C, refluxed for 48 h, cooled to 25 °C, and diluted with 50 mL of H_2O. The suspension was concentrated to 50 mL and diluted with CH_2Cl_2 (200 mL) and 10% aqueous NaCl (300 mL). After stirring for 24 h at 25 °C, the CH_2Cl_2 layer was dried ($MgSO_4$) and evaporated, and the residue, dissolved in benzene. Addition of hexane gave an amorphous solid which was filtered and dissolved in 100 mL of CH_2Cl_2. Decomplexation of any NaCl complex was performed by extracting the CH_2Cl_2 solution with 5 portions of deionized H_2O (200 mL). The organic layer was dried ($MgSO_4$) and concentrated, and EtOH was added to give 318 mg (47%) of **8**: mp >300 °C; MS (300 °C) *m/e* 646 (M^+, 100); ^1H NMR δ 1.34 (s, $C(CH_3)_3$, 9H), 2.58 (s, OCH_3, 6H), 3.02 (s, OCH_3, 3H), 3.48 (s, OCH_3, 6H), 4.03 (d, $J = 10.3$ Hz, $ArCH_2$, 2H), 4.13 (d, $J = 10.3$ Hz, $ArCH_2$, 2H), 6.88–7.49 (m, ArH, 14H). Anal. Calcd for $C_{41}H_{42}O_5S$: C, 76.13; H, 6.54. Found: C, 76.14; H, 6.60.

Hexacyclo[23.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}]tritritiaconta-1(29),2,4,6(33),7,9,-11(32),12,14,16(31),17,19,21(30),25,27-pentadecaene-23,23-dicarboxylic Acid, 9-(1,1-Dimethylethyl)-29,30,31,32,33-pentamethoxy-, Diethyl Ester (9) and Hexacyclo[23.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}]tritritiaconta-1-(29),2,4,6(33),7,9,11(32),12,14,16(31),17,19,21(30),25,27-pentadecaene-23-carboxylic Acid, 9-(1,1-Dimethylethyl)-29,30,31,32,33-pentamethoxy-, Ethyl Ester (10). A solution of 2.6 g (3.8 mmol) of dichloride **17** and 650 mg (4.1 mmol) of diethyl malonate in 0.9 L of THF was added over 40 h to a refluxing suspension of 2.4 g (50 mmol) of NaH (50% mineral oil dispersion) in 1 L of THF under Ar. The mixture was refluxed an additional 6 h and cooled to 0 °C, and excess NaH was decomposed with 1 N hydrochloric acid. The mixture was concentrated to 300 mL under reduced pressure and then diluted with $CHCl_3$ (400 mL) and 2 N aqueous NaCl (200 mL). The layers were separated, and the aqueous layer was extracted with 100 mL of $CHCl_3$. The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in 250 mL of CH_2Cl_2 and stirred for 12 h with 300 mL of 4 N aqueous NaCl solution. The CH_2Cl_2 layer was separated out, dried ($MgSO_4$), concentrated to 10 mL, and diluted with 200 mL of petroleum ether. Filtration gave 1.8 g (57%) of **9**·NaCl: mp 256 °C dec, after drying under vacuum at 25 °C; MS (**9**·NaCl) (250 °C) *m/e* 772, free **9** (loss of NaCl, 70%), 700, host **10** (loss of CO_2Et and NaCl, 100%); ^1H NMR δ 0.85 (t, OCH_2CH_3, 3H), 1.40 (s, CCH_3, 9H), 1.51 (s, OCH_2CH_3, 3H), 2.81 (s, OCH_3, 6H), 3.17 (s, OCH_3, 3H), 3.53 (s, OCH_3, 6H), 3.32 (q, OCH_2CH_3, 2H), 4.50 (q, OCH_2CH_3, 2H), 3.25–3.97 (m, $ArCH_2$, $CHCO_2Et$, 5H), 7.16–7.62 (m, ArH, 14H). The NaCl complex was decomplexed to give **9** without further purification. A solution of 300 mg (0.36 mmol) of **9**·NaCl in CH_2Cl_2 was washed with three 150-mL portions of deionized H_2O. The organic layer was dried ($MgSO_4$) and concentrated to give 250 mg (90%) of **9**, recrystallized from CH_2Cl_2–EtOH: mp 199-201 °C; MS (330 °C) *m/e* 772 (M^+, 100); ^1H NMR δ 1.14 (t, OCH_2CH_3, 3H), 1.27 (t, OCH_2CH_3, 3H), 1.33 (s, CCH_3, 9H), 2.45 (s, OCH_3, 6H), 3.05 (s, OCH_3, 3H), 3.26 (s, OCH_3, 6H), 3.98 (q, OCH_2CH_3, 2H), 4.28 (q, OCH_2CH_3, 2H), 3.21–3.82 (m, $ArCH_2$, $CHCO_2Et$, 5H), 6.87–7.49 (m, ArH, 14H). Anal. Calcd for $C_{48}H_{52}O_9$: C, 74.59; H, 6.78. Found: C, 74.24; H, 6.44.

