oriented toward the metal center as is exemplified by the structure of $[Et_4N][Te(S_2COEt)_3]$.[30] The xanthate ligands in bis(*O*-ethyl xanthato)bis(quinolin-8-olato)tin(IV), like those in $Ph_2Ge[S_2COMe]_2$, are oriented with the oxygen, not the second sulfur atom in the nonbonding position nearest the metal, and they too show similar large differences in the C=S and C—S bond lengths.[10]

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada and Imperial Oil Canada for financial support and the Ministry of Colleges and Universities of Ontario for a scholarship for M.L.Y.W.

Supplementary Material Available: Tables SI-SIII, listing full experimental details, anisotropic thermal parameters for non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms (3 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Studies of Sodium Complexes of *sym*-Dibenzo-14-crown-4 Ionizable Lariat Ethers

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Two lariat ethers of *sym*-dibenzo-14-crown-4 with acetate and propanoate pendant arms were synthesized and used to complex the Na^+ ion. The crystal structures of these two complexes and that of the Na^+ complex with (*sym*-dibenzo-14-crown-4-oxy)acetate were determined by X-ray diffraction. Molecular mechanics calculations indicated that intramolecular cation–anion bonding is possible for these complexes, but it was not found in any of these crystals. In the crystals of the acetate and propanoate derivatives there is intermolecular cation–anion bonding, and in the oxyacetate the cation is bonded to the O atom within the arm. Crystal data for $Na(C_{20}H_{21}O_6)\cdot H_2O\cdot CH_3OH$: monoclinic, $P2_1/c$, $a = 11.50\ (2)$ Å, $b = 17.40\ (3)$ Å, $c = 10.89\ (2)$ Å, $\beta = 101.72\ (1)^\circ$, $V = 2133.7$ Å^3, $Z = 4$. Refinement based on 3088 reflections with $I_o > \sigma(I_o)$ gave $R(F) = 0.052$. Crystal data for $Na(C_{21}H_{23}O_6)\cdot 2H_2O$: monoclinic, $P2_1/c$, $a = 12.95\ (1)$ Å, $b = 16.78\ (2)$ Å, $c = 9.58\ (1)$ Å, $\beta = 95.8\ (2)^\circ$, $V = 2071.0$ Å^3, $Z = 4$. Refinement based on 1273 reflections with $I_0 > 2\sigma(I_0)$ gave $R(F) = 0.065$. Crystal data for $Na(C_{20}H_{21}O_7)\cdot 3C_2H_5OH\cdot 0.5H_2O$: orthorhombic, $Pca2_1$, $a = 27.53\ (1)$ Å, $b = 12.008\ (5)$ Å, $c = 9.043\ (4)$ Å, $V = 2989.4$ Å^3, $Z = 4$. Refinement based on 1565 reflections with $I_o > 2\sigma(I_o)$ gave $R(F) = 0.060$.

Introduction

Lariat ethers were synthesized originally to increase the complexing ability of macrocyclic ethers through participation in the bonding by properly oriented side-arm donor atoms.[1-3] Later it was shown that the presence of ionizable functionalities on the side arms facilitated the phase transfer of cations by solvent extraction.[4] Crystal structure analyses have provided many examples of N-pivot lariat ethers in which an ether-coordinated cation is also bonded to one or more atoms of the sidearm.[5-11] As yet, there has appeared only one C-pivot lariat ether complex showing intramolecular bonding by the side-arm anion.[12]

Data on the kinetics and equilibria involved in the complexation of alkali-metal and alkaline-earth-metal ions in solution have been interpreted as indicating participation of the side-arm anions in intramolecular bonding for the cases of 18-crown-6 polycarboxylates[13] and (*sym*-dibenzo-16-crown-5-oxy)acetate.[14] The existence of such bonding is supported in the first case by the crystal structures of the Ca^{2+} and Sr^{2+} complexes of a similar 18-crown-6 ring substituted with two acetate ions that bond directly to these cations.[12] Relevant to the second case are the known crystal structures of complexes of closely related ligands, Li(**3**)$\cdot 7.5H_2O$[15] and Na(**4**)$\cdot H_2O\cdot 2EtOH$;[16] in neither of these is the anion bonded to the cation. There is, however, a bond between the O atom of the side arm and the Na^+ ion in Na(**4**)$\cdot 2H_2O\cdot EtOH$ and a indirect linkage through a water molecule between the Li^+ ion and the O atom of the side arm in Li(**3**)$\cdot 7.5H_2O$.

The present study of lariat ethers was done to examine the structural constraints on the interactions between side-arm carboxylate ions and cations that are coordinated by the attached macrocycle. Of special interest was whether replacing the O atom in the side arm with a C atom in a ligand such as **3** facilitates intramolecular cation–anion bonding. To this end we have synthesized the lariat ethers having acetate and propanoate groups replacing the oxy acetate as the side arm of **3** and complexed these new ligands with the Na^+ ion to produce Na(**1**)$\cdot H_2O\cdot MeOH$ and Na(**2**)$\cdot 2H_2O$. We also made Na(**3**)$\cdot 3EtOH\cdot 0.5H_2O$ for com-

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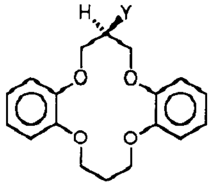

1, Y = $CH_2CO_2^-$
2, Y = $CH_2CH_2CO_2^-$
3, Y = $OCH_2CO_2^-$
4, Y = $OCH_2(C_6H_5)PO_2^-$
5, Y = H

parison with the Li^+ analogue, $Li(\mathbf{3})\cdot 7.5H_2O$. Crystal structure analyses were carried out on these three complexes, and molecular mechanics calculations were used in analyzing the configurations found.

Experimental Section

All solvents and reagents were obtained from commercial sources and used as received unless otherwise noted. Tetrahydrofuran was distilled from sodium benzophenone ketyl before use. Benzene was dried by distillation from Na/K alloy (4:1, w/w). Acetonitrile was dried by distillation from calcium hydride. Melting points were obtained on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on a JEOL FX-90Q spectrometer and IR spectra were obtained with a 1 mm path length solution cell on a Digilab FTS-60 spectrometer. These data are presented in the supplementary material; see note at end of paper.

***sym*-Methylenedibenzo-14-crown-4.** A stirred solution of 1,3-bis(2-hydroxyphenoxy)propane[15,17] (10.0 g, 38.5 mmol) in 200 mL of tetrahydrofuran and 100 mL of water was heated to reflux under an Ar atmosphere, and a solution of LiOH (3.5 g, 83 mmol) in 20 mL of water was added. After 20 min, 5.0 mL (5.4 g, 40 mmol) of 3-chloro-2-(chloromethyl)-1-propene (94%) was added by syringe pump over 2.5 h. The reaction was refluxed overnight. After being cooled to room temperature, the reaction mixture was extracted twice with 100 mL of ethyl acetate. The combined organic phases were extracted with 100 mL of 3 M NaOH, dried over sodium sulfate, and evaporated in vacuo. Recrystallization from 30 mL of isopropyl alcohol/isopropyl ether (5:1) gave 7.38 g (61.5%) of 3-methylenedibenzo-14-crown-4, mp 109–110 °C. Chromatography of the mother liquor on silica gel with ethyl acetate/hexanes gave an additional 1.00 g of product. Acidification of the combined aqueous extracts and extraction with chloroform allowed, upon evaporation, recovery of 1.24 g of starting material. Final yield: 79.7% (corrected for recovered starting material).

