Efficient Syntheses and Crystal Structures of New Benzene-Containing Cryptands

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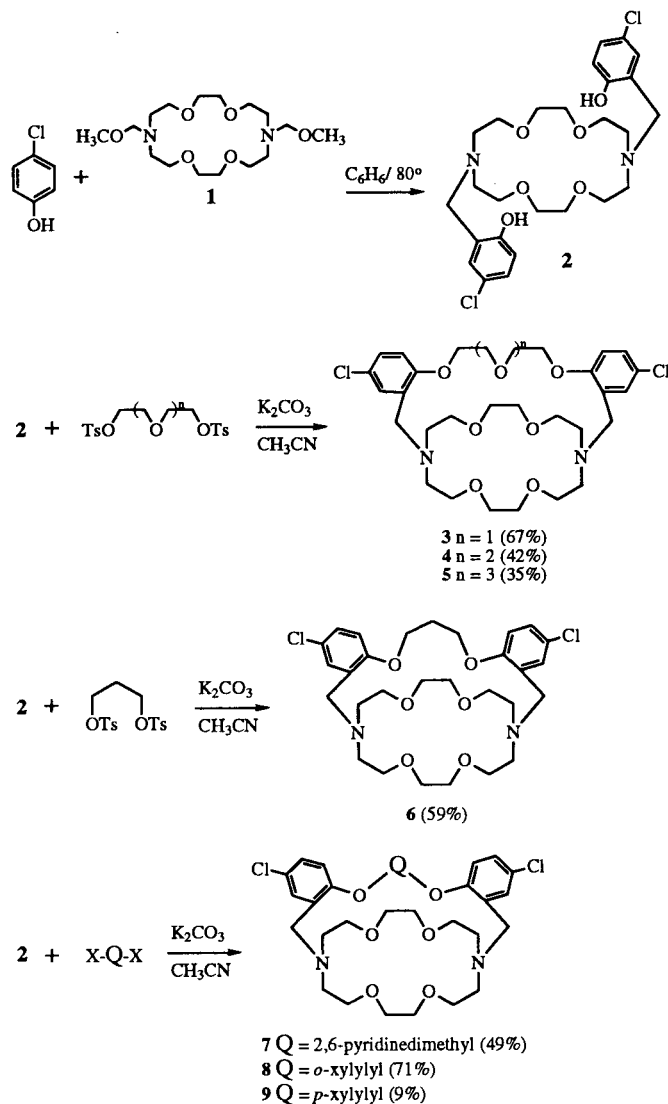**This work is dedicated to Professor N. E. Alexandrou of Thessaloniki, Greece**

Seven new cryptands **3-9** containing two or three aromatic rings in one bridge were prepared in good yields by treating N,N'-bis(p-chlorophenol)-substituted diaza-18-crown-6 (**2**) with three oligoethylene glycol ditosylates, 1,3-propanediol ditosylate, 2,6-pyridinedimethanol ditosylate, α,α'-dibromo-o-xylene and α,α'-dibromo-p-xylene. Because of the convenient synthesis of **2** from N,N'-bis(methoxymethyl)diaza-18-crown-6 (**1**) and the relative ease of isolation of the cryptand products, this is an excellent method for the design of three-dimensional cavities containing aromatic fragments. In an attempt to better understand the synthetic route to the cryptands, the crystal structures of KI•**2** and Na Picrate•**2** were determined using X-ray analysis. In addition, crystal structure analyses of cryptands **3**, **6** and **8** were used to establish their structures.

Introduction.

Cryptands are superior complexing agents for metal cations and other charged or neutral guest species. Cryptands, cryptohemispherands and other bi- and polycyclic ligands can encapsulate guest cations and thus provide more effective binding and selectivity than that provided by the unidimensional moncyclic crown ethers [1]. Cryptands in general are not accessible. Only a few of them are commercially available and they are very expensive. It is important to find convenient methods to prepare these three-dimensional ligating agents and to elaborate the conditions for their large scale syntheses.

Most of the known methods for cryptand syntheses include many steps to prepare the intermediates. Thus, the cryptands are prepared in low overall yields. In the classical approach [2-5], cyclization of diazacrowns with diacyl chlorides requires reduction of the resulting macrocyclic diamides and decomposition of the borane-cryptand complex when B_2H_6 is the reducing agent. The cyclization reaction is accompanied by polycondensation which further reduces the yield of the desired macrocycle. Template metal ions, high dilution conditions and high pressure techniques have been used to reduce polycondensation. New syntheses of three-dimensional macroheterocycles have been achieved using one-step reactions with good to excellent yields [6-10]. Self-assembly cyclization is another step toward efficient and simple syntheses of the cryptands [11,12]. Special building blocks containing self-coordinating sites in proper positions allow the synthesis of hydroxy-, amide- and phenol-containing crytands in high yields [11-14]. We have been studying a modified Mannich reaction for the synthesis of new azamacroheterocycles [11,12,14-20]. A number of bi- and tricyclic ligands have been prepared by treating the appropriate bisphenolic substances with N,N'-bis(methoxymethyl)diaza-18-crown- 6 (**1** in Scheme 1) [11,12].

Scheme I. Preparation of New Cryptands

3 n = 1 (67%)
4 n = 2 (42%)
5 n = 3 (35%)

6 (59%)

7 Q = 2,6-pyridinedimethyl (49%)
8 Q = o-xylylyl (71%)
9 Q = p-xylylyl (9%)

Results and Discussion.

Refluxing the methoxymethyl-substituted azacrown ethers with phenols in nonpolar solvents gave the phenol-substituted azacrown ethers in good yields [11]. For example, lariat diazacrown **2** was prepared in a 77% yield by treating **1** with 4-chlorophenol in refluxing benzene [19]. The phenol-containing macrocycles can have electron donor as well as electron acceptor substituents in the phenol ring [11]. Compound **2** is a key intermediate for cyclization with various bisalkylating agents to form three-dimensional macrocycles. The phenolic OH groups of **2** were alkylated by the appropriate ditosylates to form cryptands **3-6** in good yields (Scheme I). The reactions were carried out in refluxing acetonitrile using potassium carbonate as the base. Cryptands **7-9** were prepared in a similar manner using the appropriate α,α'-dibromoxylene or 2,6-pyridinedimethanol ditosylate. Techniques to prevent polycondensation, *i.e.*, high dilution, were not used in the cyclization step. The excellent yields of the cryptands must be caused by the potassuium ion acting as a template (Figure 1).
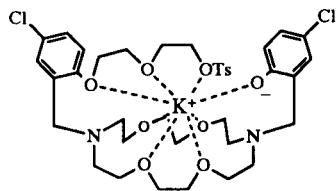

Figure 1. Possible Structure of the Intermediate in the Cyclization Step.

There are three significant advantages of this new cryptand synthesis. First, starting bisphenol-substituted diazacrown ethers, as well as the final cryptands, are obtained in good yields (except for cryptand **9**) and they are easily purified. This allows the preparation of these cryptands on a large scale. Second, a wide variation of cryptand structures are possible as shown in Scheme I and their geometric parameters can be adjusted to fit the steric requirements of the guests. Third, benzene-containing cryptands which have various functional groups on the benzene rings can be prepared in the ring-closure step. Usually, the benzene rings of benzomacrocycles are functionalized after the cyclization step. In many cases, such functionalization requires drastic conditions which can decompose the macrocycle or lead to by-products which would make it difficult to isolate the cryptand. We believe that this new method will find wide application for the preparation of azamacroheterocycles of different topologies.

