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The effects of methylene-substituents in crown ether backbones. Crystal structures of [Na(OH_2)(methylene-16-crown-5)]I, [Na(NO_2)(methylene-16-crown-5)]·0.5 (H_2O), 3,16-dimethylene-26-crown-8,[Na_4I_4(3,16-dimethylene-26-crown-8)], and [$Na_2(OH_2)_4$(3,16-dimethylene-26-crown-8)]I_2

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The effects of methylene-substituents in crown ether backbones. Crystal structures of [Na(OH_2)(methylene-16-crown-5)]I, [Na(NO_2)(methylene-16-crown-5)]•0.5 (H_2O), 3,16-dimethylene-26-crown-8,[Na_4I_4 (3,16-dimethylene-26-crown-8)], and [Na_2 $(OH_2)_4$(3,16-dimethylene-26-crown-8)]I_2

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The crystal structures of five methylene substituted crown ether compounds were investigated. [Na(OH_2)(methylene-16-crown-5)]I is orthorhombic, $P2_12_12_1$ with a = 7.920(9), b = 10.787(3), c = 20.870(5)Å, and D_{calc} = 1.54 g cm^{-3} for Z = 4. The sodium cation is coordinated to all five etheric oxygen atoms and a water molecule giving it a coordination number of six. [Na(NO_2)(methylene-16-crown-5)]•0.5(H_2O) is monoclinic, $P2_1/n$ with a = 20.566(6), b = 8.605(9), c = 20.821(7)Å, β = 115.66(3)°, and D_{calc} = 1.30 g cm^{-3} for Z = 8. Each sodium cation is seven-coordinate, coordinated to all five etheric oxygen atoms and a bidentate nitrite anion. One crown molecule is severely disordered. The macrocycles in both methylene-16-crown-5 structures have essentially the same conformations. 3,16-dimethylene-26-crown-8 is orthorhombic, Pccn with a = 18.061(4), b = 14.320(4), c = 8.659(7)Å, and D_{calc} = 1.20 g cm^{-3} for Z = 4. The crown ether has an elongated cavity generated by a series of six consecutive *anti* torsion angles. [Na_4I_4(3,16-dimethylene-26-crown-8)] is triclinic, $P\bar{1}$ with a = 7.960(2), b = 9.786(7), c = 11.499(2)Å, α = 72.66(3), β = 79.86(2), γ = 89.00(3)°, and D_{calc} = 1.98 g cm^{-3} for Z = 1. The macrocycle has a more square cavity than observed for the uncomplexed ether. Four sodium cations are coordinated to the macrocycle and participate in a polymeric Na-I network. [$Na_2(OH_2)_4$(3,16-dimethylene-26-crown-8)]I_2 is triclinic, $P\bar{1}$ with a = 10.326(8), b = 11.521(8), c = 14.031(9)Å, α = 82.33(7), β = 86.78(7), γ = 88.72(8)°, and D_{calc} = 1.56 g cm^{-3} for Z = 2. Two different macrocycle conformations are observed, each coordinating a $Na_2(OH_2)_4$ unit. One crown molecule utilizes all of its oxygen donors while the other uses only six of the eight donors. None of the four unique macrocycles in the 3,16-dimethylene-26-crown-8 structures has the same conformation.

INTRODUCTION

Separation scientists have recognized the increased complexing ability of lariat ethers containing side arm donor atoms and a flurry of activity in the preparation and characterization of lariat ethers has resulted.[1,2] While most of these have been N-pivot lariat ethers, C-pivot lariat ethers have appeared which utilize methylene-substituted crown ethers as starting materials.[3-5]

The structural chemistry of methylene-substituted crown ethers and their complexes has been virtually ignored, despite the need to properly orient the C-pivot side arm for maximum participation in coordination of a metal ion.[5] In order to get a better structural handle on methylene-crown ether conformations and possible orga-

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nization of the macrocycles during synthetic procedures we have prepared and structurally characterized the title compounds.