3-Ketodibenzo-14-crown-4. A solution of sodium metaperiodate (14 g, 65 mmol) in 100 mL of water was added dropwise over 1 h to a stirred solution of *sym*-methylenedibenzo-14-crown-4 (10.0 g, 32.0 mmol) and osmium tetraoxide (0.10 g, 0.40 mmol) in 150 mL of dioxane and 15 mL of water maintained at 25 °C in a water bath. After 1 h, 200 mL of ethyl acetate was added. The supernatant was decanted from the residue, which was washed twice with 50 mL of ethyl acetate. The combined supernatant was washed once with a saturated NaCl solution, dried over sodium sulfate, and filtered through a short column (50 g) of silica gel. The column was eluted with 500 mL of ethyl acetate, and the eluent was evaporated in vacuo to obtain 9.59 g (95.3%) of *sym*-ketodibenzo-14-crown-4 as a brown oil.

***sym*-((Ethoxycarbonyl)methylene)dibenzo-14-crown-4.** To a solution of 6.5 mL (7.3 g, 33 mmol) of triethyl phosphonoacetate in 150 mL of dry benzene maintained at 5 °C in an ice–water bath was added a suspension of sodium hydride (0.83 g, 35 mmol) in 20 mL of benzene. After 30 min, a solution of *sym*-ketodibenzo-14-crown-4 (9.51 g, 30 mmol) in 50 mL of tetrahydrofuran was added dropwise over 5 min. The reaction mixture was allowed to warm to room temperature. After 30 min, 5 mL of acetone was added, followed by 5 mL of water. The reaction mixture was washed with a saturated solution of NaCl, dried over magnesium sulfate, and evaporated in vacuo. Chromatography on silica gel and eluting with an ether/hexanes gradient (0–40% ether) gave 6.83 g (58.7%) of *sym*-((ethoxycarbonyl)methylene)dibenzo-14-crown-4 as a colorless oil.

Ethyl *sym*-Dibenzo-14-crown-4-acetate. To a solution of *sym*-((ethoxycarbonyl)methylene)dibenzo-14-crown-4 (3.4 g, 8.85 mmol) in 30 mL of absolute ethanol was added sodium borohydride (0.25 g, 6.6 mmol, 25 mmol hydride equivalent). Solid product began to precipitate after 5 min. After 15 min, 100 mL of dichloromethane was added to dissolve the precipitate. The reaction mixture was washed once with 3 M HCl and once with a saturated solution of NaCl, dried over sodium sulfate, and evaporated in vacuo to obtain 3.4 g (99%) of white solid ethyl *sym*-dibenzo-14-crown-4-acetate. Recrystallization from ethanol gave 2.52 g (74%); mp 96.0–96.5 °C.

2-(*sym*-Dibenzo-14-crown-4)acetic Acid (1). A solution of ethyl 2-(*sym*-dibenzo-14-crown-4)acetate (1.51 g, 3.91 mmol) and NaOH (1.0 N, 10 mL, 10 mmol) in 20 mL of dioxane was refluxed for 3 h (reaction was complete by TLC after 1 h). The solution was acidified with HCl (3 M, 5 mL, 15 mmol), diluted with 50 mL of water, and filtered. The white solid was dissolved in hot 2-propanol, filtered, and cooled to crystallize 1.11 g (79.3%) of *sym*-dibenzo-14-crown-4-acetic acid, mp 188 °C.

2-(*sym*-Dibenzo-14-crown-4)ethanol. To a solution of ethyl *sym*-dibenzo-14-crown-4-acetate (1.88 g, 4.86 mmol) in 100 mL of tetrahydrofuran was added $LiAlH_4$ (0.11 g, 2.9 mmol, 11 mmol hydride equivalent). After 30 min, several drops of water were added to destroy excess hydride, and then the reaction mixture was partitioned between ether and 3 M HCl. The organic phase was washed with a saturated solution of NaCl followed by a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated in vacuo. Recrystallization from methanol gave 1.55 g (92.7%) of white crystals of 2-(*sym*-dibenzo-14-crown-4)ethanol, mp 106.5–107.0 °C.

***sym*-(2-Bromoethyl)dibenzo-14-crown-4.** To a suspension of triphenylphosphine (1.50 g, 5.7 mmol) in 10 mL of dry acetonitrile was added 0.28 mL (0.87 g, 5.4 mmol) of bromine followed by a solution of 2-(*sym*-dibenzo-14-crown-4)ethanol (1.55 g, 4.5 mmol) in dry acetonitrile (10 mL). After 15 min, one drop of methanol was added to destroy excess dibromotriphenylphosphorane and the reaction mixture cooled in an ice bath. Filtration and washing with cold acetonitrile gave 1.68 g (91.6%) of white crystals of *sym*-(2-bromoethyl)dibenzo-14-crown-4, mp 121.0–121.5 °C.

3-(*sym*-Dibenzo-14-crown-4)propionitrile. A solution of *sym*-(2-bromoethyl)-dibenzo-14-crown-4 (1.50 g, 3.68 mmol) and NaCN (0.20 g, 4.0 mmol) in 5 mL of dimethyl sulfoxide was heated to 65 °C for 1 h. Hot water (20 mL) was added and the mixture cooled and filtered to obtain 1.2 g of product. The solid was dissolved in benzene, filtered, and cooled to crystallize 0.99 g (76%) of *sym*-(dibenzo-14-crown-4) propionitrile, mp 126–128 °C.

3-(*sym*-Dibenzo-14-crown-4)propanoic Acid (2). A solution of 3-(*sym*-dibenzo-14-crown-4)propionitrile (0.99 g, 2.8 mmol) and NaOH (50% in water) (1.1 g, 14 mmol) in 10 mL of ethylene glycol was heated at 150 °C under Ar for 30 min. The reaction mixture was allowed to cool, diluted with 20 mL of water, acidified with 6 mL of 3 M HCl, and extracted twice with chloroform. The combined organic extracts were dried over sodium sulfate and evaporated in vacuo. The residue was dissolved in hot methanol, treated with decolorizing carbon, filtered, and cooled to precipitate 0.76 g (73%) of white crystals of 3-(*sym*-dibenzo-14-crown-4)propanoic acid, mp 149–150 °C.

Sodium Salt of *sym*-Dibenzo-14-crown-4-acetic Acid. A solution of ethyl 2-(*sym*-dibenzo-14-crown-4)acetate (0.30 g, 0.77 mmol) and NaOH (1.0 N, 0.80 mL, 0.80 mmol) in 5 mL of 90% ethanol was refluxed for 15 min. Air evaporation left a white solid, which was used to prepare crystals for X-ray study.

Sodium Salt of Dibenzo-14-crown-4-propanoic Acid. A solution of NaOH (1.0 N, 0.80 mL, 0.80 mmol) in 5 mL of 90% ethanol was added to 3-(*sym*-dibenzo-14-crown-4)propanoic acid (0.30 g, 0.80 mmol) in 10 mL of ethanol. Air evaporation left a white solid, which was crystallized for X-ray analysis as outlined below.

Preparation of Crystals. Evaporation of a solution of Na(**1**) in wet methanol gave prismatic crystals of $Na(\mathbf{1})\cdot H_2O\cdot MeOH$ up to 1 mm in diameter. These were separated from the supernatant and surface dried; they were stable in air during data collection, but eventually lost solvent. Platelike crystals of $Na(\mathbf{2})\cdot 2H_2O$ were grown from wet methanol solution and remained stable in air indefinitely. In order to crystallize $Na(\mathbf{3})\cdot EtOH\cdot 0.5H_2O$, it was dissolved in wet EtOH and the solution placed in a desiccator with H_2SO_4 to remove the H_2O slowly. Large prisms grew as the water was removed, but they had to be removed from the supernatant, surface dried, and sealed in capillaries in order to survive. In air, they lost EtOH and disintegrated in minutes. The reason for this behavior is apparent from the structure that was found. In each of these systems we observed the presence of other crystalline phases as the alcohol:H_2O ratio was changed, but we did not attempt to elucidate the phase diagrams.

