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Structural Aspects of Rubidium Ion Selectivity by Tribenzo-21-crown-7[1a]

Jeffrey C. Bryan,* Richard A. Sachleben, Jérôme M. Lavis, and Matthew C. Davis

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831-6119

John H. Burns

Chemistry Department, University of North Carolina—Asheville, Asheville, North Carolina 28804-3299

Benjamin P. Hay*

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
Richland, Washington 99352

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The structural origins of the selectivity of rubidium ion over other alkali metal ions by tribenzo-21-crown-7 is investigated from single-crystal X-ray diffraction: data for Cs(tribenzo-21-crown-7)(NO_3), monoclinic, $P2_1/c$, $a = 9.598(2)$ Å, $b = 23.466(3)$ Å, $c = 23.973(5)$ Å, $\beta = 93.31(1)°$, $V = 5390(2)$ Å^3, $Z = 8$; data for [Rb(4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7)(dioxane)$_{1.5}$(H_2O)$_{0.18}$][Cl]·(dioxane)1.82(H_2O), triclinic, $P\bar{1}$, $a = 11.687(3)$ Å, $b = 12.800(4)$ Å, $c = 17.680(3)$ Å, $\alpha = 75.31(2)°$, $\beta = 80.01(2)°$, $\gamma = 69.09(2)°$, $V = 2379.8(10)$ Å^3, $Z = 2$; data for Na(4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7)ReO_4·0.5(*i*-PrOH), monoclinic, $P2_1/c$, $a = 24.300(5)$ Å, $b = 14.066(3)$ Å, $c = 22.676(5)$ Å, $\beta = 108.06(3)°$, $V = 7369(3)$ Å^3, $Z = 8$; data for and 4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7, monoclinic, $P2_1/n$, $a = 16.427(2)$ Å, $b = 11.3675(9)$ Å, $c = 33.137(3)$ Å, $\beta = 94.469(8)°$, $V = 6169.0(10)$ Å^3, $Z = 8$. The structures reported here are the first reported for a tribenzo-21-crown-7, and the alkali metal ion complexes are the first reported structures of these ions with any 21-crown-7 ether. Different crown conformations are observed for each structure. Molecular mechanics calculations were performed on all conformers, and the results are related to the observed extraction selectivity for rubidium.

Crown ethers have a remarkable ability to bind alkali metal ions.[1−3] Certain crowns can even discriminate between the alkali metal ions, which can lead to selective separations. There are many aspects of crown ethers that determine selectivity, including size of the macrocycle and the nature and arrangement of the donor groups.[2,3] Unfortunately, the ability to deliberately design a crown ether for the specific binding of a particular alkali metal ion remains elusive and requires considerable empirical screening of potential candidates. As part of our continuing interest in understanding recognition phenomena of crown ethers, we are studying the selective coordination of large cations by crown ether molecules.[4−6]

Extraction studies have long demonstrated that large crown ether molecules, containing seven and eight oxygen donor atoms (21-crown-7 and 24-crown-8), exhibit good selectivity for larger cations, such as Rb^+ and Cs^+, over smaller ions, such as Na^+.[1−7] While 21-crown-7 ethers have traditionally been considered "well-sized" for cesium,[7] our recent work demonstrates that tribenzo-21-crown-7 ether exhibits modest Rb^+ selectivity (Figure 1).[5] In an effort to understand the steric requirements behind this selectivity, we sought out structures of large alkali metal cations with tribenzo-21-crown-7 and other closely related crown ether ligands. Although many crystal structures of Rb^+ and Cs^+ complexes with 18-crown-6 ligands are reported,[8] there are no prior reports of any 21-crown-7 macrocycle with these cations. In fact, only a few structures of any 21-crown-7

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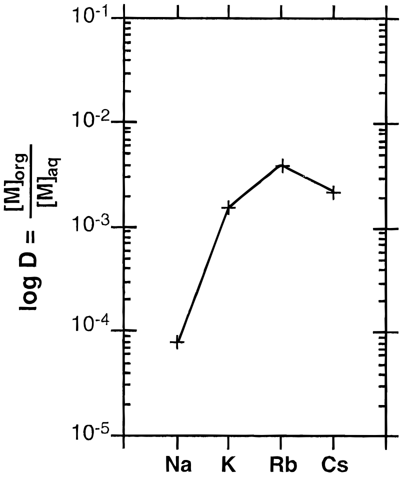

Figure 1. Competitive extraction of alkali metal nitrates by tribenzo-21-crown-7. The value for D_{Na} is approximate. Data are from ref 5.

macrocycle are reported in the literature, and only one of these involves the direct binding of a metal ion (K^+).[9-11]

Herein, we report the crystal structures of a tribenzo-21-crown-7 ether and its complexes with the alkali metal ions Na^+, Rb^+, and Cs^+. In an attempt to elucidate structural factors responsible for the Rb^+ selectivity, the structural data are analyzed in terms of binding site organization calculated by molecular mechanics.[12,13] In doing so, we focus on the relative steric energies of the ligand as a way of understanding complementarity and as a tool for crown ether design.