EXPERIMENTAL

Synthesis

Reagent quality chemicals were used as purchased without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from the sodium-benzophenone radical anion under Ar. CH_3CN and CH_3OH were separately distilled from CaH_2 and the 3:1 solution stored over 4Å molecular sieves prior to use. All samples were dried in vacuo prior to combustion analysis.

Methylene-16-crown-5

The synthesis followed the same general procedure as that described in the literature.[6] 17.2 mL (0.1 mol) of tetraethylene glycol and 11.6 mL (0.1 mol) of 3-chloro-2-chloromethyl-1-propene were dissolved in 150 mL of THF under Ar. This solution was added dropwise over a 6 h period to 7.5 g (0.312 mol) of NaH suspended in 150 mL of refluxing THF. The mixture was stirred at reflux temperature for an additional 24 h. The solution was then filtered hot to remove undissolved solids and the solvent rotary evaporated to afford a viscous yellow liquid. Anal. Calcd: C, 58.52; H, 9.00. Found: C, 58.92; H, 9.33.

3,16-Dimethylene-26-crown-8

The synthesis followed the same general procedure as that described in the literature for methylene-13-crown-4.[7] Under an Ar atmosphere 10.9 g (0.454 mol) of NaH was suspended in 500 mL of THF with stirring. The triethylene glycol was dried in vacuo for 48 h at 94°C. A slow additional funnel was charged with 17.4 mL (0.150 mol) of 3-chloro-2-chloromethyl-1-propene and 20 mL (0.150 mol) of triethylene glycol in approximately 400 mL of THF. This solution was added dropwise to the refluxing NaH suspension over a seven day period. The solution was then refluxed for an additional 3 days followed by filtrations on both Büchner funnels and glass frits. The solvent was rotary evaporated to afford a viscous liquid. The liquid was neutralized with 6 M HCl to afford a white solid and a golden brown oil. The mixture was extracted five times with $CHCl_3$ (50 mL) until the washes were clear. The $CHCl_3$ was rotary evaporated to yield a gold brown oil which was subsequently dried in vacuo. The oil was then eluted down a 5 cm i.d. × 46 cm long column packed with basic alumina using 3:1 $C_2H_5O_2CCH_3$:$(C_2H_5)_2O$ as the mobile phase. Anal. Calcd: C, 59.39; H, 8.97. Found: C, 58.48; H, 9.20. The slight discrepancy in the above values can be explained by the presence of trace $C_2H_5O_2CCH_3$ in the sample (confirmed by IR).

$[Na(OH_2)(\text{methylene-16-crown-5})]I$ (1)

0.150 g (1.0 mmol) NaI was combined with 0.246 g (≈ 1 mmol) methylene-16-crown-5 in 5 mL of 3:1 CH_3CN:CH_3OH. The solution was stirred at 60°C for 1 h and allowed to cool to room temperature. The majority of the solvent was then removed in vacuo and the remainder allowed to evaporate slowly to afford crystalline material. Anal. Calcd: C, 34.80; H, 5.84. Found: C, 31.78; H, 5.44.

$[Na(NO_2)(\text{methylene-16-crown-5})]\cdot 0.5(H_2O)$ (2)

0.069 g (1.0 mmol) $NaNO_2$ was combined with 0.246 g (≈ 1 mmol) methylene-16-crown-5 in 5 mL of 3:1 CH_3CN:CH_3OH. The solution was stirred at 60°C for 1 h and allowed to cool to room temperature. The majority of the solvent was removed in vacuo and the remainder allowed to slowly evaporate to produce crystals suitable for the diffraction study. The crystals were highly deliquescent, consequently no combustion analysis was obtained.