X-ray Diffraction and Crystal Structure Determination. After a preliminary examination of the crystals by use of a precession camera, the data for unit-cell determination and the intensity data were obtained by use of a Huber diffractometer. It was controlled by a PDP-11 computer employing a program, ORDIF, written by W. R. Busing. Operational

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Table I. Crystallographic Data for the Complexes

	Na(**1**)·H_2O·MeOH	Na(**2**)·$2H_2O$	Na(**3**)·EtOH·$0.5H_2O$
formula	$NaC_{21}H_{27}O_8$	$NaC_{21}H_{27}O_8$	$NaC_{26}H_{40}O_{10.5}$
fw	430.43	430.43	543.58
a, Å	11.50 (2)	12.95 (1)	27.53 (1)
b, Å	17.40 (3)	16.78 (2)	12.008 (5)
c, Å	10.89 (2)	9.58 (1)	9.043 (4)
β, deg	101.72 (1)	95.8 (2)	90.0
V, Å^3	2133.7	2071.0	2989.4
Z	4	4	4
space group	$P2_1/c$	$P2_1/c$	$Pca2_1$
t, °C	19.3	21.5	20.6
radiation (λ, Å)	0.709 26	0.709 26	0.709 26
d_{obsd}, g cm^{-3}	1.36	1.37	
d_{calcd}, g cm^{-3}	1.34	1.38	1.21
μ, cm^{-1}	1.16	1.16	0.97
trans coeff	0.961–0.973	0.973–0.997	0.964–0.969
no. of reflcns	3088	1273	1565
$R(F)$	0.052	0.065	0.060
$R_w(F)$	0.062	0.066	0.068

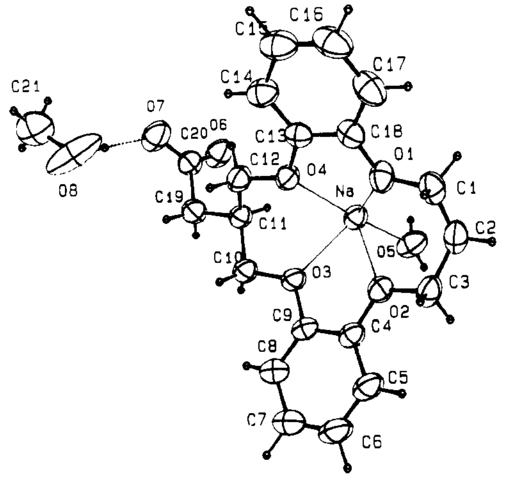

Figure 1. One molecule of Na(**1**)·H_2O·MeOH. Atoms are represented by 50% probability thermal ellipsoids except for H atoms, which are shown as small spheres. The dotted line is a hydrogen bond.

details and crystal data are given in Table I. The space groups for Na(**1**)·H_2O·MeOH and Na(**2**)·$2H_2O$ were deduced from systematic absences, but for Na(**3**)·3EtOH·$0.5H_2O$, a choice of the noncentrosymmteric space group was based on consideration of the density and the unlikelihood of the molecules having a plane of symmetry. Each of the structures was solved by the use of MULTAN82 plus Fourier syntheses. These calculations were done with the Enraf-Nonius Structure Determination Package.[18]

The positions and anisotropic thermal parameters of non-hydrogen atoms were adjusted by full-matrix least-squares methods to yield the values given in Tables II–IV. Although some of the H atoms could be detected in electron-density maps, calculated positions for these atoms were used in the refinements and isotropic B values equal to $1.3B_{eq}$ of the atom on which they ride were employed. No H atom parameters were varied in the refinement.

Compound Na(**3**)·3EtOH·$0.5H_2O$ has two of its EtOH molecules disordered. Three sites for each C atom of these molecules (no H atoms were included) were obtained from electron density difference maps, and several cycles of least squares were carried out with the sites one-third occupied by atoms with isotropic thermal motion and the EtOH geometry restrained[19] toward ideal values. These molecules were then held fixed during the full-matrix refinement of the rest of the structure. In a subsequent difference Fourier map the highest peak amounted to 0.6 e Å^{-3}. From the environment of the site of this peak, it was deduced to be partially occupied by a H_2O molecule that is H bonded to O7. On addition to the refinement of half an O atom at this site, the largest peaks in the resulting difference map were ±0.2 e Å^{-3}. Because the crystal structure is noncentrosymmetric, the enantiomorph was refined by least-squares methods; however, its agreement indices were not significantly different, and the absolute configuration is not known.

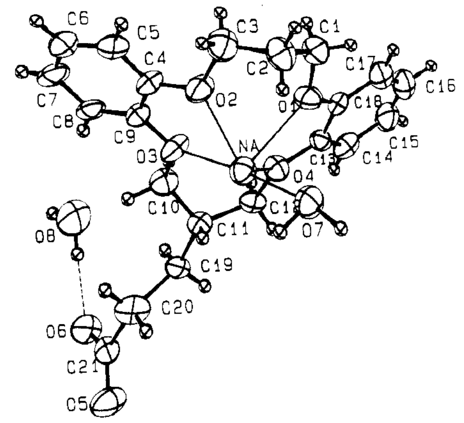

Figure 2. One molecule of Na(**2**)·$2H_2O$. Atoms are represented by 50% probability thermal ellipsoids except for H atoms, which are shown as small spheres. The dashed line is a hydrogen bond.

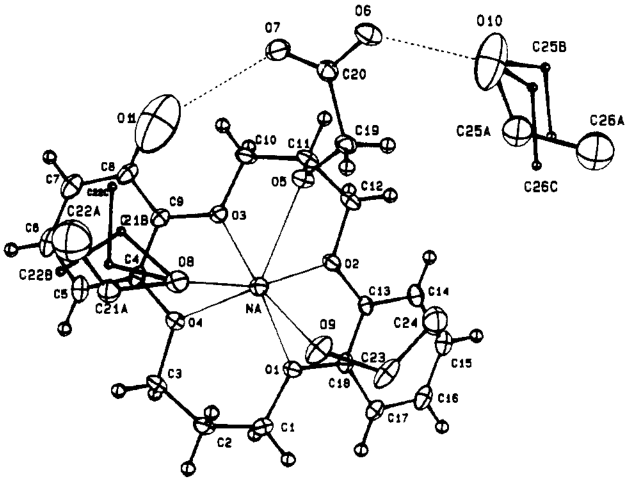

Figure 3. One molecule of Na(**3**)·3EtOH·$0.5H_2O$. Atoms are represented by 10% probability thermal ellipsoids. Hydrogen atoms are depicted as small spheres. Molecules of EtOH (containing O8 and O10) are pictured with two of the alternate sites shown with small spheres in each case.

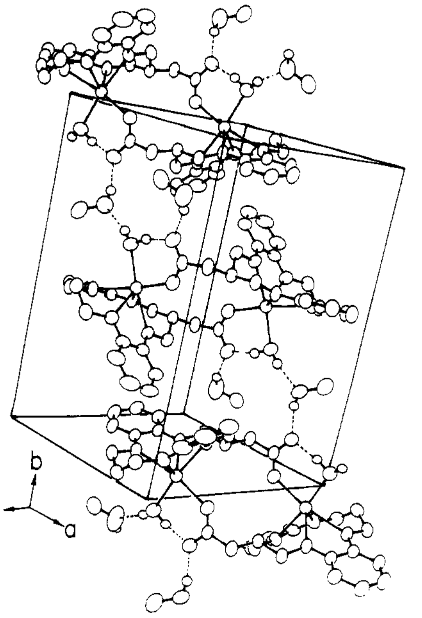

Figure 4. One unit cell of Na(**1**)·H_2O·MeOH. Hydrogen bonds are shown as dotted lines and connect the dimers into chains along the *b* axis. Only H atoms involved in such bonding are shown.