Crystal structure studies of the KI•**2** complex, referred to as K⁺•**2**, and the Na Picrate•**2** complex, referred to as Na⁺•**2**, were initiated in order to investigate the role of a template cation in the synthesis of these cryptands. Both complexes in

the solid state exist with the phenol arms on opposite sides of the diaza-18-crown-6 ring (*trans* form) (see Figures 2 and 3).
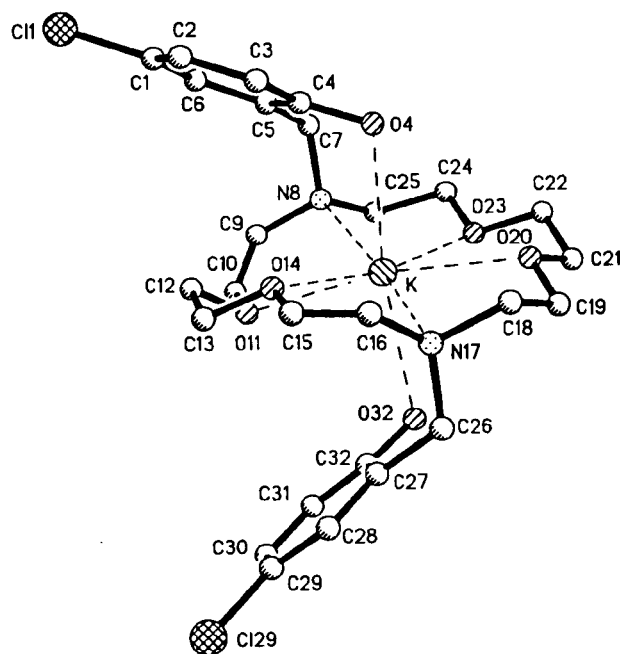

Figure 2. A computer drawing of K⁺•**2** with hydrogen atoms and the disordered I⁻ omitted for clarity.
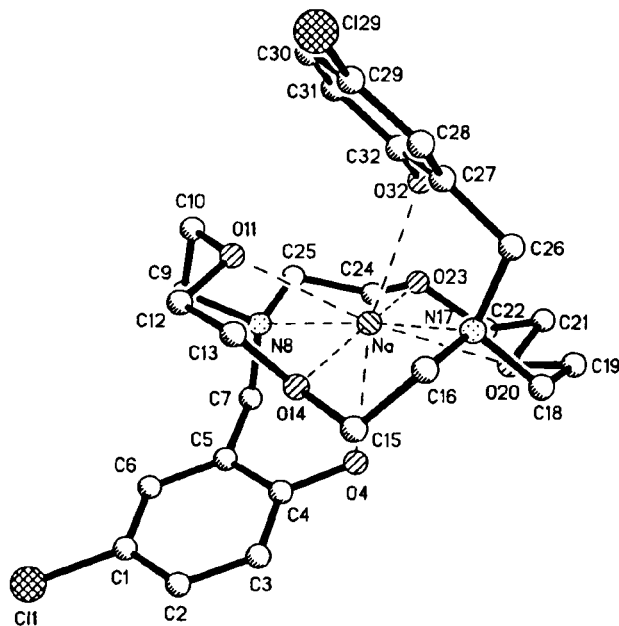

Figure 3. A computer drawing of Na⁺•**2** with hydrogen atoms, the picrate anion an the methanol solvent molecule omitted for clarity. Only one position of each disordered atom is shown.

In the solid state structure of K⁺•**2**, the K⁺ is coordinated by the six donor atoms of the crown ring as well as the phenol oxygens. The K⁺···donor atom interatomic distances are

Donor Atom	K⁺•2 (Å)	Na⁺•2 (Å)
O4	2.76(1)	2.523(5)
N8	2.93(1)	2.763(5)
O11	2.73(1)	2.570(4)
O14	2.68(1)	2.506(5)
N17	2.94(1)	2.809(5)
O20	2.68(1)	2.480(4)
O23	2.72(2)	2.510(5)
O32	2.76(1)	2.540(5)

included in Table 1. The iodide ion is disordered in the structure with a partial iodide, I, located at a site near O4 and with the other partial iodide, I′, located at a site near O32. The occupancy factors of the two sites were refined in such a manner that their sum was required to be 1.0. The refined values for the occupancies were 0.50 ±0.01. The iodides in both sites are involved in hydrogen bonds with their neighboring oxygen atoms. The hydrogen bond data are listed in Table 2. The disorder of this atom does not mean that there is one-half an iodide in each site, but rather that there is one iodide ion associated with each complex and that half of these molecules have the iodide at the site near O4 and a vacancy at the site near O32 while the other half of the molecules have the opposite arrangement. X-ray studies give a time averaged structure so that it appears that there are half atoms in each site of the structure.

The structure of Na⁺•2 is similiar to that of K⁺•2 (see Figures 2 and 3). The cation is coordinated by the eight donor atoms of 2 and the interatomic distances between the Na⁺ and the donor atoms are included in Table 1. In this structure, the phenol oxygen atoms are also involved in hydrogen bonds. These interactions link O4 to O38 of the picrate anion and O32 to O39 of a methanol of solvation. The data for these H-bonds are listed in Table 2.

plane [19]. The high yields of 3-8 were unexpected because the starting intermediate has the interacting groups in a *trans* conformation which is unfavorable for cyclization. Evidently, in the reaction solution containing potassium carbonate, the *p*H of the solution is high enough to deprotonate the phenols so that hydrogen bonding is not possible. In this situation, the *cis* form of the complex (the aromatic fragments are located on the same side of the diazacrown ring) is likely because of the coordinating role of the potassium cation acting as a template (Figure 1).

The structures of cryptands 3, 6 and 8 were also determined by X-ray diffraction. The three cryptands were synthesized using 2 as the major building block and, therefore, the three structures have the diaza-18-crown-6 ring and the phenol arms in common. However, they differ in the organic bridge joining the phenol oxygen atoms. Because of the phenol groups of 2, the third branch of the cryptand contains at least two, three in 8, benzene rings. There are two chemically identical but crystallographically different molecules of 3 in its asymmetric unit, so there are a total of four different cryptand molecules that will be discussed. In the structure of 3, the molecule containing atoms N1 through C39 is referred to as molecule 3-A while the molecule containing atoms N51 through C89 is called molecule 3-B. Computer drawings of 3-A, 3-B, 6 and 8 are shown in Figures 4, 5, 6 and 7, respectively. The labels of chemically similiar atoms of the diaza-crown ring and one benzo-containing arm are the same in 3, 6, and 8. In order to identify similar atoms of 3-A and 3-B, 50 was added to the atom label numbers of 3-A to give the atom label numbers of 3-B. Thus N51 in 3-B corresponds to N1 in 3-A. The conformation of 3-A differs considerably from that of 3-B. Molecule 3-A is much more elliptical (see Figures 4 and 5). It is apparent that all the

O	H	A	O···A(Å)	H···A(Å)	O-H···A(Å)
		K⁺•2			
O4	H4	I	3.41	2.60	137
O32	H32	I′	3.36	2.54	138
		Na⁺•2			
O4	H4	O38	2.751	1.82	164
O32	H32	O39	2.674	1.56	169