Experimental Section

Materials. All chemicals were used as supplied. Tribenzo-21-crown-7[14] and bis-*tert*-butylbenzo, benzo-21-crown-7[11] were prepared as described elsewhere.

X-ray Crystallography: General Considerations. A summary of crystallographic data is given in Table 1, and selected bond lengths and angles are given in Table 2. Complete tabulations of crystallographic data, bond lengths and angles, atomic coordinates, thermal parameters, and completely labeled ball-and-stick diagrams are available as Supporting Information. Data were obtained at −110 °C using an Enraf-Nonius CAD4 diffractometer, with the exception of Cs(tribenzo-21-crown-7)(NO_3), for which data were obtained at room temperature. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied based on a set of ψ scans. Calculations were carried out using XCAD4[15] (data reduction), SHELXTL[16] (absorption correction, structure solution/refinement, and molecular graphics), and PLATON[17] (structure analysis). Each H atom was placed in a calculated position, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (C*H*, CH_2) or 1.5 (CH_3, O*H*) times the equivalent isotropic displacement parameter of the atom to which it is attached. When warranted, methyl H atomic positions were allowed to rotate about the adjacent C−C bond. Full-matrix least-squares refinement against $|F|^2$ of the quantity $\sum w(F_o^2 - F_c^2)^2$ was used to adjust the positions and anisotropic thermal parameters of all non-hydrogen atoms.

X-ray Structure Determination for Cs(tribenzo-21-crown-7)(NO_3). Crystals were prepared by adding 21 mg (0.11 mmol) of $CsNO_3$ in 0.22 mL of H_2O to 50 mg (0.11 mmol) of tribenzo-21-crown-7 in 10 mL of EtOH and allowing the solution to slowly evaporate. A clear plate, measuring 0.14 × 0.28 × 0.29 mm^3, was mounted on a glass fiber. Unit-cell dimensions were refined by use of the settings of 21 reflections in the range $22 < 2\theta < 28°$. Intensities were measured by $\omega-2\theta$ scans. A total of 3405 reflections were collected ($2\theta \leq 40°$, $+h$, $+k$, $\pm l$). The data were averaged over $2/m$ symmetry ($R_{int} = 4.3\%$). The cesium atoms were located by Patterson methods, and subsequent Fourier syntheses were used to determine other non-hydrogen atomic positions. Two oxygen atoms on each nitrate ion are disordered over two sites. All N−O bonds are restrained to be approximately equal, and all nitrate O···O 1,3-distances are restrained to approximately 1.732 times the average N−O distance. Additionally, each nitrate orientation is restrained to be planar. Due to the limited amount of data, arene carbon atoms and disordered nitrate oxygen atoms are refined isotropically.

X-ray Structure Determination for [Rb(4,4′-bis-*tert*-butylbenzo, benzo-21-crown-7)(dioxane)$_{1.5}$(H_2O)$_{0.18}$][Cl]·(dioxane)1.82(H_2O). Crystals were prepared by dissolving 10 mg (0.083 mmol) of RbCl and 50 mg (0.088 mmol) of bis-*tert*-butylbenzo,benzo-21-crown-7 in 10 mL of 1:1 1,4-dioxane/methanol and allowing the solution to slowly evaporate. A clear plate, measuring 0.16 × 0.33 × 0.61 mm^3, was mounted on a glass fiber. Unit-cell dimensions were refined by use of the settings of 25 reflections in the range $20 < 2\theta < 30°$. Intensities were measured by ω scans. A total of 9802 reflections were collected ($2\theta \leq 30°$, $\pm h$, $\pm k$, $\pm l$, and $30 \leq 2\theta \leq 50°$, $\pm h$, $-k$, $\pm l$). The data were averaged over $\bar{1}$ symmetry ($R_{int} = 3.2\%$). The structure was solved by direct methods, and subsequent Fourier syntheses were used to determine remaining non-hydrogen atomic positions. Water hydrogen atoms were not located and are not present in the refinement. One dioxane molecule exhibits 2-fold (59:41) disorder, sharing a common oxygen atom (O11) bound to Rb^+. The water molecule bound to Rb^+ (O14) is assigned 18% occupancy, and its U_{ij} components are restrained to approximate isotropic behavior. Cl^- is apparently disordered over four sites, and lattice water, over seven. These eleven sites of disordered chloride and water are clustered in three distinct volumes of space within the asymmetric unit. Assignment of element and occupancy for chloride and lattice water has some uncertainty but is based on one Cl^- per Rb^+, whole numbers of atoms in the unit cell, and ≤100% occupancy in any one volume. Disordered atoms within 0.7 Å of each other are restrained to have similar U_{ij} components. Lattice water atoms O16A−D are refined isotropically.