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Table II. Positional and Equivalent Isotropic Thermal Parameters for Na(**1**)·H_2O·MeOH, with Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
Na	0.28308 (7)	−0.01216 (5)	0.17469 (8)	3.70 (2)
O1	0.1160 (1)	−0.09098 (9)	0.0895 (2)	4.21 (4)
O2	0.1916 (1)	−0.0515 (1)	0.3503 (1)	4.01 (3)
O3	0.4101 (1)	−0.07919 (9)	0.3413 (1)	3.71 (3)
O4	0.3314 (1)	−0.13571 (9)	0.0975 (1)	3.68 (3)
O5	0.2490 (2)	0.1110 (1)	0.2267 (2)	5.50 (4)
O6	0.6792 (2)	−0.0403 (1)	0.0084 (2)	5.82 (4)
O7	0.7114 (2)	−0.1643 (1)	−0.0087 (2)	6.46 (5)
O8	0.2326 (2)	0.1973 (1)	0.4301 (2)	10.94 (6)
C1	−0.0017 (2)	−0.0812 (2)	0.1132 (2)	4.47 (6)
C2	0.0036 (2)	−0.0229 (2)	0.2168 (2)	4.65 (6)
C3	0.0669 (2)	−0.0471 (2)	0.3465 (2)	4.52 (5)
C4	0.2653 (2)	−0.0687 (1)	0.4640 (2)	3.64 (5)
C5	0.2291 (2)	−0.0721 (2)	0.5782 (2)	4.76 (6)
C6	0.3116 (3)	−0.0892 (2)	0.6869 (2)	5.34 (6)
C7	0.4280 (2)	−0.1032 (2)	0.6825 (2)	5.04 (6)
C8	0.4652 (2)	−0.1004 (2)	0.5676 (2)	4.20 (5)
C9	0.3838 (2)	−0.0832 (1)	0.4593 (2)	3.45 (5)
C10	0.5248 (2)	−0.1064 (1)	0.3276 (2)	3.91 (5)
C11	0.5342 (2)	−0.1013 (1)	0.1904 (2)	3.52 (5)
C12	0.4529 (2)	−0.1568 (1)	0.1039 (2)	4.05 (5)
C13	0.2467 (2)	−0.1698 (1)	0.0061 (2)	3.46 (5)
C14	0.2711 (2)	−0.2248 (1)	−0.0778 (2)	4.51 (6)
C15	0.1787 (3)	−0.2538 (2)	−0.1690 (2)	5.37 (6)
C16	0.0639 (3)	−0.2295 (2)	−0.1738 (3)	5.92 (7)
C17	0.0388 (2)	−0.1759 (2)	−0.0877 (3)	5.11 (6)
C18	0.1304 (2)	−0.1461 (1)	0.0015 (2)	3.74 (5)
C19	0.6631 (2)	−0.1195 (2)	0.1814 (2)	4.32 (5)
C20	0.6865 (2)	−0.1064 (1)	0.0499 (2)	4.02 (5)
C21	0.1488 (3)	0.1680 (2)	0.4885 (3)	7.05 (8)

Table III. Positional and Equivalent Isotropic Thermal Parameters for Na(**2**)·2H_2O, with Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
Na	0.7710 (2)	−0.5018 (2)	−0.2723 (3)	3.88 (7)
O1	0.7795 (4)	−0.6294 (3)	−0.1597 (5)	3.8 (1)
O2	0.5962 (4)	−0.5510 (3)	−0.3012 (6)	4.4 (1)
O3	0.6431 (4)	−0.4359 (3)	−0.1319 (5)	3.8 (1)
O4	0.8358 (4)	−0.5000 (3)	−0.0262 (5)	3.8 (1)
O5	0.8867 (4)	−0.0876 (3)	−0.0517 (6)	5.4 (2)
O6	0.7627 (4)	−0.1098 (3)	0.0880 (6)	4.6 (1)
O7	0.8995 (4)	−0.5527 (3)	−0.4077 (6)	5.6 (2)
O8	0.5871 (5)	−0.2892 (4)	−0.3761 (8)	7.8 (2)
C1	0.7237 (7)	−0.6974 (5)	−0.2180 (9)	4.7 (2)
C2	0.6697 (7)	−0.6746 (5)	−0.3617 (9)	5.1 (2)
C3	0.5697 (7)	−0.6279 (5)	−0.360 (1)	5.7 (3)
C4	0.5142 (6)	−0.5036 (5)	−0.2696 (8)	3.7 (2)
C5	0.4121 (6)	−0.5163 (5)	−0.3265 (9)	4.7 (2)
C6	0.3342 (6)	−0.4665 (5)	−0.288 (1)	5.1 (2)
C7	0.3581 (6)	−0.4071 (5)	−0.1902 (9)	4.8 (2)
C8	0.4618 (6)	−0.3953 (5)	−0.1327 (9)	4.1 (2)
C9	0.5409 (6)	−0.4429 (4)	−0.1744 (8)	3.3 (2)
C10	0.6752 (6)	−0.3724 (5)	−0.0367 (9)	4.1 (2)
C11	0.7903 (6)	−0.3618 (4)	−0.0317 (8)	2.9 (2)
C12	0.8506 (6)	−0.4261 (4)	0.0523 (8)	3.5 (2)
C13	0.8731 (6)	−0.5693 (4)	0.0367 (8)	3.3 (2)
C14	0.9339 (6)	−0.5734 (5)	0.1635 (9)	4.3 (2)
C15	0.9670 (6)	−0.6469 (5)	0.2165 (9)	4.9 (2)
C16	0.9400 (7)	−0.7145 (5)	0.143 (1)	5.1 (2)
C17	0.8778 (6)	−0.7133 (5)	0.0149 (9)	4.3 (2)
C18	0.8435 (6)	−0.6394 (5)	−0.0365 (8)	3.4 (2)
C19	0.8191 (6)	−0.2798 (4)	0.0311 (9)	3.5 (2)
C20	0.7989 (7)	−0.2117 (5)	−0.0753 (8)	4.3 (2)
C21	0.8181 (6)	−0.1298 (4)	−0.0064 (8)	3.7 (2)

Relevant bond lengths and angles for all three crystals are given in Tables V–VII. Observed and calculated structure factors, anisotropic thermal parameters, and calculated H atom positions are given in the supplementary material.