Both complexes reported here exist in the *trans* form and in each structure there are hydrogen bonds involving the lariat arms. It appears that in the solid state, the hydrogen bonds are important in determining the conformation of the complexes. In the structure of uncomplexed 2, intramolecular hydrogen bonding also is a factor in causing the *trans* relationship of the phenol arms relative to the diazacrown
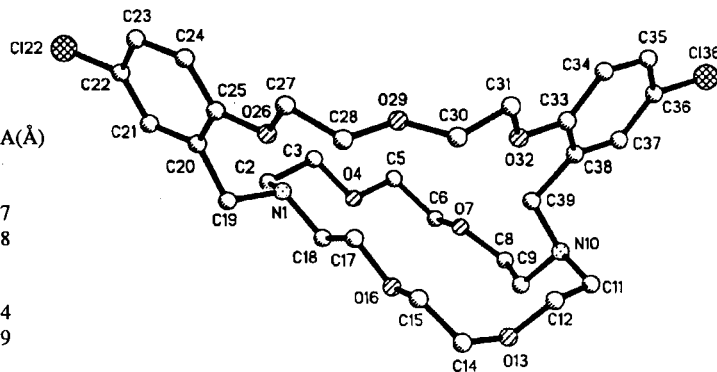

Figure 4. A computer drawing of 3-A with hydrogen atoms omitted for clarity.

molecules have some similarities and also some major differences. Each cryptand contains the atoms of 2 as a basis. The bridge joining the phenol oxygens consists of five atoms in the two molecules of 3, three atoms in 6 (see
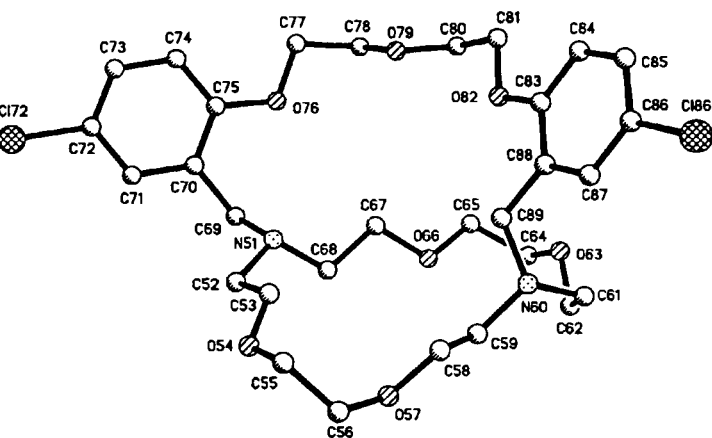
Figure 5. A computer drawing of **3-B** with hydrogen atoms omitted for clarity. The atoms labels of **3-B** are obtained by adding 50 to the atom label of the corresponding atom of **3-A**.
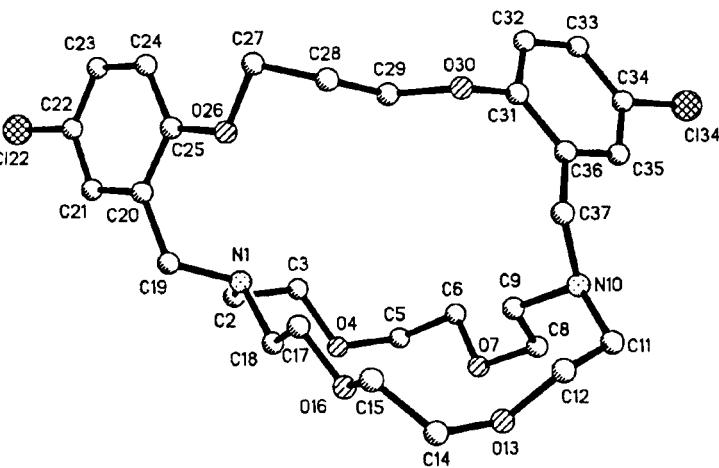

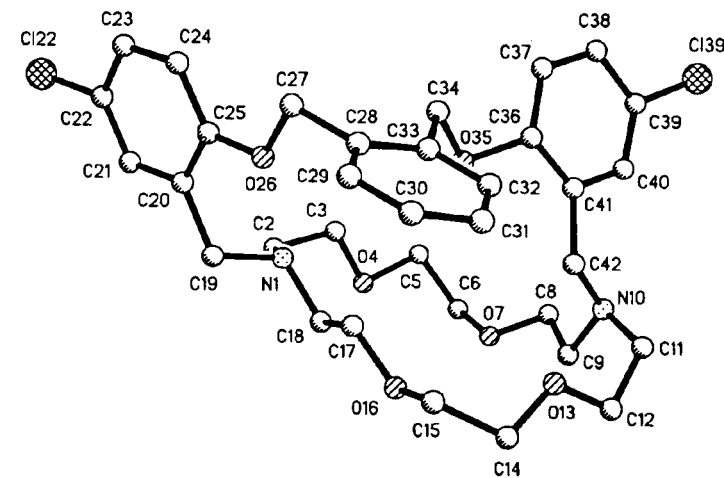Figure 6. A computer drawing of **6** with hydrogen atoms omitted for clarity.

Figure 7. A computer drawing of **8** with hydrogen atoms omitted for clarity. Only one position of each disorded atom is shown.

Figure 6), and four atoms in **8** which includes two carbon atoms of an *ortho* bonded benzene group (see Figure 7). There are few common conformational features in the diaza-18-crown-6 rings of the four molecules. The rings are not preorganized for complexation. The torsion angles of the diaza-18-crown-6 rings in the four molecules are compared in Table 3. These angles generally have low energy values but each molecule contains several exceptions to the values commonly found in pre-organized ligands and in crowns and cryptands which are complexing metal ions. In such ligands, D-C-C-D (D represents a donor O or N atom) torsion angles have values close to 60°, while the C-D-C-C torsion angles have values near 180°. It is interesting to note that in the four cryptands, the lone pair of electrons of N1 (N51 in **3-B**) point into the cavity (endo), while similar electrons of N10 (N60 in **3-B**) point out of the cavity (exo). In the uncomplexed cryptand, 2.2.2, both nitrogen atoms are in the endo form and in the disubstituted BH_3 derivative of 2.2.2 both nitrogens are in the exo form [21]. While 2.2.2 is not a model molecule for these cryptands, each benzo-cryptand does have one 18-crown-6 ring which is identical to the rings in 2.2.2.