3,16-Dimethylene-26-crown-8 (3)

Crystals of this ligand were isolated from the attempted synthesis of a LiCl complex. 0.0430 g (1.0 mmol) LiCl was dissolved in 5 mL of 3:1 CH_3CN:CH_3OH followed by the addition of 184 μL (≈ 0.5 mmol) 3,16-dimethylene-26-crown-8. The solution was stirred at 60°C for 1 h followed by storage at 3°C for 9.5 h and -10°C for 28 h. Approximately 4 mL of solvent was removed in vacuo followed by slow evaporation to afford diffraction quality crystalline material.

$[Na_4I_4(\text{3,16-dimethylene-26-crown-8})]$ (4)

The complex was isolated from a mixture of reaction products. 0.0747 g (0.50 mmol) NaI was added to 306 μL of a mixture of 3,16-dimethylene-26-crown-8 and triethylene glycol in 5 mL of 3:1 CH_3CN:CH_3OH. The mixture was stirred at 60°C for 1 h followed by storage at 3°C for 25 h and -10°C for 24 h. Approximately 75% of the solvent was removed in vacuo followed by further storage at 3°C for 22 h. Slow evaporation yielded crystalline material. Anal. Calcd: C, 23.92; H, 3.61. Found: C, 29.62; H, 5.69. The crystals submitted for analysis were removed from an oily mixture presumed to be the ligand, and this could account for the high values obtained for C and H.

$[Na_2(OH_2)_4(\text{3,16-dimethylene-26-crown-8})]I_2$ (5)

0.1507 g (1.0 mmol) NaI was dissolved in 5 mL of 3:1 CH_3CN:CH_3OH followed by the addition of 184 μL (≈

0.5 mmol) 3,16-dimethylene-26-crown-8. The solution was stirred at 60°C for 1 h followed by storage at 3°C for 9.5 h and -10°C for 28 h. Approximately 4 mL of solvent was removed in vacuo and then slow evaporation afforded crystalline material. Anal. Calcd: C, 30.94; H, 5.71. Found: C, 29.62; H, 5.69.

X-ray data collection, structure determination, and refinement

Single crystals of the title compounds were mounted in thin-walled glass capillaries, flushed with Ar, and transferred to the goniometer. The space groups were uniquely determined from the systematic absences for 1 – 3. The solution and successful refinements of 4 and 5 were carried out in the centric space group P$\bar{1}$. A summary of data collection parameters is given in Table 1. Conditions unique to each crystallographic study are detailed below.

[Na(OH$_2$)(methylene-16-crown-5)]I (1)

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. Methylene and water hydrogen atoms were not included in the final refinement. The final values of the positional parameters are given in Table 2.

[Na(NO$_2$)(methylene-16-crown-5)]•0.5(H$_2$O) (2)

The cations, anions, water molecule, and one complete crown ether molecule were readily located and refined. It then became apparent that the second crown ether was disordered such that there were two possible positions of the methylene group: either between O(9) and O(10) (C(15), C(21b), C(22b), C(24b)) or between O(8) and O(12) (C(21a), C(22a), C(23), C(24a)). The location of the methylene groups in each disordered conformation is also evident from the intramolecular O • • • O contacts. In the ordered crown ether, the O(1) • • • O(5) (methylene substituent bridged) contact is 3.15(2)Å vs. an average 2.73(2)Å for the remaining O • • • O contacts. In the disordered crown ether the two proposed methylene substituent sites have O • • • O contacts between these extremes (O(8) • • • O(12) = 2.90(2)Å, O(9) • • • O(10) = 2.86(2)Å, remaining O • • • O contacts = 2.72(2)Å).

The disorder is also manifested in each of the ethylene units. It was not possible to resolve disorder of the oxygen atoms. O(8)–O(12) actually refined well with only a slight elongation noticeable in the thermal ellipsoid for O(8) and O(10). C(14), C(15), C(17), C(20), and C(21a) could not be resolved into alternate positions and were refined at full occupancy. All other carbon atoms in this crown ether were refined at 50% occupancy in alternate least squares cycles from their disordered counterpart. All of the carbon atoms in this molecule were refined isotropically only. This disorder may be one of the reasons crystals of this complex diffract so poorly. The hydrogen atoms were not included in the final refinement. Final refinement was carried out with anisotropic temperature factors except for the carbon atoms in the disordered crown molecule: C(13)–C(20), C(21a), C(22a), C(23), C(24a), C(13)', C(18)', C(19)', C(23)', C(21b), C(22b), and C(24b). The final values of the positional parameters are given in Table 3.