Table IV. Positional and Equivalent Isotropic Thermal Parameters for Na(**3**)·3EtOH·0.5H_2O, with Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
Na	0.38633 (9)	0.9105 (2)	0.0000	5.28 (6)
O1	0.4730 (2)	0.8506 (3)	0.0377 (5	5.4 (1)
O2	0.4086 (1)	0.8018 (4)	0.2251 (6)	5.7 (1)
O3	0.3743 (2)	1.0182 (3)	0.2269 (6)	5.9 (1)
O4	0.4394 (2)	1.0742 (3)	0.0418 (5)	5.7 (1)
O5	0.3157 (2)	0.8517 (4)	0.1398 (6	6.3 (1)
O6	0.1934 (2)	0.7510 (4)	0.1356 (7)	7.6 (1)
O7	0.2239 (2)	0.9089 (4)	0.2139 (9)	9.3 (2)
O8	0.6518 (2)	0.9739 (4)	0.3274 (9)	10.4 (2)
O9	0.3876 (2)	0.7818 (5)	−0.1995 (7)	8.8 (1)
O10	0.1825 (4)	0.5524 (6)	−0.009 (1)	19.3 (3)
O11[a]	0.260 (1)	0.090 (2)	0.032 (5)	32 (1)
C1	0.5099 (3)	0.8939 (6)	−0.056 (1)	7.5 (2)
C2	0.4915 (3)	0.9918 (7)	−0.1416 (9)	7.2 (2)
C3	0.4805 (3)	1.0958 (6)	−0.0515 (9)	7.0 (2)
C4	0.4201 (3)	1.1607 (5)	0.1239 (9)	5.5 (2)
C5	0.4357 (3)	1.2720 (6)	0.110 (1)	7.4 (2)
C6	0.4136 (4)	1.3512 (6)	0.198 (1)	9.5 (3)
C7	0.3778 (3)	1.3213 (7)	0.298 (1)	9.3 (3)
C8	0.3626 (3)	1.2099 (6)	0.311 (1)	7.3 (2)
C9	0.3839 (2)	1.1317 (6)	0.2266 (9)	5.6 (2)
C10	0.3374 (3)	0.9799 (7)	0.3243 (9)	6.7 (2)
C11	0.3283 (3)	0.8599 (7)	0.2940 (8)	6.1 (2)
C12	0.3698 (3)	0.7796 (6)	0.3267 (9)	6.4 (2)
C13	0.4476 (2)	0.7322 (5)	0.2252 (9)	5.0 (1)
C14	0.4542 (3)	0.6414 (6)	0.3181 (9)	6.5 (2)
C15	0.4971 (3)	0.5772 (6)	0.304 (1)	8.1 (2)
C16	0.5314 (3)	0.6062 (6)	0.202 (1)	8.5 (2)
C17	0.5251 (3)	0.6956 (6)	0.110 (1)	6.7 (2)
C18	0.4831 (2)	0.7586 (5)	0.1243 (9)	5.2 (2)
C19	0.2767 (2)	0.7769 (6)	0.110 (1)	6.1 (2)
C20	0.2278 (2)	0.8173 (6)	0.1583 (9)	5.8 (2)
C21A[b]	0.650	0.867	0.273	7.0 (6)[c]
C2uB	0.680	0.873	0.369	11 (1)[c]
C21C	0.666	0.863	0.304	14 (1)[c]
C22A	0.697	0.819	0.241	21 (2)[c]
C22B	0.670	0.795	0.240	18 (2)[c]
C22C	0.707	0.851	0.418	13 (1)[c]
C23	0.4052 (3)	0.6670 (7)	−0.186 (1)	9.1 (2)
C24	0.3778 (4)	0.5966 (8)	−0.086 (1)	10.1 (3)
C25A	0.230	0.500	−0.015	10.4 (8)[c]
C25B	0.200	0.466	0.091	14 (1)[c]
C25C	0.215	0.482	0.088	18 (2)[c]
C26A	0.234	0.379	−0.043	18 (2)[c]
C26B	0.251	0.441	0.093	10.4 (8)[c]
C26C	0.259	0.462	0.008	17 (1)[c]

[a] Occupancy of 0.5. [b] Atoms named with a letter suffix have occupancy factors of 0.333. [c] Isotropic thermal parameters were refined.

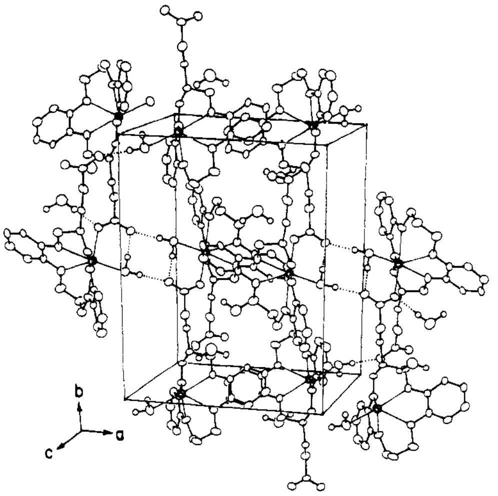

Figure 5. One unit cell of Na(**2**)·2H_2O. The only H atoms shown are those involved in H bonds (dotted lines).

Description and Discussion of the Structures

Molecular Structures. Individual molecules of each complex are illustrated in Figures 1–3, and the intermolecular bonding and packing are shown in Figures 4–6. There are some broad similarities among these structures although they differ in important details. In each complex, the dibenzo-14-crown-4 ring is V-shaped and folded along the C2–C11 line. This results in the four ether

Table V. Bond Lengths (Å) and Angles (deg) in Na(**1**)·H_2O·MeOH

Bond Lengths			
Na–O1	2.389 (2)	C9–O3	1.381 (3)
Na–O2	2.460 (2)	C10–O3	1.437 (3)
Na–O3	2.390 (2)	C10–C11	1.522 (3)
Na–O4	2.414 (2)	C11–C12	1.528 (3)
Na–O5	2.271 (2)	C11–C19	1.539 (3)
Na–O6	2.313 (2)	C12–O4	1.433 (3)
O1···O4	2.581 (2)	C13–O4	1.378 (2)
O1···O2	2.879 (2)	C13–C14	1.391 (3)
O2···O3	2.581 (2)	C13–C18	1.391 (3)
O3···O4	2.803 (2)	C14–C15	1.394 (3)
		C15–C16	1.377 (4)
C1–O1	1.439 (3)	C16–C17	1.394 (4)
C1–C2	1.511 (4)	C17–C18	1.381 (3)
C2–C3	1.511 (3)	C18–O1	1.389 (3)
C3–O2	1.428 (3)	C19–C20	1.526 (3)
C4–O2	1.385 (2)	C20–O6	1.233 (3)
C4–C5	1.390 (3)	C20–O7	1.255 (3)
C4–C9	1.396 (3)	C21–O8	1.357 (4)
C5–C6	1.390 (3)		
C6–C7	1.371 (3)	O7···O8	2.594 (3)
C7–C8	1.402 (3)	O5···O7	2.674 (3)
C8–C9	1.381 (3)	O5···O8	2.713 (3)
Bond Angles			
O1–C1–C2	108.5 (2)	C12–C11–C19	107.9 (2)
C1–C2–C3	116.7 (2)	C12–O4–C13	117.6 (2)
C2–C3–O2	109.4 (2)	O4–C13–C14	124.4 (2)
C3–O2–C4	117.8 (2)	O4–C13–C18	115.5 (2)
O2–C4–C5	124.7 (2)	C13–C14–C15	119.4 (2)
O2–C4–C9	115.5 (2)	C13–C18–O1	115.4 (2)
C5–C4–C9	119.8 (2)	C14–C13–C18	120.1 (2)
C4–C5–C6	119.6 (2)	C14–C15–C16	120.1 (2)
C5–C6–C7	120.7 (2)	C15–C16–C17	120.6 (2)
C6–C7–C8	120.1 (2)	C16–C17–C18	119.5 (2)
C7–C8–C9	119.5 (2)	C17–C18–C13	120.2 (2)
C8–C9–C4	120.3 (2)	C17–C18–O1	124.3 (2)
C8–C9–O3	124.5 (2)	C18–O1–C1	117.0 (2)
O3–C9–C4	115.2 (2)	C11–C19–C20	112.6 (2)
C9–O3–C10	117.3 (2)	O6–C20–O7	124.6 (2)
O3–C10–C11	109.4 (2)	O6–C20–C19	118.1 (2)
C10–C11–C12	114.3 (2)	O7–C20–C19	117.2 (2)
C10–C11–C19	108.2 (2)		
C11–C12–O4	109.6 (2)		

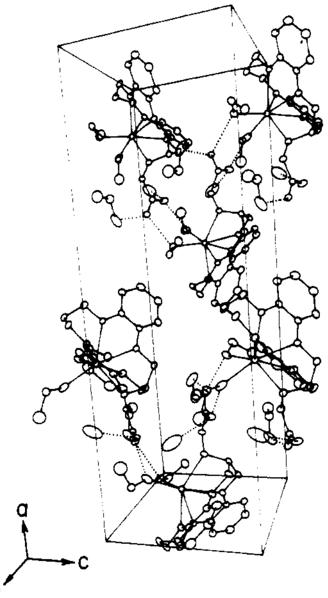

Figure 6. One unit cell of Na(**3**)·3EtOH·0.5H_2O. H atoms are omitted. EtOH molecules are shown in only one of the disordered sites. H bonds are indicated by dashed lines.