X-ray Structure Determination for Na(4,4′-bis-*tert*-butylbenzo, benzo-21-crown-7)ReO_4·0.5(*i*-PrOH). Crystals were prepared by dissolving 24 mg (0.088 mmol) of $NaReO_4$ and 50 mg (0.088 mmol) of bis-*tert*-butylbenzo,benzo-21-crown-7 in 10 mL of 2-propanol and allowing the solution to slowly evaporate. A clear plate, measuring 0.18 × 0.37 × 0.46 mm^3, was mounted on a glass fiber. Unit-cell dimensions were refined by use of the settings of 25 reflections in the range $19 < 2\theta < 32°$. Intensities were measured by ω scans. A total of 13 652 reflections were collected ($2\theta \leq 32°$, $\pm h$, $-k$, $\pm l$, and $32 \leq 2\theta \leq 50°$, $\pm h$, $-k$, $+l$). The data were averaged over $2/m$ symmetry ($R_{int} = 2.6\%$). The rhenium atoms were located by Patterson methods, and subsequent Fourier syntheses were used to determine other non-hydrogen atomic positions. The methyl carbon atoms on one *tert*-butyl

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Table 1. Summary of Crystallographic Data

complex	bB$_2$B21C7	Na$^+$•bB$_2$B21C7	Rb$^+$•bB$_2$B21C7	Cs$^+$•B$_3$21C7
empirical formula	$C_{34}H_{44}O_7$	$C_{35.5}H_{48}NaO_{11.5}Re$	$C_{44}H_{68}ClO_{14}Rb$	$C_{26}H_{28}CsNO_{10}$
a, Å	16.427(2)	24.300(5)	11.687(3)	9.598(2)
b, Å	11.3675(9)	14.066(3)	12.800(4)	23.466(3)
c, Å	33.137(3)	22.676(5)	17.680(3)	23.973(5)
α, deg			75.31(2)	
β, deg	94.469(8)	108.06(3)	80.01(2)	93.31(1)
γ, deg			69.09(2)	
V, Å^3	6169.0(10)	7369(3)	2379.8(10)	5390(2)
Z	8	8	2	8
fw	564.69	867.93	941.90	647.42
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
T, °C	−110	−110	−110	26
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.22	1.56	1.31	1.60
μ, cm^{-1}	0.84	33.7	11.6	14.2
R^a	0.041	0.043	0.052	0.042
$wR2^b$	0.117	0.122	0.140	0.126

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, based on $F_o^2 > 2\sigma F_o^2$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Torsion Angles (deg) for M$^+$•BB$_2$B21C7 (M$^+$ = Rb$^+$, Na$^+$) and Cs$^+$•B$_3$21C7

complex	Cs$^+$•B$_3$21C7	Rb$^+$•bB$_2$B21C7	Na$^+$•bB$_2$B21C7
M$^+$−O$_{crown}$ (range)	3.022(7)−3.335(7)	2.980(3)−3.086(3)	2.432(5)−2.630(5)
M$^+$−O$_{crown}$ (average)^a	3.20(10)	3.03(4)	2.52(6)
M$^+$−O$_{dioxane}$		2.858(4), 2.860(4)	
M$^+$−O$_{water}$		2.812(17)	
M$^+$−O$_{anion}$ (range)	3.09(4)−3.286(14)		2.423(7)−2.70(3)
M$^+$−O$_{anion}$ (average)	3.12(2)		2.55(12)
M$^+$−centroid(O$_{crown}$)	0.711(8), 0.664(8)	0.173(3)	0.475(5), 0.487(5)
		Crown Ether Torsion Angles	
O−C•••C−O (range)	0(2)−3.2(15)	0.6(6)−2.5(6)	3.3(9)−9.9(10)
O−CH$_2$−CH$_2$−O (range)	66.1(12)−71.2(12)	65.2(5)−69.7(5)	54.2(7)−62.1(7)

[a] Uncertainties quoted for M$^+$−O (average) are σ values based on the statistical distribution of M$^+$−O$_{crown}$.

group (C31−C34) exhibit 2-fold disorder (56:44) and are refined isotropically. One perrhenate anion is also disordered over two sites (85:15) and is refined anisotropically, although U_{ij} components of bonded atoms or atoms within 0.7 Å of each other are restrained to be similar. The lattice 2-propanol molecule is refined isotropically and exhibits 3-fold disorder about the methine carbon atom (C75). All equivalent 1,2 and 1,3 distances within disordered groups are restrained to be equal.

X-ray Structure Determination for Bis-*tert*-butylbenzo,benzo-21-crown-7. Crystals were prepared by dissolving 50 mg (0.088 mmol) bis-*tert*-butylbenzo,benzo-21-crown-7 in 10 mL of 1:1 CH_2Cl_2/EtOH and allowing the solution to slowly evaporate. A clear plate, measuring 0.14 × 0.34 × 0.60 mm^3, was mounted on a glass fiber. Unit-cell dimensions were refined by use of the settings of 25 reflections in the range $19 < 2\theta < 24°$. Intensities were measured by ω scans. A total of 11 951 reflections were collected ($2\theta \leq 34°$, $\pm h$, $+k$, $\pm l$, and $34 \leq 2\theta \leq 48°$, $+h$, $+k$, $\pm l$). The data were averaged over $2/m$ symmetry ($R_{int} = 4.1\%$). The structure was solved by direct methods, and subsequent Fourier syntheses were used to determine remaining non-hydrogen atomic positions. The methyl carbon atoms on one *tert*-butyl group (C67−C70) exhibit 2-fold disorder (80:20). All 1,2 C−C and 1,3 C•••C distances within each conformer of the disordered *tert*-butyl group are restrained to be equal. All non-hydrogen atoms were refined anisotropically.