3,16-Dimethylene-26-crown-8 (3)

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. The methylene hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5Å^2). The final values of the positional parameters are given in Table 4.

[Na$_4$I$_4$(3,16-dimethylene-26-crown-8)] (4)

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. The methylene hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5Å^2). The final values of the positional parameters are given in Table 5.

[Na$_2$(OH$_2$)$_4$(3,16-dimethylene-26-crown-8)]I$_2$ (5)

The small size and poor overall crystal quality led to an observed to measured ratio of only 0.27, severely affecting the overall esd's. The data to parameter ratio is only 4.8 and coupled with the poor crystal quality results in high R factors. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. The methylene and aquo hydrogen atoms were not included in the final refinement. The final values of the positional parameters are given in Table 6.

RESULTS

[Na(OH$_2$)(methylene-16-crown-5)]I (1)

An ORTEP illustration of the cation environment in 1 is illustrated in Fig. 1. The Na$^+$ ion has an irregular 6-coordinate geometry which resembles a pentagonal based pyramid with the water molecule coordinated at the apex (Na-O(6) = 2.311(7)Å). The Na$^+$ ion is not symmetrically placed over the macrocycle, but located closer to the side containing the methylene group. O(3) is farthest

Table 1 Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Cmpd	[Na(OH$_2$)(methylene-16-crown-5)]I (1)	[Na(NO$_3$)(methylene-16-crown-5)]•0.5(H$_2$O) (2)	3,16-dimethylene-26-crown-8 (3)	[Na$_4$I$_4$(3,16-dimethylene-26-crown-8] (4)	[Na$_2$(OH$_2$)$_4$(3,16-dimethylene-26-crown-8)]I$_2$ (5)
Color/Shape	Colorless/parallelepiped	Colorless/parallelepiped	Colorless/parallelepiped	Yellow/parallelepiped	Colorless/parallelepiped
For. wt.	414.21	324.31	404.50	1004.1	776.35
Space group	$P2_12_12_1$	$P2_1/n$	Pccn	$P\bar{1}$	$P\bar{1}$
Temp., °C	18	20	20	22	20
Cell Constants[a]					
a, Å	7.920(9)	20.566(6)	18.061(4)	7.960(2)	10.326(8)
b, Å	10.787(3)	8.605(9)	14.320(4)	9.786(7)	11.521(8)
c, Å	20.870(5)	20.821(7)	8.659(7)	11.499(2)	14.031(9)
α, deg				72.66(3)	82.33(7)
β, deg		115.66(3)		79.86(2)	86.78(7)
γ, deg				89.00(3)	88.72(8)
Cell vol, Å^3	1783	3321	2240	841.1	1651.5
Formula units/unit cell	4	8	4	1	\
D_{calc}, g cm^{-3}	1.54	1.30	1.20	1.98	1.56
μ_{calc}, cm^{-1}	18.6	1.37	0.98	38.4	20.1
Diffractometer/Scan	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ
Range of relative trans. factors, %	94/100			76/100	65/100
Radiation, graphite monochromator	MoKα(λ=0.71073)	MoKα(λ=0.71073)	MoKα(λ=0.71073)	MoKα(λ=0.71073)	MoKα(λ=0.71073)
Max crystal dimensions, mm	0.25 × 0.30 × 0.35	0.20 × 0.40 × 0.40	0.35 × 0.38 × 0.53	0.08 × 0.18 × 0.20	0.05 × 0.30 × 0.30
Scan width	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ
Standard reflections	600;080;0,0,18	800;$\bar{2}\bar{2}$2;008	10,0,2;0,$\bar{6}$,4;12,0,0; 1,$\bar{9}$,0;10,$\bar{2}$,1;5,$\bar{1}$,4	400;050;003	600;020;002
Decay of standards	±2%	±3%	±2%	±3.5%	±2%
Reflections measured	1842	6419	2285	2954	5822
2θ range, deg	2≤2θ≤50	2≤2θ≤50	2≤2θ≤50	2≤2θ≤50	2≤2θ≤50
Range of h, k, l	+9, +12, +24	+24, +10, ±24	+21, -17, +10	+9, ±11, ±13	+12, ±13, ±16
Reflections observed[$F_o \geq 5\sigma(F_o)$][b]	1368	1313	869	1369	1567
Computer programs[c]	SHELX[8]	SHELX	SHELX	SHELX	SHELX
Structure solution	SHELXS[9]	SHELXS	SHELXS	SHELXS	SHELXS
No. of param. varied	181	304	127	163	325
Weights	$[\sigma(F_o)^2 + 0.0009F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0028F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00013F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$
GOF	1.25	1.13	0.50	1.67	0.85
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.034	0.081	0.049	0.051	0.061
R_w	0.048	0.101	0.051	0.055	0.068
R inverse config.	0.040				
Largest feature final diff. map	0.3e$^-$ Å^{-3}	0.4e$^-$ Å^{-3}	0.2e$^-$ Å^{-3}	0.8e$^-$ Å^{-3}	0.8e$^-$ Å^{-3} near I(2)