Table VI. Bond Lengths (Å) and Angles (deg) in Na(**2**)·2H_2O

Bond Lengths			
Na–O1	2.394 (6)	O3–C10	1.436 (8)
Na–O2	2.398 (6)	C10–C11	1.50 (1)
Na–O3	2.494 (6)	C11–C12	1.52 (1)
Na–O4	2.421 (6)	C11–C19	1.53 (1)
Na–O6	2.298 (7)	C12–O4	1.453 (8)
Na–O7	2.371 (6)	O4–C13	1.374 (8)
O1···O4	2.586 (8)	C13–C14	1.38 (1)
O1···O2	2.923 (8)	C13–C18	1.40 (1)
O2···O3	2.555 (7)	C14–C15	1.38 (1)
O3···O4	2.810 (7)	C15–C16	1.36 (1)
		C16–C17	1.40 (1)
O1–C1	1.434 (9)	C17–C18	1.39 (1)
O1–C18	1.383 (9)	C19–C20	1.54 (1)
C1–C2	1.53 (1)	C20–C21	1.53 (1)
C2–C3	1.52 (1)	C21–O5	1.249 (9)
C3–O2	1.436 (9)	C21–O6	1.256 (9)
O2–C4	1.385 (9)		
C4–C5	1.39 (1)		
C4–C9	1.39 (1)	O7···O5	2.733 (8)
C5–C6	1.39 (1)	O7···O5	2.895 (8)
C6–C7	1.38 (1)	O6···O8	2.885 (9)
C7–C8	1.41 (1)		
C8–C9	1.39 (1)		
C9–O3	1.350 (8)		
Bond Angles			
C1–O1–C18	118.0 (7)	C11–C12–O4	107.4 (6)
O1–C1–C2	108.5 (7)	C12–O4–C13	118.2 (6)
C1–C2–C3	115.6 (8)	O4–C13–C14	125.0 (8)
C2–C3–O2	107.4 (7)	O4–C13–C18	115.1 (8)
C3–O2–C4	116.3 (7)	C14–C13–C18	120.0 (8)
O2–C4–C5	123.0 (8)	C13–C14–C15	119.7 (8)
O2–C4–C9	114.8 (7)	C14–C15–C16	119.8 (9)
C5–C4–C9	122.2 (8)	C15–C16–C17	122.6 (9)
C4–C5–C6	119.3 (8)	C16–C17–C18	117.3 (9)
C5–C6–C7	119.7 (8)	O1–C18–C13	115.7 (8)
C6–C7–C8	120.3 (8)	O1–C18–C17	123.6 (8)
C7–C8–C9	120.4 (8)	C13–C18–C17	120.7 (8)
C8–C9–O3	126.3 (8)	C11–C19–C20	112.9 (7)
C4–C9–O3	115.7 (7)	C19–C20–C21	111.8 (7)
C8–C9–C4	118.0 (8)		
O3–C10–C11	109.4 (7)	O5–C21–O6	125.3 (8)
C10–C11–C12	112.9 (7)	O5–C21–C20	116.7 (8)
C10–C11–C19	108.7 (7)	O6–C21–C20	118.0 (8)
C19–C11–C12	109.9 (6)		

O atoms (planar within ±0.11 Å) being extended to one side of the ring where, in each case, they are bonded to a Na^+ ion. The coordination sphere of this cation, Figures 4–6, also contains one H_2O and one monodentate carboxylate ion in the structures of Na(**1**)·H_2O·MeOH and Na(**2**)·2H_2O; in Na(**3**)·3EtOH·0.5H_2O, it contains an O atom from the side arm plus two EtOH molecules. The halves of the macrocyclic molecule are planar in each complex, within ±0.02 Å; the dimensions of the V-shaped molecules plus three previously determined ones are listed in Table VIII. The "V" angles exhibit considerable variability, and molecular mechanics (see below) has shown that the crown actually can invert without breaking bonds.

Pendant Side Arms. Because the Na(Li)–O–C10–C11–C12–O portion of each lariat ether complex has a pseudo-boat conformation, it is convenient to describe the pendant arms at C11 as being in pseudoaxial (A) or pseudoequatorial (E) sites. For these designations, the acetate and propanoate sidearms are in E sites with their carboxylate anions directed away from the Na^+ ion, which is coordinated by the crown ether. In Na(**1**)·H_2O·MeOH the carboxylate ion of one lariat ether forms a monodentate bond to the Na^+ ion held by a nearby lariat ether, which, in turn, forms a similar bond in reciprocal fashion, producing dimers in this structure (Figure 4). Molecules of Na(**2**)·2H_2O form similar intramolecular Na–carboxylate bonds, but each complex is bonded to two different neighbors so that polymers along the *b* axis are formed (Figure 5). Thus, in neither of these complexes is there *intra*molecular cation–anion bonding. In Na(**3**)·3EtOH·0.5H_2O, as in the previously reported Li(**3**)·7.5H_2O and Na(**4**)·2H_2O·2EtOH structures,[15,16] the ether O atom of the side arm is bonded to the cation, but the anion on this same pendant arm is directed away from the cation. Neither are there *inter*molecular cation–anion bonds in these structures, including the present case (Figure 6).

Table VII. Bond Lengths and Angles in $Na(\mathbf{3})\cdot 3EtOH\cdot 0.5H_2O$

	Bond Lengths		
Na–O1	2.515 (4)	C13–C14	1.389 (9)
Na–O2	2.495 (5)	C13–C18	1.374 (9)
Na–O3	2.448 (5)	C14–C15	1.41 (1)
Na–O4	2.479 (4)	C15–C16	1.37 (1)
Na–O5	2.423 (5)	C16–C17	1.37 (1)
Na–O8	2.337 (5)	C17–C18	1.387 (8)
Na–O9	2.376 (5)	C18–O1	1.383 (7)
O1···O2	2.521 (6)	C19–O5	1.427 (7)
O1···O4	2.840 (6)	C19–C20	1.497 (8)
O2···O3	2.765 (6)	C20–O6	1.255 (7)
O3···O4	2.543 (6)	C20–O7	1.215 (8)
		O9–C23	1.468 (9)
O1–C1	1.419 (8)	C23–C24	1.44 (1)
C1–C2	1.50 (1)	O8–C21A	1.37
C2–C3	1.52 (1)	O8–C21B	1.49
C3–O4	1.436 (7)	O8–C21C	1.41
O4–C4	1.382 (7)	O10–C25A	1.46
C4–C5	1.410 (9)	O10–C25B	1.45
C4–C9	1.407 (9)	O10–C25C	1.50
C5–C6	1.38 (1)	C21A–C22A	1.45
C6–C7	1.38 (1)	C21B–C22B	1.52
C7–C8	1.41 (1)	C21C–C22C	1.53
C8–C9	1.342 (9)	C25A–C26A	1.48
C9–O3	1.389 (7)	C25B–C26B	1.46
O3–C10	1.421 (7)	C25C–C26C	1.45
C10–C11	1.49 (1)	O8···O7	2.642 (8)
C11–C12	1.52 (1)	O9···O6	2.706 (7)
C11–O5	1.439 (8)	O10···O6	2.735 (9)
C12–O2	1.434 (7)	O11···O7	2.90 (5)
O2–C13	1.361 (7)		
	Bond Angles		
O1–C1–C2	110.8 (6)	C13–C14–C15	118.9 (8)
C1–C2–C3	115.7 (6)	C14–C15–C16	119.9 (8)
C2–C3–O4	108.9 (5)	C15–C16–C17	121.5 (7)
C3–O4–C4	118.9 (5)	C16–C17–C18	118.4 (8)
O4–C4–C5	123.1 (8)	C17–C18–C13	122.0 (7)
O4–C4–C9	116.2 (6)	C17–C18–O1	123.4 (7)
C4–C5–C6	117.7 (9)	C18–O1–C1	119.0 (5)
C5–C6–C7	120.8 (8)	C12–C11–O5	108.9 (6)
C6–C7–C8	120.8 (8)	C11–O5–C19	114.0 (5)
C7–C8–C9	119.4 (8)	O5–C19–C20	114.7 (6)
C8–C9–C4	120.6 (7)	C19–C20–O6	115.3 (7)
C8–C9–O3	127.1 (8)	C19–C20–O7	119.6 (7)
C9–O3–C10	117.0 (5)	O6–C20–O7	125.1 (7)
O3–C10–C11	108.7 (5)	O9–C23–C24	115.5 (8)
C10–C11–C12	116.8 (6)	O8–C21A–C22A	114
C10–C11–O5	106.5 (7)	O8–C21B–C22B	102
C11–C12–O2	108.5 (5)	O8–C21C–C22C	101
C12–O2–C13	118.3 (5)	O10–C25A–C26A	120
O2–C13–C14	125.8 (7)	O10–C25B–C26B	118
O2–C13–C18	114.8 (6)	O10–C25C–C26C	108