Table 3
Torsion Angles of the Diaza-18-Crown-6 Ring of Each Cryptand (Å)

Atoms				3-A	3-B	6	8
C18	N1	C2	C3	-71	75	-79	-71
N1	C2	C3	O4	74	-162	84	94
C2	C3	O4	C5	180	179	-174	178
C3	O4	C5	C6	171	-98	89	164
O4	C5	C6	O7	-63	56	72	-62
C5	C6	O7	C8	-173	79	-179	-94
C6	O7	C8	C9	-160	-172	82	174
O7	C8	C9	N10	-88	175	180	-135
C8	C9	N10	C11	-162	144	-83	-166
C9	N10	C11	C12	-76	54	-67	-59
N10	C11	C12	O13	65	79	75	-57
C11	C12	O13	C14	-165	-160	-161	172
C12	O13	C14	C15	85	117	93	-159
O13	C14	C15	O16	52	-77	61	74
C14	C15	O16	C17	-173	166	-165	-147
C15	O16	C17	C18	-170	171	-176	-180
O16	C17	C18	N1	179	167	-168	-175
C17	C18	N1	C2	162	-159	167	163

A structural feature that is often used in comparing cryptands is the N···N interatomic distance. It was expected that there would be a correlation between the N···N distance and number of atoms bridging the two oxygen atoms in the benzene-containing branches. This was not found to be the case, as the longest (6.65Å) and the shortest (5.82Å) N···N interatomic distances are found in molecules **3-A** and **3-B**, respectively, which are the molecules with the same number of bridging atoms (5 atoms). The other N···N interatomic distances are 6.39Å in **6** with 3 bridging atoms and 6.27Å in **8** which has 4 bridging

Table 4
Crystal Data and Experimental Details for the Structures Reported

	K⁺•2	Na⁺•2	3	6	8
Formula	[K(C$_{26}$H$_{36}$N$_2$O$_6$Cl$_2$)]I	[Na(C$_{26}$H$_{36}$N$_2$O$_6$Cl$_2$)] (C$_6$H$_2$N$_3$O$_7$)•CH$_3$OH	C$_{30}$H$_{42}$Cl$_2$N$_2$O$_7$	C$_{29}$H$_{40}$Cl$_2$N$_2$O$_6$	C$_{34}$H$_{42}$Cl$_2$N$_2$O$_6$
Crystal Size(mm)	0.30 x 0.48 x 0.58	0.40 x 0.42 x 0.50	0.20 x 0.30 x 0.42	0.20 x 0.32 x 0.56	0.10 x 0.40 x 0.46
Space Group	P$\bar{1}$	P2$_1$/c	P2$_1$/c	P$\bar{1}$	P2$_1$/c
Unit Cell Dimension	a = 10.234(4)Å	a = 11.855(8)Å	a = 29.222(11)Å	a = 9.430(3)Å	a = 14.230(10)Å
	b = 11.413(5)Å	b = 15.450(9)Å	b = 13.044(5)Å	b = 12.701(5)Å	b = 13.733(9)Å
	c = 14.947(7)Å	c = 21.497(12)Å	c = 16.831(8)Å	c = 14.693(6)Å	c = 16.965(8)Å
	α = 87.52(3)Å	β = 96.72(5)°	β = 105.04(3)°	α = 68.21(A)°	β = 90.05(5)°
	β = 83.57(3)°			β = 72.80(2)°	
	γ = 74.92(3)°			γ = 68.50(3)°	
Volume	1674.8(12)Å³	3910(4)Å³	6196(4)Å³	1494.3(9)Å³	3315(3)Å³
Z	2	4	8	2	4
Formula Weight	709.5	826.6	613.6	583.5	645.6
Density (Calcd.) (Mg/m³)	1.407	1.404	1.315	1.297	1.293
Absorption Coefficient (mm⁻¹)	1.277	0.249	0.257	0.261	0.242
2θ range (°)	4.0 to 45.0	4.0 to 45.0	4.0 to 40.0	4.0 to 45.0	4.0 to 40.0
Reflections Collected	4672	5674	6431	4202	4826
Independent Reflections	4377(R$_{int}$ = 1.13%)	5137 (R$_{int}$ = 1.31%)	5812(R$_{int}$ = 3.86%)	3917(R$_{int}$ = 1.32%)	4391(R$_{int}$ = 2.86%)
Observed Reflections	2630(F>6.0σ(F))	3521(F>3.0σ(F))	3609(F>3.0σ(F))	3000(F>4.0σ(F))	2129(F>3.0σ(F))
Quantity Minimized	Σw(F$_o$-F$_c$)²	Σw (F$_o$-F$_c$)²	Σw(F$_o$-F$_c$)²	Σw(F$_o$-F$_c$)²	Σw(F$_o$-F$_c$)²
Extinction Correction	N/A	N/A	N/A	χ = 0.0015(6) where: F* = F[1+0.002χ F²/sin(2θ)]⁻¹/⁴	χ = 0.00032(9) where: F* = F[1+0.002χ F²/sin(2θ)]⁻¹/⁴
Weighting Scheme	unit weights	w⁻¹ =σ²(F) + 0.0007F²	w⁻¹ = σ²(F) + 0.0005F²	w⁻¹ = σ²(F) + 0.0003 F²	w⁻¹ =σ²(F) + 0.0003 F²
Final R Indices	R = 10.30%	R = 6.87% Rw = 8.04%	R = 6.73% Rw = 6.24%	R = 4.59% Rw = 5.62%	R = 7.78% Rw = 6.14%
Goodness of fit	2.69	1.96	1.48	2.07	1.68
Largest and mean Δ/σ	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000
Data to parameter ratio	7.5:1	7.5:1	Block 1 9.3:1 Block 2 9.3:1	8.5:1	5.4:1
Largest Difference Peak (eÅ⁻³)	1.68	0.72	0.46	0.40	0.31
Largest Difference Hole (eÅ⁻³)	-0.41	-0.45	-0.33	-0.29	-0.25

Table 5
Postitional Coordinates (x10⁴) and Equivalent Isotropic Displacement Coefficients (Å² x 10³) for Non-hydrogen Atoms and Isotropic Displacement Coefficients (Å² x 10³) for Hydrogen Atoms Involved in Hydrogen Bonds of K⁺•2

	x	y	z	U(eq) [a]
K	2664(3)	2483(3)	7660(2)	71(1)
I	-93(2)	1304(2)	5270(2)	108(1)
I'	4408(3)	5449(4)	8988(2)	157(2)
C1	5354(18)	-2260(14)	6405(10)	75(7)
Cl1	6391(6)	-3724(4)	6510(4)	128(3)
C2	3988(21)	-2129(15)	6461(10)	89(9)
C3	3140 (17)	-973(18)	6389(10)	88(8)
C4	3684(15)	36(16)	6226(9)	68(7)
O4	2907(10)	1179(9)	6110(7)	82(5)
C5	5089(15)	-142(14)	6188(8)	64(7)
C6	5895(16)	-1327(17)	6264(9)	79(7)
C7	5700(14)	933(13)	6025(9)	75(7)
N8	5471(11)	1704(11)	6816(7)	71(5)
C9	6288(17)	1123(19)	7524(12)	113(10)
C10	5882(23)	1027(3)	8360(16)	248(24)
O11	4532(14)	1102(13)	8699(8)	118(7)
C12	4384(22)	-73(20)	8758(14)	125(11)
C13	2945(23)	-12(17)	9168(10)	110(10)
O14	2054(13)	580(10)	8570(9)	100(6)
C15	679(26)	651(20)	8891(20)	173(17)

Table 5 (continued)

	x	y	z	U(eq) [a]
C16	-255(21)	1560(20)	8579(19)	157(15)
N17	-137(12)	2775(12)	8500(9)	80(6)
C18	-947(21)	3390(22)	7789(16)	136(13)
C19	-572(25)	4459(25)	7436(17)	165(16)
O20	746(15)	4165(12)	6895(9)	118(7)
C21	1246(31)	5166(22)	6529(19)	174(17)
C22	2513(30)	4756(20)	5967(16)	148(14)
O23	3511(17)	4092(12)	6492(8)	111(7)
C24	4780(26)	3657(19)	5963(14)	130(13)
C25	5737(19)	2886(18)	6545(13)	108(10)
C26	-587(15)	3443(14)	9343(11)	84(7)
C27	396(14)	3133(13)	10054(12)	72(7)
C28	46(15)	2614(14)	10875(13)	82(8)
C29	950(20)	2344(14)	11519(11)	88(8)
Cl29	484(6)	1704(4)	12545(3)	126(3)
C30	2192(19)	2607(15)	11386(12)	90(9)
C31	2518(16)	3144(14)	10605(13)	85(8)
C32	1641(17)	3413(14)	9921(12)	79(7)
O32	1940(10)	3985(9)	9130(8)	88(5)
H4	2113	1659	5784	80 [b]
H32	2364	4632	8842	80 [b]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U$_{ij}$ tensor. [b] Isotropic U.