Molecular Mechanics Calculations. Molecular mechanics (MM) calculations were performed using the MM3(96) program[18] with an extended parameter set for the treatment of polydentate ether ligands and their complexes with alkali metal cations.[19,20] This model has been further modified to include 1,5 CH_2•••O interactions by defining a hydrogen bond between type 5 hydrogen and both types of ether oxygen (the aliphatic ether type 6 and the conjugated ether type 41). The hydrogen bond parameters, $\epsilon = 1.35$ kcal/mol and $r^* = 2.57$ Å, reproduce the potential surface reported for this interaction in a dimethyl ether dimer.[21]

The initial series of calculations were performed on the two conformations of the uncomplexed ligand, on the Na$^+$ and Rb$^+$ complexes, and on both Cs$^+$ complexes observed in the asymmetric unit. Input files for these calculations were generated using Cartesian coordinates from the crystal structures. When present, a *tert*-butyl group was replaced with a hydrogen atom. Control calculations showed that this substitution had little to no effect on the rest of the structure. When present, other inner-sphere ligands (e.g. solvent and anions) were omitted from the metal complexes. Again, control calculations revealed that with the relatively long M−O distances found in these complexes (≥2.5 Å), steric interactions between the macrocycle and other inner-sphere ligands were minimal, i.e., the presence or absence of auxiliary ligands did not significantly alter the results of the calculation. Comparison between experimental and calculated structures obtained in this manner revealed the expected degree of agreement: bond lengths to within ±0.03 Å, bond angles to within ±2°, and torsion angles to within ±5°.[19,20,22,23]

Steric energies of the ligands when bound to the metal ions were obtained by removing the metal ion from the optimized complex and

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(18) The calculations were carried out with MM3(96). The program may be obtained from Tripos Associates, 1699 S. Hanley Road, St. Louis, MO 63144, for commercial use, and it may be obtained from the Quantum Chemistry Program Exchange, Mr. Richard Counts, QCPE, Indiana University, Bloomington, IN 47405, for noncommercial users.

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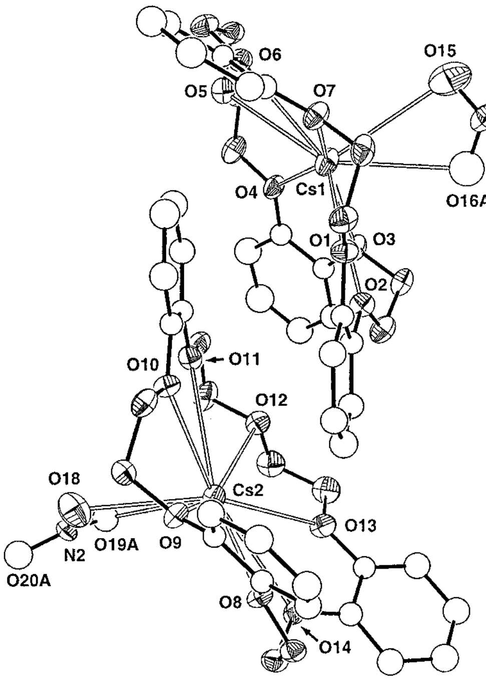

Figure 5. ORTEP drawing (25% probability ellipsoids) of Cs(tribenzo-21-crown-7)(NO_3). Atoms refined isotropically are represented as spheres. Hydrogen atoms and atoms that are minor components of a disordered pair are omitted.

performing an initial energy calculation on the remaining ligand coordinates.[12] Structures and steric energies for the uncomplexed binding conformations were computed by removing the metal ion from complexes and optimizing the resulting set of coordinates. Cavity radii were computed from these structures by averaging the distances from the seven oxygen atoms to their centroid.

A second series of calculations were performed in an attempt to identify complexes in which the observed cation was replaced with the other two cations in this study. Attempts to locate heptadentate complexes of the Na^+ with the ligand binding conformations that occur for Rb^+ and Cs^+ failed. Although heptadentate Na^+ complexes with these conformers were not stable, we note the possibility that Na^+ could form lower denticity complexes. Calculations on such complexes were not performed. Similarly, while Rb^+ and Cs^+ are interchangeable in the three large cavity conformers, neither cation minimizes to a stationary point with the conformation observed with Na^+.