Table VIII. Molecular Dimensions for Complexes of Dibenzo-14-crown-4 and Derivatives

compd	"V" angle, deg	$d(M^+\cdots O_4$ plane), Å	ref
$Na(\mathbf{1})\cdot H_2O\cdot MeOH$	135.3	1.47	this work
$Na(\mathbf{2})\cdot 2H_2O$	126.7	1.48	this work
$Na(\mathbf{3})\cdot 3EtOH\cdot 0.5H_2O$	135.4	1.61	this work
$Na(\mathbf{4})\cdot 2EtOH\cdot 2H_2O$	120.7	1.52	16
$Li(\mathbf{3})\cdot 7.5H_2O$	118.6	0.84	15
$Li(\mathbf{5})\cdot SCN$	121	0.79	20

Solvent Molecules and Hydrogen Bonding. In the structures reported here, each Na^+ ion includes in its coordination sphere either one H_2O or two EtOH molecules. These solvent molecules form H bonds to O atoms of other complex molecules or to other solvent molecules in between complexes and thereby play a basic role in linking the complexes into crystals. In $Na(\mathbf{1})\cdot H_2O\cdot MeOH$, the dimers are joined by H bonds between the inner-sphere H_2O molecule and an outer-sphere MeOH molecule to produce a chain of dimers along the crystal *b* axis (Figure 4). The H bonding in the structure of $Na(\mathbf{2})\cdot H_2O$ is between inner-sphere H_2O molecules in adjacent complexes and includes as well H bonds to one of the carboxylate O atoms of these neighbors (Figure 5). This produces a double layer of complexes parallel to (010). In $Na(\mathbf{3})\cdot 3EtOH\cdot 0.5H_2O$ the inner sphere of the Na^+ ion contains two EtOH molecules, one of which is disordered. These two EtOH molecules form H bonds to the carboxylate O atoms of an adjacent complex. Each carboxylate O atom also receives H bonds from an additional molecule: O6 from the EtOH containing O10 and O7 from the H_2O containing O11 (Figure 6). The disorder, partial occupancy, and large thermal motion of the two EtOH molecules and the half H_2O molecule suggest that these are all held loosely in the crystal. This may explain why the crystals were difficult to isolate, losing EtOH and H_2O and disintegrating quickly when left out in air. Even though the samples used for X-ray diffraction were sealed in glass, they may have lost some of the solvent before use.[21]

Molecular Mechanics Calculations

In order to study why these complexes do not show intramolecular cation–anion bonding we calculated the minimum-energy configurations of various isolated molecules. Ten different starting models were used. Each contained the sodium dibenzo-14-crown-4 ring and attached to it were acetate, propanoate, and oxyacetate side arms in A and E sites, respectively. Where available, the molecular structures found in the crystals were used; the other models were hypothesized. Coordinated solvent molecules were also included where found in the crystals or in analogous sites in hypothetical models. For the energy calculation and minimization, the program WMIN by Busing[22] was used as described previously.[23] The potential function was of the conventional force-field type and included Coulombic forces, nonbonded attraction and repulsion, and the bonded terms for stretching, bending, and torsion. Hydrogen atoms were treated individually. All parameters used in the calculation are given in the supplementary material. Consistent with earlier work on crown ether complexes,[23,24] the charges were assigned as follows: Na, +1.0; O in ether −0.6; O in carboxylate, −0.65; C adjacent to O, +0.3; other atoms, 0.0. The minimization of energy was continued until the change in total energy was less than 0.1% for each type of molecule.

The configurations of minimum energy for each of the molecules are shown in Figure 7. From these calculations, it thus appears that Na complexes of dibenzo-14-crown-4 having pendant acetate or propanoate side arms in A sites are able to form *intra*molecular cation–anion bonds. The presence of inner-sphere H_2O determines whether the carboxylate anion forms mono- or bidentate bonds to the Na^+ ion. With these side arms in the E site, however, such bonding does not occur, although the carboxylate ion is available to form *inter*molecular bonds, and this is what is found in the crystal structure of these complexes. The oxyacetate side arm behaves differently because of the presence of the oxy moiety. When the side arm is in the A site, this moiety bonds to the Na^+ ion. The carboxylate ion also bonds to it if there is H_2O present in the inner sphere but is inhibited from doing so if there are two EtOH molecules instead. The latter situation is that found in the crystal. The hypothetical oxyacetate hydrate with the side arm in the E site still forms an intramolecular cation–anion bond, but the oxy moiety is not bonded to the Na^+ ion.

It should be emphasized that the calculations are for isolated molecules (and also have the assumptions and approximations listed) and are useful only in assessing the possible configurations resulting from intramolecular force fields. The presence of neighboring molecules in crystals or in solution will obviously be very important in determining the bonding pattern there. The calculations are useful to the extent that among the minimum-energy structures they produce are the configurations actually

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(21) The final difference Fourier map contains a number of small peaks (<0.2 e/Å^3) in the region of the disordered EtOH molecules, suggesting that our model may not completely account for the disorder or vacancies that the crystal may have.