The filtrate from the crystallization of **9**·NaCl was evaporated under reduced pressure and the residue dissolved in 25 mL of CH_2Cl_2. This solution was added to a silica gel column (150 g) made up in CH_2Cl_2. Elution of the column with CH_2Cl_2–acetone (4:1) gave 0.4 g (15%) of **10**: mp 260–262 °C; MS (250 °C) *m/e* 700 (M^+, 100); ^1H NMR δ 0.77 (t, OCH_2CH_3, 3H), 1.35 (s, CCH_3, 9H), 2.57 (s, OCH_3, 6H), 3.06 (s, OCH_3, 3H), 3.35 (s, OCH_3, 6H), 2.74–3.81 (m, OCH_2, $ArCH_2$, $CHCO_2Et$, 7H), 6.87–7.53 (m, ArH, 14H). Anal. Calcd for $C_{45}H_{48}O_7{\cdot}0.5H_2O$: C, 76.22; H, 6.82. Found: C, 75.88; H, 7.28.

A similar experiment to that described above in which the addition of dichloride **17** and diethyl malonate was extended to 72 h and the additional reflux period to 48 h gave 35% of **10** and no isolable **9**·NaCl.

Association Constants and Free Energies of Binding. The standard extraction-picrate colorimetric method was applied[8] except that the vortexing of the $CDCl_3$–D_2O layers was extended to 6 min for Li^+ and Na^+ and to 3 min for the other ions to ensure that equilibrium was reached.

Complexation of Diester 9 and Ester 10. One equivalent of **9** and $LiClO_4$ or $NaClO_4$ dissolved in 98% $CDCl_3$–2% $(CD_3)_2SO$ were mixed to produce a 0.064 M solution of **9**·$LiClO_4$ and **9**·$NaClO_4$, respectively, whose ^1H NMR spectral data (25 °C) are as follows: **9**·$LiClO_4$, δ 0.78 (t, OCH_2CH_3, 3H), 1.43 (s, CCH_3, 9H), 1.48 (t, OCH_2CH_3, 3H), 2.91 (s, OCH_3, 6H), 3.20 (s, OCH_3, 3H), 3.27 (q, OCH_2CH_3, 2H), 3.51 (s, OCH_3, 6H), 3.18–3.92 (m, $ArCH_2$, $CHCO_2Et$, 5H), 4.46 (q, OCH_2CH_3, 2H), 7.24–7.66 (m, ArH, 14H); **9**·$NaClO_4$, δ 0.86 (t, OCH_2CH_3, 3H), 1.41 (s, CCH_3, 9H), 1.51 (t, OCH_2CH_3, 3H), 2.82 (s, OCH_3, 6H), 3.12 (s, OCH_3, 3H), 3.31 (q, OCH_2CH_3, 2H), 3.47 (s, OCH_3, 6H), 3.15–3.98 (m, $ArCH_2$, $CHCO_2Et$, 5H), 4.48 (q, OCH_2CH_3, 2H), 7.18–7.65 (m, ArH, 14H).

Identical experiments applied to ester **10** gave the following complexes, whose ^1H NMR spectral data are as follows: **10**·$LiClO_4$, δ 0.92 (t, OCH_2CH_3, 3H), 1.42 (s, $C(CH_3)_3$, 9H), 2.89 (s, OCH_3, 6H), 3.27 (s, OCH_3, 3H), 3.65 (s, OCH_3, 6H), 2.57–3.87 (m, OCH_2CH_3, $ArCH_2$, $CHCO_2Et$, 7H), 7.21–7.69 (m, ArH, 14H); **10**$NaClO_4$, δ 1.00 (t, OCH_2CH_3, 3H), 1.35 (s, $C(CH_3)_3$, 9H), 2.83 (s, OCH_3, 6H), 3.12 (s, OCH_3, 3H), 3.54 (s, OCH_3, 6H), 2.53–2.83 (m, OCH_2CH_3, $ArCH_2$, $CHCO_2Et$, 7H), 7.16–7.64 (m, ArH, 14H).