Results

Crystal Structures. The structures of 4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7 (bB_2B21C7), its $NaReO_4$ and RbCl complexes, and the $CsNO_3$ complex with tribenzo-21-crown-7 (B_321C7) are illustrated in Figures 2−5. In all but the rubidium complex, two formula units make up the crystallographic asymmetric unit; only one is shown in Figure 3 ($Na^+\cdot bB_2B21C7$), as the crown ether ligands in these two formula units adopt nearly identical conformations.

The structure of bB_2B21C7 (Figure 2) illustrates that the free crown is collapsed in on itself, as is generally observed for uncomplexed crown ethers.[3,9,11,24] As a result, each of the two conformations exhibits two 1,5 $CH_2\cdots O$ interactions with a range of $H\cdots O$ distances of 2.43−2.58 Å. The collapse of the cavity is accomplished largely due to the anti O5−C17−C18−O6 torsion angle while all other O−C−C−O torsion angles are gauche. The gauche $O-CH_2-CH_2-O$ torsion angles range from 66.6(2) to 69.1(2)° and average 68.5°, close to the value of 72° calculated for 1,2-dimethoxyethane.[19] Guest complexation requires all O−C−C−O torsion angles to be gauche, i.e., all oxygen donors have their lone pairs directed inward, toward the center of the crown cavity. If the conformation observed

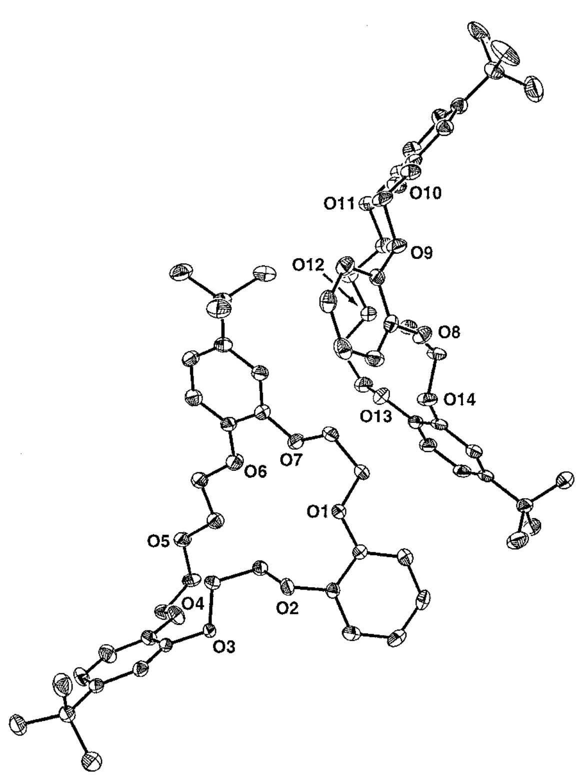

Figure 2. ORTEP drawing (50% probability ellipsoids) of 4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7 (bB_2B21C7). Hydrogen atoms and atoms that are minor components of a disordered pair are omitted.

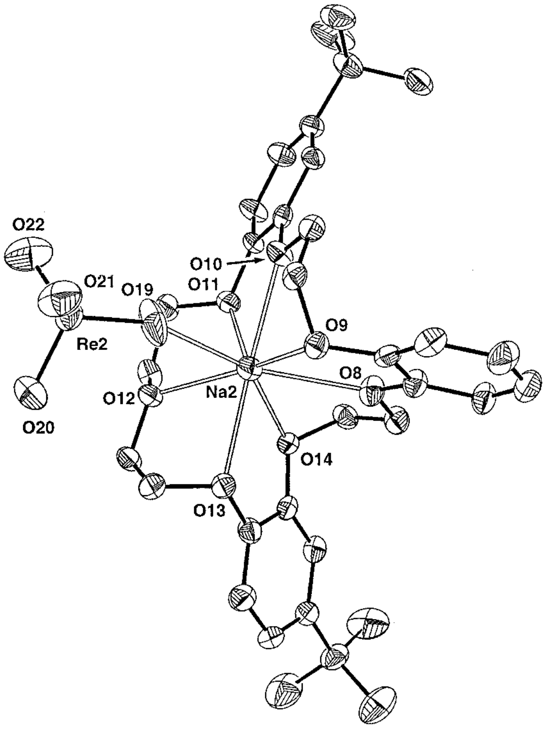

Figure 3. ORTEP drawing (50% probability ellipsoids) of Na(4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7)$ReO_4\cdot 0.5$(*i*-PrOH). Only one complex from the asymmetric unit is shown, and hydrogen atoms and the solvate molecule are omitted.