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections θ > 20° (1), 16° (2), 18° (3), 19° (4), 15° (5).
[b] Corrections: Lorentz-polarization (1 – 5) and absorption (1, 4, 5) (empirical, psi scan).
[c] Neutral scattering factors and anomalous dispersion corrections from ref 10.

Table 2 Final Fractional Coordinates for [Na(OH_2)(methylene-16-crown-5)]I (1)

Atom	*x/a*	*y/b*	*z/c*	*B(eqv)*[a]
I	0.01573(8)	-1.23654(5)	-0.66919(3)	5.76
Na	0.3020(4)	-1.1228(3)	-0.8858(1)	4.25
O(1)	0.5560(8)	-1.2288(5)	-0.8436(2)	5.18
O(2)	0.5399(7)	-0.9913(5)	-0.8923(3)	5.69
O(3)	0.2967(8)	-0.9767(5)	-0.9794(3)	5.05
O(4)	0.0590(7)	-1.1505(5)	-0.9513(2)	4.68
O(5)	0.2124(8)	-1.3396(5)	-0.8858(3)	4.77
O(6)	0.155(1)	-1.0447(7)	-0.7990(3)	6.74
C(1)	0.657(1)	-1.1315(9)	-0.8183(4)	5.81
C(2)	0.693(1)	-1.042(1)	-0.8700(6)	6.98
C(3)	0.556(1)	-0.9043(8)	-0.9431(5)	6.48
C(4)	0.384(1)	-0.8665(8)	-0.9638(5)	6.38
C(5)	0.126(1)	-0.9549(8)	-0.9955(5)	6.10
C(6)	0.046(1)	-1.0758(8)	-1.0088(4)	5.22
C(7)	0.002(1)	-1.2738(7)	-0.9591(4)	5.65
C(8)	0.032(1)	-1.3397(8)	-0.8980(4)	5.67
C(9)	0.252(1)	-1.4140(8)	-0.8303(4)	5.89
C(10)	0.441(1)	-1.4324(9)	-0.8253(4)	5.79
C(11)	0.540(2)	-1.327(1)	-0.7986(4)	7.07
C(12)	0.511(2)	-1.5435(9)	-0.8387(5)	8.91

[a] $B(eqv) = (8\pi^2/3)\,[a^2U_{11}(a^*)^2 + b^2U_{22}(b^*)^2 + c^2U_{33}(c^*)^2 + ab(\cos\gamma)U_{12}a^*b^* + ac(\cos\beta)U_{13}a^*c^* + bc(\cos\alpha)U_{23}b^*c^*]$

from Na at 2.511(6)Å while O(2) (2.364(6)Å) and O(4) (2.380(6)Å) are closest followed by O(5) (2.442(6)Å) and O(1) (2.475(6)Å). The range in Na-O(crown ether) distances, 0.147Å, is quite large (Table 7).