Table 6

Positional Coordinates (x 10⁴) and Equivalent Isotropic Displacement
Coefficients (Å² x 10³) for Non-hydrogen Atoms and Isotropic
Displacement Coefficients (Å² x 10³) for Hydrogen Atoms
Involved in Hydrogen Bonds of Na⁺•2

	x	y	z	Ueq [a]
Na	3247(2)	12034(1)	1081(1)	52(1)
C1	2745(4)	8477(4)	582(3)	56(2)
Cl1	2017(1)	7535(1)	337(1)	89(1)
C2	3219(5)	8568(4)	1191(3)	63(3)
C3	3811(5)	9311(4)	1376(3)	61(2)
C4	3923(4)	9968(4)	953(3)	47(2)
O4	4494(3)	10710(21)	1109(2)	59(2)
C5	3456(4)	9868(4)	326(2)	43(2)
C6	2867(4)	9120(4)	151(3)	49(2)
C7	3641(4)	10563(4)	-145(3)	50(2)
N8	2928(3)	11329(3)	-108(2)	48(2)
C9	1723(4)	11122(4)	-292(3)	58(2)
C10	957(5)	11754(4)	-9(3)	75(3)
O11	1162(3)	11758(3)	651(2)	71(2)
C12	690(5)	11046(5)	940(3)	84(3)
C13	1019(5)	11105(5)	1630(3)	79(3)
O14	2219(3)	11034(3)	1740(2)	62(2)
C15	2675(5)	11038(14)	2383(3)	63(3)
C16	2673(5)	11918(4)	2675(2)	55(2)
N17	3308(3)	12540(3)	2339(2)	46(2)
C18	4518(4)	12487(4)	2571(2)	62(2)
C19	5288(5)	12930(4)	2161(3)	64(2)
O20	5125(3)	12561(3)	1560(2)	80(2)
C21	5637(11)	13226(9)	1140(6)	62(4) [b]
C21'	5885(11)	12739(10)	1128(6)	75(4) [b]
C22	5603(10)	12812(9)	538(6)	66(3) [b]
C22'	5207(10)	13311(9)	638(6)	68(3) [b]
O23	4332(4)	12780(3)	301(2)	76(2)
C24	4409(5)	12402(4)	-284(3)	71(3)
C25	3289(6)	12015(4)	-519(3)	69(3)
C26	2898(5)	13427(4)	2414(3)	58(2)
C27	1722(5)	13561(4)	2081(3)	54(2)
C28	789(6)	13620(4)	2418(3)	73(3)
Cl29	-1431(2)	13759(2)	2553(1)	129(1)
C30	-474(6)	13770(4)	1478(4)	86(3)
C31	432(5)	13726(4)	1131(3)	73(3)
C32	1531(5)	13625(3)	1431(3)	57(2)
O32	2453(3)	13559(3)	1109(2)	61(2)
C33	7676(5)	10898(4)	2435(3)	64(3)
N33	7751	10987	1750	107(2) [b]
O331	8147	11613	1578	81(3) [b]
O332	7548	10409	1454	171(5) [b]
O333	8418	10386	1512	172(5) [b]
O334	6918	10900	1382	187(6) [b]
C34	8649(6)	11033(4)	2821(3)	74(3)
C35	8646(5)	10949(4)	3457(3)	57(2)
N35	9691(5)	11050(4)	3863(3)	78(3)
O351	9698(3)	10903(3)	4424(2)	86(2)
O352	10549(4)	11255(5)	3632(3)	128(3)
C36	7665(5)	10766(3)	3703(3)	51(2)
C37	6677(4)	10648(3)	3314(3)	48(2)
N37	5666(5)	10485(4)	3613(3)	67(2)
O371	5690(4)	10612(4)	4162(3)	121(3)
O372	4838(5)	10194(4)	3315(3)	129(3)
C38	6599(5)	10675(4)	2635(3)	54(2)
O38	5722(4)	10531(3)	2270(2)	74(2)
C39	2838(6)	14568(5)	-413(3)	96(4)
O39	2061(4)	14238(4)	-40(2)	99(2)

Table 6 (continued)

	x	y	z	Ueq [a]
H4	4912	10761	1518	80 [b]
H32	2206	13796	611	80 [b]

[a] Equivalent isotropic U defined as one third of the trace of the
orthogonalized U_{ij} tensor. [b] Isotropic U.

Table 7

Positional Coordinates (x10⁴) and Equivalent Isotropic Displacement
Coefficients (Å² x 10³) for Nonhydrogen Atoms of 3

	x	y	z	Ueq [a]
N1	79(2)	2310(4)	4455(3)	43(3)
C2	531(3)	1812(5)	4482(5)	55(4)
C3	531(3)	654(6)	4570(5)	54(4)
O4	287(2)	173(4)	3833(3)	52(2)
C5	281(3)	-914(5)	3895(5)	53(4)
C6	-47(3)	-1319(6)	3129(5)	68(4)
O7	-517(2)	-944(4)	3091(4)	76(3)
C8	-864(3)	-1365(7)	2445(5)	76(5)
C9	-1301(3)	-713(6)	2249(5)	68(4)
N10	-1637(2)	-955(4)	2725(4)	50(3)
C11	-2111(2)	-547(7)	2358(4)	88(5)
C12	-2184(3)	635(8)	2452(6)	94(5)
O13	-1916(2)	1155(6)	2038(4)	92(3)
C14	-1869(4)	2199(8)	2260(8)	106(6)
C15	-1521(5)	2445(8)	2938(8)	144(8)
O16	-1079(3)	2118(5)	2988(4)	105(3)
C17	-764(4)	2316(7)	3750(6)	88(5)
C18	-279(3)	2110(6)	3691(5)	61(4)
C19	153(3)	3435(5)	4583(4)	51(4)
C20	305(3)	3739(5)	5473(5)	43(4)
C21	776(3)	3973(5)	5845(5)	52(4)
C22	914(3)	4267(6)	6658(5)	53(4)
Cl22	1515(1)	4508(2)	7130(2)	91(1)
C23	595(3)	4377(5)	7112(5)	52(4)
C24	124(3)	4157(5)	6747(5)	50(4)
C25	-21(3)	3840(5)	5941(5)	39(3)
O26	-482(2)	3598(3)	5535(3)	54(2)
C27	-839(3)	3835(6)	5944(5)	64(4)
C28	-1315(3)	3581(6)	5407(5)	67(4)
O29	-1389(2)	2509(4)	5421(3)	60(3)
C30	-1870(3)	2231(6)	5109(5)	60(4)
C31	-1947(3)	1137(6)	5278(5)	63(4)
O32	-1776(2)	512(4)	4732(3)	59(2)
C33	-1858(3)	-526(6)	4734(5)	50(4)
C34	-2049(3)	-1004(8)	5316(5)	62(4)
C35	-2116(3)	-2051(8)	5289(5)	65(4)
C36	-1999(3)	-2613(6)	4684(6)	52(4)
Cl36	-2091(1)	-3945(2)	4659(2)	86(1)
C37	-1806(3)	-2159(6)	4113(5)	51(4)
C38	-1724(3)	-1110(7)	4145(4)	47(4)
C39	-1455(3)	-629(6)	3582(4)	52(3)
N51	5198(2)	7546(4)	5744(3)	39(2)
C52	4803(3)	8064(5)	5966(5)	55(4)
C53	4847(3)	9225(6)	5874(5)	83(5)
O54	4605(3)	9730(5)	6263(4)	109(4)
C55	4649(3)	10839(6)	6204(6)	84(5)
C56	4983(3)	11276(6)	6901(6)	74(5)
O57	5448(2)	10914(4)	7120(3)	70(3)
C58	5745(3)	11295(6)	6638(5)	71(4)
C59	6192(3)	10725(6)	6864(5)	62(4)