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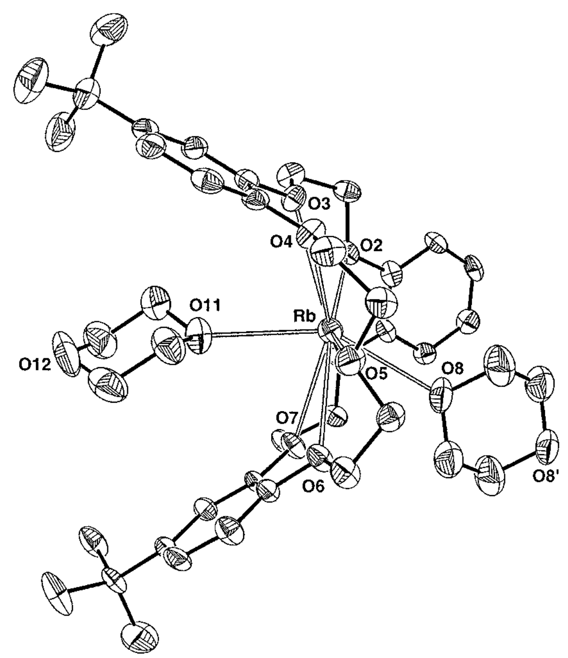

Figure 4. ORTEP drawing (50% probability ellipsoids) of [Rb(4,4′-bis-*tert*-butylbenzo,benzo-21-crown-7)(dioxane)$_{1.5}$(H$_2$O)$_{0.18}$]-[Cl]·(dioxane)1.82(H$_2$O). Atoms with less than 50% occupancy and hydrogen atoms are omitted.

in the solid state (Figure 2) is representative of a low-energy conformation in solution, then some reorganization will be required of this molecule before it can complex electropositive guests.

To accommodate the relatively small sodium ion, bB$_2$B21C7 collapses to form a three-dimensional cavity ((Na$^+$·bB$_2$B21C7, Figure 3). This has been previously observed, albeit rarely, when the ion is small relative to the crown ether.[3,25,26] The sodium ion is well enclosed by the crown in this conformation; however, an area large enough for monodentate coordination of the perrhenate anion is left exposed. The average Na−O$_{crown}$ distance of 2.52(6) Å is identical to an average value recently reported for several Na(O−CH$_2$−CH$_2$−O)$_x$ chelate rings,[12] but the individual Na−O$_{crown}$ distances vary by 0.20 Å, suggesting that the Na$^+$ does not bind equally to all crown oxygen donors. Additionally, Na$^+$ is displaced by almost 0.5 Å (0.475(5) Å Na1, 0.487(5) Å Na2) from the calculated centroid of the seven crown oxygen atoms.

The tribenzo crown ether bB$_2$B21C7 forms a more conventional crown-alkali metal ion complex with the larger rubidium ion (Rb$^+$·bB$_2$B21C7). The crown oxygen donors form a "belt" around the ion (Figure 4). In doing so, a considerable surface of the alkali metal ion remains exposed above and below the belt. These exposed spaces are filled by coordinating solvents: two 1,4-dioxane molecules and a site partially occupied by water. A crystallographic inversion center is located at the centroid of one of the coordinated 1,4-dioxane molecules, where it serves as a bridge to another Rb$^+$·bB$_2$B21C7·1,4-dioxane, forming dimers. The Rb−O$_{crown}$ distances average 3.03(4) Å, very close to the reported average Rb−O$_{crown}$ distance of 2.95 Å.[19] The Rb−O$_{dioxane}$ distances are significantly shorter, 2.858(4) and 2.860(4) Å, reflecting the stronger basicity of the dioxane oxygen donor relative to crown ether oxygen donors. The Rb−O$_{crown}$ distances vary by only 0.11 Å, indicating that the cation and the oxygen atoms are able to arrange themselves so that they are roughly equidistant from Rb$^+$. The distance between Rb$^+$ and the calculated centroid of the seven crown oxygen atoms is also quite small at 0.173(3) Å. These results show that the crown can form a symmetric cavity, well-sized for Rb$^+$.

Table 3. Ligand Steric Energies (kcal/mol)[a] and Cavity Radii (Å)[b] for Observed Conformations of M$^+$·B$_3$21C7 (M = Cs$^+$, Rb$^+$, Na$^+$) and B$_3$21C7

macrocycle conformer	cavity radius	U_{crown}	M$^+$	$U_{M^+ \cdot crown}$	ΔU
bB$_2$B21C7-1		21.9			
bB$_2$B21C7-2		20.7			
Cs$^+$·B$_3$21C7-1	3.20	21.8	Cs$^+$	23.8	2.0
			Rb$^+$	24.5	2.7
Cs$^+$·B$_3$21C7-2	3.19	22.5	Cs$^+$	24.7	2.2
			Rb$^+$	25.5	3.0
Rb$^+$·bB$_2$B21C7	3.16	20.6	Cs$^+$	23.1	2.5
			Rb$^+$	24.0	3.4
Na$^+$·bB$_2$B21C7	2.86	28.7	Na$^+$	36.2	7.5

[a] Steric energies, U, of the ligand when in the uncomplexed and complexed state. The value ΔU ($U_{M^+ \cdot crown} - U_{crown}$) is the ligand strain caused by metal ion coordination with the specified conformation. [b] Cavity radii for the ligand in the uncomplexed state are computed as the average distance of the seven oxygen atoms to their centroid.