A side view of the cation (Fig. 2) reveals how the sodium cation has adapted to the crown's conformation. All five crown ether oxygen atoms are planar only to 0.29Å with Na^+ 0.58Å out of this mean plane. The four oxygen atoms O(1), O(2), O(4), and O(5), however, are planar to 0.004Å and Na^+ is 0.45Å out of this mean plane.

The conformation of the crown ether as defined by its torsion angles (Table 8) has several features in common with unsubstituted crown ethers. The torsion angles around the C-C bonds alternate ±gauche (±60°), including O(5)-C(9)-C(10)-C(11) (79.1°) and C(9)-C(10)-C(11)-O(1) (-74.5°), although these latter angles are expanded by about 15–20° over the O-C-C-O values. All of the C-O-C-C torsion angles are anti (180°). In the unsubstituted analog, 15-crown-5, a similar conformation is often observed, however, due to the odd number of ethylene linkages two consecutive O-C-C-O torsion angles must be of the same sign and this usually forces one of the C-O-C-C torsion angles between them to a near gauche value.

The coordinated water molecule donates hydrogen bonds to two iodide anions related by -x, 1/2+y, -z-3/2. The two O(6) • • • I contacts and I • • • O(6) • • • I^a angle are 3.585(7)Å, 3.650(7)Å, and 123.3(2)°, respectively.

Table 3 Final Fractional Coordinates for [Na(NO_2)(methylene-16-crown-5)]· 0.5(H_2O) (2)