Table 7 (continued)

	x	y	z	Ueq [a]
N60	6512(2)	10987(4)	6355(4)	53(3)
C61	7006(3)	10976(6)	6823(5)	69(4)
C62	7189(3)	9996(8)	7301(5)	85(5)
O63	7282(2)	9260(5)	6776(3)	74(3)
C64	7297(3)	8218(6)	7073(5)	67(4)
C65	6908(3)	7607(6)	6520(5)	66(4)
O66	6474(2)	7858(4)	6698(3)	64(2)
C67	6072(3)	7507(6)	6079(5)	67(4)
C68	5637(3)	7669(6)	6400 (4)	53(4)
C69	5084(2)	6445(5)	5587(4)	41(3)
C70	4768(3)	6234(5)	4747(5)	37(3)
C71	4291(3)	6041(5)	4650(5)	46(4)
C72	4000(3)	5784(5)	3883(6)	53(4)
Cl72	3401(1)	5538(2)	3765(2)	98(1)
C73	4187(3)	5721(5)	3217(5)	56(4)
C74	4657(3)	5892(5)	3303(5)	48(4)
C75	4948(3)	6142(5)	4059(5)	41(4)
O76	5427(2)	6317(3)	4217(3)	49(2)
C77	5643(3)	6000(5)	3588(5)	51(3)
C78	6160(3)	6201(5)	3865(5)	61(4)
O79	6233(2)	7284(3)	3819(3)	54(2)
C80	6715(3)	7524(5)	3972(5)	57(4)
C81	6776(3)	8628(6)	3759(5)	56(4)
O82	6648(2)	9257(4)	4363(3)	55(2)
C83	6712(3)	10306(6)	4320(5)	45(3)
C84	6873(3)	10746(7)	3704(5)	59(4)
C85	6931(3)	11794(8)	3685(5)	67(4)
C86	6834(3)	12375(6)	4292(6)	62(4)
Cl86	6914(1)	13718(2)	4288(2)	102(1)
C87	6672(3)	11937(6)	4914(5)	53(4)
C88	6614(2)	10891(6)	4941(5)	43(3)
C89	6427(2)	10382(6)	5598(4)	51(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Positional Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3) for Nonhydrogen Atoms of **6**

	x	y	z	Ueq [a]
N1	8469(3)	7962(2)	239(2)	47(1)
C2	8994(3)	6931(2)	1097(2)	55(2)
C3	10154(3)	5869(3)	824(3)	58(2)
O4	11675(2)	5958(2)	560(2)	60(1)
C5	12783(4)	5020(3)	191(2)	63(2)
C6	12988(4)	5271(3)	-910(2)	63(2)
O7	13777(3)	6135(2)	-1415(2)	69(1)
C8	14002(4)	6441(3)	-2488(3)	79(2)
C9	12616(4)	7312(3)	-2866(2)	65(2)
N10	12846(3)	7633(2)	-3967(2)	57(1)
C11	13642(4)	8532(3)	-4544(3)	67(2)
C12	12837(4)	9792(3)	-4496(3)	70(2)
O13	12897(3)	9880(2)	-3578(2)	75(1)
C14	11806(6)	10873(3)	-3312(3)	103(3)
C15	10405(5)	10693(3)	-2707(3)	109(3)
O16	10637(3)	9812(2)	-1773(2)	77(1)
C17	9327(4)	9419(3)	-1273(3)	72(2)
C18	9624(4)	8577(3)	-272(2)	57(2)
C19	6961(3)	8721(3)	557(2)	54(2)
C20	5652(3)	8175(2)	863(2)	44(1)
C21	5015(3)	7751(3)	1863(2)	54(2)
C22	3836(3)	7240(3)	2141(2)	57(2)

Table 8 (continued)

	x	y	z	Ueq [a]
Cl22	3113(1)	6673(1)	3407(1)	89(1)
C23	3245(3)	7161(3)	1438(2)	58(2)
C24	3831(3)	7592(3)	437(2)	53(2)
C25	5046(3)	8083(3)	144(2)	46(1)
O26	5730(2)	8493(2)	-825(1)	55(1)
C27	5048(4)	8541(3)	-1593(2)	61(2)
C28	6183(4)	8747(3)	-2566(2)	61(2)
C29	7502(4)	7639(3)	-2602(2)	64(2)
O30	8301(3)	7737(2)	-3602(2)	72(1)
C31	9463(4)	6722(3)	-3738(2)	58(2)
C32	9095(4)	5708(3)	-3602(3)	68(2)
C33	10243(5)	4716(3)	-3772(3)	70(2)
C34	11744(4)	4749(3)	-4072(2)	60(2)
C134	13215(1)	3512(1)	-4327(1)	88(1)
C35	12123(4)	5749(3)	-4207(2)	58(2)
C36	10974(4)	6764(3)	-4051(2)	54(2)
C37	11402(4)	7887(3)	-4268(3)	65(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9