Equilibrations Involving Diester 9, Ester 10, Hosts 8 and 19, $LiClO_4$, and $NaClO_4$. Attempted Na^+ picrate extractions from D_2O into $CDCl_3$ solutions of **10** and **11** at 25 °C (vortexing for 1 h) failed to reach equilibrium. Accordingly, $NaClO_4$ or $LiClO_4$ was partitioned (equilibrated) between two hosts, one host of known K_a (M^{-1}) and the other, **9**, of unknown K_a. From the results, the $-\Delta G°$ value at 25 °C for binding for the unknown host was estimated.[9] The solvent in all experiments was 98% $CDCl_3$ and 2% $(CD_3)_2SO$; equivalent amounts of a complex and a host at about 0.01 M concentration were employed; the guest exchange was monitored by changes in the ^1H NMR spectra. When **9**·$NaClO_4$ and **8** were equilibrated for 12 h, only **9** and **8**$NaClO_4$ could be detected at equilibrium. Hence, $-\Delta G°$ is <14.4 kcal mol-1. When **9** was equilibrated with **19**·$NaClO_4$ for 36 h at 25 °C, [**9**·$NaClO_4$]:[**9**] = 70:30. When **9**·$NaClO_4$ was equilibrated with **19**, [**9**·$NaClO_4$]:[**9**] = 60:40. Since the $-\Delta G°$ value for **18** binding Na^+ picrate[9] is 13.3 kcal mol-1 in $CDCl_3$ at 25 °C, we estimate **9** to have a $-\Delta G°$ value of about 13.4 kcal mol^{-1}. This estimate involves the assumption that the equilibrium points are independent of the counterion (picrate vs perchlorate). When **9**·$LiClO_4$ was equilibrated at 60 °C for 12 days with **19**, [**9**·$LiClO_4$]:[**9**] = 1:1. Since $-\Delta G°$ of **19**·$LiClO_4$ is 16.8 kcal mol^{-1}, that of **9**·$LiClO_4$ appears to be similar. Equilibrations at 25 °C were too slow to be studied.

A solution of ester **10** and 2 equiv of $NaClO_4$ gave an ^1H NMR spectrum for only **10**·$NaClO_4$. When 0.2 equiv of $LiClO_4$ was added, the two complexes equilibrated at 25 °C for 24 h gave [**10**·$NaClO_4$]:[**10**·$LiClO_4$] = 4:1. When 1 equiv of $LiClO_4$ was substituted in the above experiment for the 0.2 equiv, only **10**·$LiClO_4$ was detected, although the total of equivalents of $NaClO_4$ and $LiClO_4$ present was 2:1.

Crystal Structure Data. Compound **7** crystallized as colorless plates in the monoclinic system $P2_1/c$. Unit cell dimensions are as follows: $a = 31.684(5)$ Å, $b = 10.864(3)$ Å, $c = 21.328(4)$ Å, $\beta = 108.34(1)°$, $V = 6969$ Å^3, $Z = 8$ (2 independent molecules). The crystal was examined on a modified Syntex $P\bar{1}$, diffractometer with CuKα radiation at 298 K. The structure was determined by direct methods. Refinement of 424 + 424 parameters (2 blocks, 6230 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.103.

Compound **8** crystallized from CH_2Cl_2–EtOH as colorless parallelepipeds in the monoclinic system $P2_1/n$. Unit cell dimensions are as follows: $a = 15.128(2)$ Å, $b = 11.897(1)$ Å, $c = 19.615(2)$ Å, $\beta = 95.291(2)°$, $V = 3515$ Å^3, $Z = 4$. The crystal was examined on a modified Syntex $P\bar{1}$ diffractometer with CuKα radiation at 298 K. The structure was determined by direct methods. Refinement of 269 parameters (2790 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.089. Details will be published elsewhere.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **7** and **8** (13 pages). Ordering information is given on any current masthead page.