The structure of cesium nitrate in tribenzo-21-crown-7 (Cs$^+$·B$_3$21C7) contains two different ligand conformations. Like the Rb$^+$ complex, the crown adopts a belt-like conformation around the large ion; the crown forms a shallow inverted bowl with Cs$^+$ emerging from its apex. In each formula unit, the cesium ion sits roughly 0.7 Å (0.711(8) Å Cs1, 0.664(8) Å Cs2) above the least-squares plane for the seven crown oxygen atoms and is dislocated about the same distance from their calculated centroid. Large areas of the ion are exposed, with the larger "upper" space occupied by an η^2-nitrate anion (disordered) and the smaller "lower" space inside the bowl filled by an arene group from a neighboring complex. Some of the Cs···C$_{arene}$ contacts (about 3.7 Å, roughly equal to the sum of the ionic radius of Cs$^+$ and the van der Waals radius of carbon) are short enough to suggest that the arene π-cloud may be acting as a donor to the large, diffuse cesium cation.[27]

Molecular Mechanics. The results from molecular mechanics calculations are presented in Table 3. When two different ligand conformers are observed in the asymmetric unit for a single structure, they were calculated and represented separately ("1" and "2" in Table 3). For the metal complexes the radius of the crown cavity and the steric energies of the ligand in both the binding conformation ("U_{crown}") and the complexed state ("$U_{M^+ \cdot crown}$") were determined and are presented in Table 3. In addition, calculations of ligand steric energies were attempted for complexes in which the observed cation was replaced with the other two cations in this study (also under "$U_{M^+ \cdot crown}$" column in Table 3). Attempts to identify heptadentate complexes of the sodium ion with the ligand conformations that occur for Rb$^+$ and Cs$^+$ failed. Similarly, while Rb$^+$ and Cs$^+$

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are interchangeable in the three large cavity conformers, neither ion minimizes to a local minimum with the conformation observed for Na^+. No entry appears for $U_{M^+\cdot crown}$ energy (Table 3) when the metal ion proved incompatible with the crown conformation. Finally, the difference between the ligand energies in the complexed state and in the binding conformation (ΔU in Table 3) was determined to provide an indication of the complementarity of that particular conformation for the specified metal ion.[12]

Discussion

Only a few structures of any 21-crown-7 ether as a free ligand or as a metal complex are reported in the literature.[9−11] The structures reported here are the first reported for any tribenzo-21-crown-7, and the alkali metal ion complexes are the first reported structures of these particular ions with any 21-crown-7 ether.

Three of the structures here involve the 4,4′-*tert*-butyl substituted tribenzo-21-crown-7, while the Cs^+ structure involves the unsubstituted crown. Extraction studies indicate that the addition of bulky *tert*-butyl or *tert*-octyl groups at the 4 or 5 positions on the arene rings has no significant effect on the extraction ability of these crown ether molecules.[5,6] The structural studies are consistent with these results, at least in a purely steric sense, as the alkyl groups are well removed from the macrocycle cavity, and MM calculations reveal that their presence does not significantly affect the crown conformation in any of the structures reported here. This allows comparison of the structures observed in this study.

These crystal structures attest to the conformational flexibility of this large ring with no less than six different conformers of the 21-crown-7 ring appearing in the four structures: two conformations each for $Cs^+\cdot B_321C7$ and bB_2B21C7 and a single conformation observed for the Na^+ and the Rb^+ complexes. This conformational flexibility arises despite the presence of three relatively rigid benzo groups on the crown ether backbone.[28]

The MM approach provides a means of assessing the degree of ligand binding site organization for metal ion complexation.[12,29] A new formalism for the application and interpretation of MM calculations in the structural design of ligands uses ligand strain energies as a measure of the degree of ligand binding site organization.[12,13] In this approach, two contributions to ligand strain are evaluated. These are the ligand strain energies associated with conformational reorganization on going from the lowest energy free ligand conformer to the binding conformer and the ligand strain energy associated with metal ion complexation on going from the binding conformer to the bound form. The application of this formalism to a variety of multidentate ether ligands has yielded correlations between metal ion binding affinity and ligand structure for series of ligands in which structural effects are expected to be the primary factor responsible for the reactivity differences, i.e., constant number and type of donor group, one metal ion, and a fixed set of experimental conditions.[12,13] Here this approach is applied to quantitatively assess the degree of binding site organization of tribenzo-21-crown-7 for the alkali cations Na^+, Rb^+, and Cs^+.

The results of the MM calculations, summarized in Table 3, suggest that the structural origins of this selectivity for the larger rubidium and cesium ions over the smaller sodium ion involve both conformational reorganization and complementarity. Conformational reorganization is discussed first. With the exception of the crown conformation observed in the $Na^+\cdot bB_2B21C7$ structure, the energies for all the uncomplexed ligand conformations are roughly comparable. The Na^+ conformer is 6−8 kcal/mol higher in energy than the others. Thus, the crown is forced to adopt an unfavorable conformation to form a heptadentate complex with the smaller sodium ion. The modeling results suggest that this conformational reorganization is a major factor in the destabilization of the $Na^+\cdot bB_2B21C7$ complex.