Positional Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3)for Nonhydrogen Atoms of **8**

	x	y	z	Ueq [a]
N1	4560(4)	2425(4)	10763(3)	48(2)
C2	5374(5)	3044(6)	10903(4)	62(3)
C3	5205(6)	4111(6)	10832(5)	80(4)
O4	5007(4)	4536(3)	11541(3)	89(3)
C5	4902(13)	5574(11)	11357(7)	73(5) [b]
C5'	5144(16)	5530(16)	11786(17)	90(9) [b]
C6	4409(11)	6065(10)	12047(9)	72(4) [b]
C6'	4332(14)	6006(16)	11489(14)	71(7) [b]
O7	3549(6)	5711(5)	12158(4)	119(4)
C8	2810(11)	6102(10)	11852(8)	177(9)
C9	1936(9)	5579(10)	11963(7)	148(7)
N10	1297(9)	5460(7)	11291(5)	110(5)
C11	418(11)	5145(10)	11563(9)	153(9)
C12	331(7)	4237(10)	12008(7)	122(6)
O13	672(5)	3455(6)	11613(4)	117(4)
C14	721(6)	2582(8)	12042(5)	98(5)
C15	1404(7)	1949(7)	11651(5)	96(5)
O16	2325(4)	2275(5)	11789(3)	95(3)
C17	2945(6)	2115(6)	11177(4)	73(4)
C18	3879(5)	2488(5)	11402(4)	58(3)
C19	4873(5)	1418(5)	10622(4)	52(3)
C20	5303(6)	1268(5)	9819(4)	50(3)
C21	6254(6)	1169(5)	9720(4)	59(3)
C22	6637(5)	1036(5)	8983(5)	58(3)
Cl22	7849(2)	930(2)	8880(1)	105(1)
C23	6061(6)	978(5)	8334(5)	65(3)
C24	5107(6)	1060(5)	8416(4)	63(3)
C25	4728(6)	1209(5)	9154(5)	54(3)
O26	3789(3)	1292(4)	9286(3)	65(2)
C27	3166(5)	1183(5)	8625(4)	61(3)
C28	2194(5)	1341(6)	8908(4)	49(3)
C29	1618(9)	564(7)	9041(5)	91(5)
C30	763(11)	679(13)	9292(7)	153(9)
C31	398(9)	1553(15)	9437(8)	154(10)
C32	950(10)	2358(9)	9290(6)	118(6)
C33	1866(7)	2276(6)	9043(4)	66(4)
C34	2477(9)	3139(6)	8853(6)	146(6)

Table 9 (continued)

	x	y	z	Ueq [a]
O35	2613(8)	3867(8)	9524(6)	72(3) [b]
O35'	2013(8)	3800(8)	9413(6)	66(3) [b]
C36	2183(6)	4799(6)	9301(6)	75(4)
C37	2338(5)	5194(6)	8578(5)	68(4)
C38	2179(5)	6182(7)	8467(5)	74(4)
C39	1865(6)	6729(5)	9082(6)	65(4)
C139	1678(2)	7969(2)	8939(2)	110(1)
C40	1726(6)	6333(6)	9795(5)	77(4)
C41	1865(7)	5358(6)	9917(4)	87(4)
C42	1329(13)	4782(12)	10624(9)	78(5) [b]
C42'	2047(12)	4962(12)	10743(9)	71(5) [b]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic thermal parameter.

atoms. Despite the rigidity of the benzene groups in one branch of the cryptand, there is enough flexibility in that branch to allow for expansion and contraction of the molecule. These N···N distances are all shorter than similar N···N interatomic distances of 6.87Å found in 2.2.2 and 6.76Å found in the disubstituted BH_3 derivative of 2.2.2 [21]. The bond distances and angles in these molecules are well characterized and therefore are not listed.

EXPERIMENTAL

Melting points were determined on Thomas-Hoover capillary tube melting point apparatus and are uncorrected. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Arizona. The nmr spectra were obtained on a Varian Gemini 200 MHz spectrometer. High resolution mass spectroscopy (CI) was used to obtain the mass spectra. Starting materials were purchased from commercial sources where available. N,N'-Bis(methoxymethy)-diaza-18-crown-6 (1) [20], bisphenol 2 [19] and 2, 6- pyridine-dimethanol ditosylate [22] were synthesized as described.

Cryptand 3 (Scheme 1).

Compound 2 (2 g, 3.7 mmoles), 6 g of potassium carbonate and 1.5 g (3.7 mmoles) of diethylene glycol ditosylate were refluxed in 100 ml of acetonitrile for 4 days. The solvent was removed under reduced pressure. The residue was treated with 150 ml of a 1:3 mixture of water and chloroform. The water phase was separated and extracted twice with 50-ml portions of chloroform. The organic layers were combined, dried over anhydrous sodium sulfate and evaporated. Crude cryptand 3 was purified on neutral alumina using chloroform/tetrahydrofuran: 2/1 as eluent to give a 67% yield, mp 142-144°; ^{1}H nmr (deuteriochloroform): δ 2.89 (m, 8 H), 3.56-3.70 (m, 16 H), 3.86 (s, 4 H), 3.95 (m, 4 H), 4.10 (m, 4 H), 6.72 (d, 2H), 7.10 (dd, 2 H), 7.33(d, 2 H), ms: m/z 614 [M+1]+.

Anal. Calcd. for $C_{30}H_{42}Cl_2N_2O_7$: C, 58.73; H, 6.85. Found C, 58.79; H, 7.05.

Cryptand 4 (Scheme 1).

Compound 4 was prepared in the same manner as 3 using 2 g (3.7 mmoles) of 2, 6 g of potassium carbonate and 1.7 g (3.7 mmoles) of triethylene glycol ditosylate. The product was an oil

(42%); ^{1}H nmr (deuteriochloroform): δ 2.90 (t, 8 H), 3.59-3.69 (m, 20 H), 3.79 (s, 4 H), 3.89 (m, 4 H), 4.10 (m, 4 H), 6.74 (d, 2 H), 7.11 (dd, 2 H), 7.31 (d, 2 H); ms: m/z 658 [M+1]+.

Anal. Calcd. for $C_{32}H_{46}Cl_2N_2O_8$: C, 58.45; H, 7.00. Found: C, 58.37; H, 7.15.

Cryptand 5 (Scheme 1).

Compound 5 was prepared in the same manner as 3 using 2 g (3.7 mmoles) of 2, 6 g of potassium carbonate and 1.85 g (3.7 mmoles) of tetraethylene glycol ditosylate. The product was an oil, (35%); ^{1}H nmr (deuteriochloroform): δ 2.90 (t, 8 H), 3.60-3.80 (m, 28 H), 3.86 (m, 4 H), 4.10 (m, 4 H), 6.75 (d, 2 H), 7.14 (dd, 2 H), 7.38 (d, 2 H); ms: m/z 702 [M+1]+.

Anal. Calcd. for $C_{34}H_{50}Cl_2N_2O_9$: C, 58.20; H, 7.13. Found C, 57.99; H, 7.18.

Cryptand 6 (Scheme 1).

Compound 6 was prepared in the same manner as 3 using 2 g (3.7 mmoles) of 2, 6 g of potassium carbonate and 1.3 g (3.7 mmoles) of 1,3-propanediol ditosylate. Crude cryptand 6 was purified on silica gel using chloroform/tetrahydrofuran: 10/1 than 1/1 as eluents. The resulted compound was recrystallized from ethanol/ethyl acetate: 1/1 to give 6 in 59% yield, mp 130-131°; ^{1}H nmr (deuteriochloroform): δ 2.36 (m, 2 H), 2.90 (m 8 H), 3.50-3.70 (m, 16 H), 3.84 (s, 4 H), 4.17 (t, 4 H), 6.80 (d, 2 H), 7.15 (dd, 2 H), 7.32 (d, 2 H); ms: m/z 583, M+.

Anal. Calcd. for $C_{29}H_{40}Cl_2N_2O_6$: C, 59.69; H, 6.86. Found: C, 59.81; H, 7.00.

Cryptand 7 (Scheme 1).