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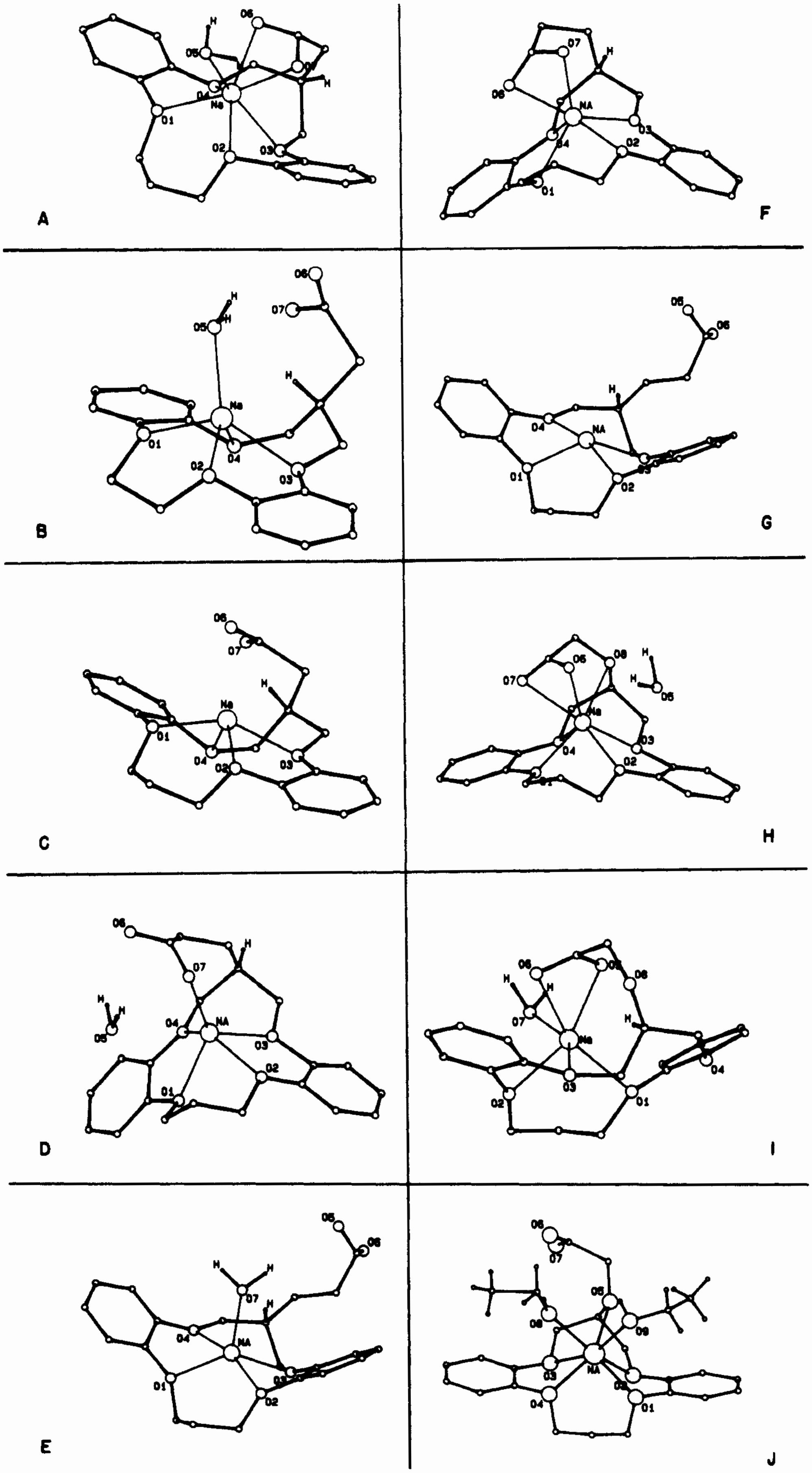

Figure 7. Schematic representations of complexes of minimum energy: (A) Na(**1**)·H_2O, axial; (B) Na(**1**)·H_2O, equatorial; (C) Na(**1**), equatorial; (D) Na(**2**)·H_2O, axial; (E) Na(**2**)·H_2O, equatorial; (F) Na(**2**), axial; (G) Na(**2**), equatorial; (H) Na(**3**)·H_2O, axial; (I) Na(**3**)·H_2O, equatorial; (J) Na(**3**)·2EtOH, axial.

found in the crystal structures reported here. Of some interest is the fact that in three cases (Figure 7A,E,I) the folding of the macrocyclic ring was reversed as the Coulombic forces exceeded the strain energy induced in the ring during its inversion. Such configurations have not been found experimentally as yet.

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Supplementary Material Available: Table SI (NMR and IR data), Table SII (complete crystal data and experimental details), Tables SIII–SV (anisotropic thermal parameters), Tables SVI–SVIII (calculated H atom positions), and Table SXII (molecular mechanics parameters (11 pages); Tables SIX–SXI (observed and calculated structure factors) (32 pages). Ordering information is given on any current masthead page.

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Synthesis and Single-Crystal X-ray Structural Investigation of 1,1-Bis(pentacarbonylmanganio)-3,4-dimethylgermacyclopent-3-ene and Bis[1-(tetracarbonylferrio)-3,4-dimethylgermacyclopent-3-ene]: The First Evidence for a Puckered Ground-State Conformation in Germacyclopent-3-enes

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The crystal and molecular structures of 1,1-bis(pentacarbonylmanganio)-3,4-dimethylgermacyclopent-3-ene (I) and bis[1-(tetracarbonylferrio)-3,4-dimethylgermacyclopent-3-ene] (II) have been determined in the solid state by single-crystal X-ray diffraction. The yellow compound I, chemical formula $C_{16}H_{10}O_{10}Mn_2Ge$, crystallizes in the triclinic crystal system with space group $P\bar{1}$, where $a = 7.1603$ (2) Å, $b = 9.6364$ (4) Å, $c = 16.491$ (5) Å, $\alpha = 74.68$ (2)°, $\beta = 87.87$ (2)°, $\gamma = 71.90$ (2)°, and $Z = 2$; R refined to 4.0%. Orange plates of II, chemical formula $C_{20}H_{20}O_8Fe_2Ge_2$, crystallize in the triclinic crystal system with space group $P\bar{1}$, where $a = 9.949$ (3) Å, $b = 8.372$ (2) Å, $c = 7.777$ (2) Å, $\alpha = 72.41$ (1)°, $\beta = 106.77$ (1)°, $\gamma = 94.75$ (1)°, and $Z = 1$; R refined to 2.5%. The germacyclopent-3-ene rings of both molecules are severely strained and adopt a puckered ground-state conformation with puckering angles, δ, of 29.7° for I and 30.2° for II. These data provide the first evidence for a nonplanar equilibrium conformation in species containing germacyclopent-3-ene rings.

Introduction

The ground-state conformations of small ring molecules have been studied intensely for well over 20 years.[1] While cyclopentene exhibits a nonplanar ring structure,[2] the equilibrium structures of its heavier group 14 congomers are quite different, according to the literature.[3] Gas-phase, liquid-phase, and solid-state (77 K) vibrational analyses of 1,1-disubstituted silacyclopent-3-enes have been found consistent with a planar, C_{2v}, rather than a puckered, C_s, ground-state ring conformation.[4] Electron diffraction studies on these molecules have also been interpreted in terms of C_{2v} ring structures but with deviations from planarity that were largest for the 1,1-difluoride and smallest for the 1,1-dichloride.[5] Two- and three-dimensional potential energy surface calculations[6] have shown that cyclopentene, 3-phospholene, silacyclopentane, and 1,3-disilacyclobutane are puckered, whereas silacyclopent-3-ene possesses a planar ring structure. The stability of the planar ring conformation of silacyclopent-3-ene has been attributed to various effects, including an increase in stability that results from reduction of the eclipsing strain of the two CH_2 groups with the SiX_2 group due to the relatively long Si–C length compared to the C–C distance in the cyclopentene analogue. This is consistent with the planar conformation adopted by 2,5-dihydrofuran. At the same time, however, the longer Si–C bonds of silacyclopent-3-enes are also expected to result in a decrease of the C—Si—C angle and an increase the C=C—C angles if the ring remains planar. A smaller C–E–C angle is likely to become more favorable as group 14 is descended due to a reduction in stability gained from hybridization of s and p orbitals. Distortion to a puckered conformation would relieve this strain to some extent. Other explanations favoring the planar conformation have invoked interactions between vacant Si 3d orbitals and π orbitals of the double bond.[4]

It might be expected that the subtle tradeoff between these opposing factors would be manifest in the ground-state conformation of *germa*cyclopent-3-enes. However, the only reported structural study of these molecules is the liquid phase vibrational analysis of 1,1-disubstituted germacyclopent-3-enes, which have been interpreted in terms of planar, C_{2v}, ring structures.[7] We now report the first solid-state single-crystal X-ray diffraction study of two classes of 1,1-dimetal-substituted germacyclopent-3-enes, which demonstrates that the ground-state ring conformation in these molecules is puckered.

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