Of the other ligand conformations, the one observed in the Rb^+ complex is found to be the lowest steric energy conformation (20.6 kcal/mol). While this is consistent with the observed Rb^+ selectivity, the energetic preference is small, on the order of 1−2 kcal/mol. We note that these steric energies were obtained on isolated ligands and that this difference in energy is within the range where corrections for solvent effects and crystal packing forces could alter the relative conformer stabilities.[23]

The complexation of a metal ion with a given conformation may cause further changes in structure that give rise to additional ligand strain. This strain provides a measure of structural complementarity, i.e., a measure of how well the ligand fits the metal ion.[12] These values, designated as ΔU in Table 3, reveal that in addition to the unfavorable conformational reorganization, the complexation of Na^+ with the crown conformation observed in its crystal structure causes further structural changes that result in additional ligand strain of 7.5 kcal/mol. This value can be compared with the 2.7−3.4 kcal/mol range observed for the complexation of Rb^+ and the 2.0−2.5 kcal/mol range observed for Cs^+ with the crown conformations observed in the large ion crystal structures.

In the case of aliphatic crown ethers, the additional ligand strain caused by metal ion complexation mainly arises from changes in macrocyclic ring torsion angles, as has been discussed previously.[19,30] In these earlier studies, calculations on metal ion complexes of dimethoxyethane, DME, revealed that the degree of torsion angle change is related to the metal ion size. For example, calculated $O-CH_2-CH_2-O$ torsion angles in DME decrease from a maximum of 72° for uncomplexed DME to 65° when complexed with cesium, to 63° when complexed with rubidium, and to 58° when complexed with sodium. The same trend was noted in a statistical analysis of the crystal structures of crown ether complexes where the $O-CH_2-CH_2-O$ torsion angles decreased from 69° in uncomplexed crowns to 68° in Cs^+ complexes, 66° in Rb^+ complexes, and 61° in Na^+ complexes.[19] This behavior is observed in the crystal structures reported here (Table 2), where the average gauche $O-CH_2-CH_2-O$ torsion angle is 69° for the Cs^+ complexes, 67° for the Rb^+ complexes, and 59° for the Na^+ complexes.

The MM results establish that there are clear structural origins for the preference of tribenzo-21-crown-7 to complex larger ions, both in terms of conformational preference and complementarity. However, the MM results do not indicate a steric preference for Rb^+ over Cs^+. Examination of the ΔU values in Table 3 reveal that in every case the complexation of Cs^+ causes slightly less ligand strain, from 0.7 to 0.9 kcal/mol, than the complexation of Rb^+. The modeling results indicate that regardless of conformation, this ligand exhibits a weak steric preference to complex Cs^+ over Rb^+. Thus, the modest selectivity for Rb^+

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over Cs^+ observed experimentally (Figure 1)[5] is not explained by a consideration of the ligand architecture alone.

Selectivities for one metal ion over another are controlled by both steric and electronic factors, and the MM analysis employed here addresses only the former. Since the strength of the M−O interactions are expected to decrease with increasing size of the cation, the observed Rb^+ selectivity over Cs^+ can be rationalized as a consequence of slightly stronger M−O interactions in the Rb^+ complex, i.e., a balance of steric and electronic factors. The MM calculations reveal that the binding sites in tribenzo-21-crown-7 are arranged so that a difference of only 0.15 kcal/mol per M−O interaction would be enough to overcome the calculated steric preference for Cs^+.

Conclusion

The previously observed[5] alkali metal ion selectivity of tribenzo-21-crown-7 (B_321C7) can be understood from crystallographic and molecular mechanics studies. The dramatic selectivity for the larger Rb^+ and Cs^+ over the smaller Na^+ can be largely attributed to steric factors. The crown must adopt an energetically unfavorable conformation to achieve heptadentate coordination with optimum Na−O distances, and coordination of Na^+ with this conformation causes a further significant increase in ligand strain. The modest selectivity for Rb^+ over Cs^+ can be rationalized by a balance of steric and electronic factors wherein slightly stronger M−O bonds for Rb^+ relative to Cs^+ outweigh the small (0.7 to 0.9 kcal/mol) steric preference for Cs^+ over Rb^+.

This study provides further evidence of the utility of MM in the analysis of steric effects associated with ligands and metal ion complexation. The MM model includes both M−O distance preferences as well as oxygen orientation preferences, and it correctly predicts the changes in ligand structure on metal ion complexation. Ligand strain energies provide a quantitative measure of structural complementarity for a metal ion. Ligand strain energies also allow an energetic ranking of the ligand conformers and a quantitative measure of the effect of conformational reorganization.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $CsNO_3 \cdot B_321C7$, $Rb(bB_2B21C7)(dioxane)_{1.5}(H_2O)_{0.18}][Cl] \cdot (dioxane)1.82(H_2O)$, $Na(bB_2B21C7)ReO_4 \cdot 0.5$(*i*-PrOH), and bB_2B21C7 are available on the Internet only. Access information is given on any current masthead page.

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