Compound 7 was prepared in the same manner as 3 using 2 g (3.7 mmoles) of 2, 6 g of potassium carbonate and 1.65 g (3.7 mmoles) of 2,6-pyridinedimethanol ditosylate. Crude cryptand 7 was recrystallized from toluene/ethyl acetate: 1/1 to give a 49% yield, mp 163-165°; ^{1}H nmr (deuteriochloroform): δ 2.74 (t, 8 H), 3.29-3.47 (m, 16 H), 3.70(s, 4 H), 5.10 (s, 4 H), 6.94 (d, 2 H), 7.20 (dd, 2 H), 7.31 (d, 2 H), 7.52 (d, 2 H), 7.84 (t, 1 H); ms: m/z 647 [M+1]+.

Anal. Calcd. for $C_{33}H_{41}Cl_2N_3O_6$: C, 61.30; H, 6.35. Found: C, 61.50; H, 6.55.

Cryptand 8 (Scheme 1).

Compound 2 (2 g, 3.7 mmoles), 6 g of potassium carbonate and 0.97 g (3.7 mmoles) of α,α'-dibromo-o-xylene were refluxed in 100 ml of acetonitrile for 2 days. The solvent was removed under reduced pressure. The residue was treated with 150 ml of a 1/3 mixture of water and chloroform. The water phase was separated and extracted twice with 50-ml portions of chloroform. The combined organic layers were dried over anhydrous sodium sulfate and evaporated. The solid residue was dissolved in 10 ml of hot toluene and cooled to room temperature. A small amount of oil precipitated. The toluene solution was separated and evaporated to 5 ml and cooled. The resulting crystals were filtered and washed twice with a 1:1 mixture of methanol and ethyl acetate. Cryptand 8 was recrystallized form ethyl acetate to give a 71% yield, mp 178-180°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.68 (m, 8 H), 3.10-3.44 (m, 16 H). 3.69 (s, 4 H), 5.28 (s, 4, H), 7.05-7.60 (m, 10 H); ms: m/z 646 [M+1]+.

Anal. Calcd. for $C_{34}H_{42}Cl_2N_2O_6$: C, 63.26; H, 6.51. Found: C, 63.48; H, 6.69.

Cryptand **9** (Scheme 1).

Compound **9** was prepared in the same manner as **8** using 2 g (3.7 mmoles) of **2**, 6 g of potassium carbonate and α,α'-dibromo-p-xylene (0.97 g, 3.7 mmoles). After evaporation of acetonitrile and extraction with chloroform (see procedure for cryptand **8**), the resulting oil was passed through a short column packed with 8 g of neutral aluminum oxide using chloroform/tetrahydrofuran: 1/2 as eluent. The crude cryptand was allowed to stand for 2 days where it solidified. The crystals were filtered, washed with chloroform and recrystallized from ethyl acetate to give **9** in a 9% yield, ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.71 (m, 8 H), 3.39-3.51 (m, 16 H), 3.66 (s, 4 H), 5.20 (s, 4 H), 7.08-7.59 (m, 10 H); ms: m/z 646 [M+1]$^+$.

Anal. Calcd. for $C_{34}H_{42}Cl_2N_2O_6$: C, 63.26; H, 6.51. Found: C, 63.44; H, 6.72.

X-ray Crystal Structure Determinations.

Crystals of K$^+$•**2**, Na$^+$•**2**, **3**, **6**, and **8** which were suitable for X-ray studies were prepared and studied using a Siemens R3m/V automated diffractometer. Graphite crystal monochromated Mo-Kα X-radiation (λ=0.71073Å) was used in the five studies. The lattice parameters and the orientation matrix of each crystal were calculated using a least-squares procedure involving angles of a suitable number of carefully centered reflections for each crystal. Intensity data for the five studies were collected using a variable speed θ-2θ scanning mode with the scan rates determined by the intensities of the reflections. Crystal data and experimental conditions for the five studies are summarized in Table 4. Compounds Na$^+$•**2**, **3**, and **8** crystallized in the monoclinic space group P2$_1$/c. This space group was determined unambiguously by the systematic absences of the intensity data. K$^+$•**2** and **6** crystallized in the triclinic crystal system. Intensity statistics suggested that the centrosymmetric P1̄ space group was the proper one for both of the structures and the two structures were solved successfully using that space group. The crystal data for **3** indicated that the asymmetric unit of that structure contained of two chemically identical but crystallographically independent molecules (See Table 4). Weights based on counting statistics were applied to all of the data sets except for that of K$^+$•**2**. Unit weights were used for that data set. An emperical correction for secondary extinction was applied to data sets of **6** and **8**.

Trial structures of Na$^+$•**2**, **3**, **6** and **8** were obtained using direct methods. The difference map showed that the asymmetric unit of Na$^+$•**2** also included a methanol molecule of solvation. Efforts to solve K$^+$•**2** using heavy atom methods were complicated by the disorder of the iodide ion. This disorder has been discussed earlier. However, it was possible to solve the structure of this compound using that method. Positional and thermal parameters of the nonhydrogen atoms of K$^+$•**2**, Na$^+$•**2**, **3**, **6**, and **8** are listed in Tables 5 through 9, respectively. It is not uncommon to find disorder in molecules of the size of those reported here. The disorder of the following light atoms was resolved using difference maps: in Na$^+$•**2** C21, C22 and the oxygens of the N33 NO$_2$ group; and in **8** C5, C6, O35 and C42. These atoms and N33 were refined isotropically. The positional parameters of the atoms including N33 of the disordered NO$_2$ group in Na$^+$•**2** were not refined. The magnitude of the site occupancies of the disordered light atoms in the structures were estimated from the values of their initial isotropic thermal parameters. The occupancy parameters for all these disordered atoms were assigned values of 0.50, except for

C5 and C6 in **8**, where C5 and C6 were assigned occupancy values of 0.60, while occupancies of C5´ and C6´ were given values of 0.40. The site occupancies of I and I´ in K$^+$•**2** were refined and found to be 0.50 for each atom site. Both I and I´ were refined anisotropically. The large thermal motion of several of the atoms of the diaza-crown ring of K$^+$•**2** and also some atoms in other molecules strongly indicated that other atoms in the compounds were disordered, but this disorder could not be resolved. The disorder of the atoms is at least one cause of the rather large R value for K$^+$•**2**. Non-hydrogen, non-disordered atoms of the compounds were refined anisotropically. Because **3** contains a large number of atoms compared to the number of observed data, that structure was refined in two blocks in an alternating mode. Each block contained the scale factor and the atomic parameters of one of the crystallographically independent molecules. Positions for hydrogen atoms bonded to carbon atoms were calculated using known stereochemical geometry. Positions for hydrogen atoms bonded to disordered carbon atoms were calculated for one orientation at a time. For example, when positions for hydrogen atoms bonded to C5 and C6 of molecule **8** were calculated, carbon atoms C5´ and C6´ were omitted from the atom list. Positions for hydrogen atoms of C34 carbon bonded to the disordered O35 were not calculated. The hydrogen atoms bonded to the phenol oxygen of Na$^+$•**2** and K$^+$•**2** and the alcohol oxygen atom of the methanol molecule in the Na$^+$•**2** structure were located in difference maps. All hydrogen atoms were allowed to ride on their neighboring atoms during the refinement process. Each hydrogen atom was assigned an isotropic U value of 0.08Å^2 and these values were not refined. Atomic scattering factors were obtained from the International Tables for X-ray Crystallography [23]. All programs used in solution, refinement and display of these structures are included in the SHELXTL-PLUS program package [24].

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