Atom	*x/a*	*y/b*	*z/c*	*B(eqv)*
Na(1)	0.7065(3)	-0.4077(6)	1.0985(3)	4.65
Na(2)	0.6143(3)	0.0762(7)	0.6911(3)	4.75
O(1)	0.5970(5)	-0.323(1)	1.1136(5)	4.81
O(2)	0.6730(6)	-0.587(1)	1.1703(5)	5.65
O(3)	0.8123(7)	-0.531(2)	1.1988(6)	8.30
O(4)	0.8206(6)	-0.306(2)	1.1083(6)	8.60
O(5)	0.7036(7)	-0.118(1)	1.0772(6)	6.69
O(6)	0.6392(8)	-0.432(2)	0.9717(7)	8.90
O(7)	0.6995(9)	-0.628(2)	1.0216(8)	10.70
O(8)	0.5185(5)	0.260(1)	0.6838(6)	6.66
O(9)	0.6363(5)	0.190(1)	0.8083(5)	5.38
O(10)	0.7431(6)	0.039(1)	0.7772(6)	7.89
O(11)	0.6972(6)	0.073(1)	0.6353(6)	7.62
O(12)	0.5669(6)	0.216(1)	0.5732(5)	6.97
O(13)	0.5761(7)	-0.163(1)	0.7330(7)	7.84
O(14)	0.562(1)	-0.171(2)	0.6323(8)	13.11
O(15)	0.5455(7)	-0.274(2)	0.8450(7)	11.75
N(1)	0.654(1)	-0.562(3)	0.965(1)	10.75
N(2)	0.5566(9)	-0.239(2)	0.679(1)	8.27
C(1)	0.5607(9)	-0.467(2)	1.113(1)	6.75
C(2)	0.608(1)	-0.549(2)	1.1796(9)	6.61
C(3)	0.729(1)	-0.652(2)	1.2325(9)	8.83
C(4)	0.792(1)	-0.679(3)	1.212(1)	9.85
C(5)	0.870(1)	-0.539(4)	1.176(1)	12.20
C(6)	0.883(1)	-0.370(4)	1.162(1)	10.63
C(7)	0.826(1)	-0.137(3)	1.098(1)	10.11
C(8)	0.750(1)	-0.092(3)	1.0448(9)	9.14
C(9)	0.633(1)	-0.046(2)	1.033(1)	7.31
C(10)	0.584(1)	-0.067(3)	1.0708(8)	7.23
C(11)	0.548(1)	-0.220(2)	1.0603(9)	6.31
C(12)	0.574(1)	0.056(2)	1.106(1)	10.51
C(13)	0.533(1)	0.312(3)	0.763(1)	3.5(6)[a]
C(14)	0.5638(9)	0.215(2)	0.8074(9)	7.0(5)
C(15)	0.676(1)	0.090(2)	0.868(1)	7.2(5)
C(16)	0.763(2)	0.076(5)	0.857(2)	6(1)
C(17)	0.790(1)	-0.001(2)	0.748(1)	6.9(5)
C(18)	0.770(2)	0.069(5)	0.668(2)	5.2(8)
C(19)	0.664(2)	0.066(4)	0.567(2)	2.9(7)
C(20)	0.600(1)	0.166(2)	0.5316(9)	6.8(4)
C(21a)	0.503(1)	0.297(2)	0.548(1)	8.4(5)
C(22a)	0.455(2)	0.308(4)	0.573(2)	4.2(7)
C(23)	0.466(2)	0.365(4)	0.644(2)	4.5(7)
C(24a)	0.386(2)	0.258(4)	0.520(2)	5.9(8)
C(13)'	0.524(2)	0.358(4)	0.734(2)	6.5(9)
C(18)'	0.758(2)	-0.027(5)	0.681(2)	6.2(9)
C(19)'	0.670(2)	0.150(6)	0.553(2)	8(1)
C(23)'	0.489(2)	0.362(4)	0.613(2)	5.9(9)
C(21b)	0.768(2)	-0.007(5)	0.842(2)	7(1)
C(22b)	0.735(2)	0.095(3)	0.879(1)	3.2(6)
C(24b)	0.792(2)	0.161(4)	0.945(2)	6.2(8)

[a]The carbon atoms of the disordered crown ether were refined isotropically only.

The hydrogen bonding forms zigzag polymeric chains which propagate along the b unit cell direction.

[Na(NO_2)(methylene-16-crown-5)]•0.5(H_2O) (2)

An ORTEP illustration of the asymmetric unit in 2 is illustrated in Fig. 3. 2 crystallizes as tight ion pairs with

Table 4 Final Fractional Coordinates for 3,16-dimethylene-26-crown-8 (3)

Atom	*x/a*	*y/b*	*z/c*	*B(eqv)*
O(1)	0.3817(1)	0.0846(2)	0.2392(3)	4.01
O(2)	0.3503(2)	-0.0445(2)	0.5825(3)	4.06
O(3)	0.3726(1)	-0.1425(2)	0.8654(3)	4.07
O(4)	0.4694(2)	-0.1597(2)	1.1138(3)	3.85
C(1)	0.3983(3)	0.0148(3)	0.3489(5)	4.49
C(2)	0.3500(2)	0.0351(3)	0.4876(5)	3.92
C(3)	0.3056(2)	-0.0327(3)	0.7150(5)	3.83
C(4)	0.3024(2)	-0.1212(3)	0.8051(5)	4.03
C(5)	0.3702(2)	-0.2201(3)	0.9679(5)	4.23
C(6)	0.4469(2)	-0.2384(3)	1.0257(5)	3.93
C(7)	0.5464(2)	-0.1587(3)	1.1488(5)	4.48
C(8)	0.5959(2)	-0.1510(3)	1.0090(5)	3.25
C(9)	0.5729(2)	-0.0778(3)	0.8947(5)	3.82
C(10)	0.6553(2)	-0.2028(3)	0.9955(5)	4.38

two crown complexed Na(NO_2) moieties bridged via a hydrogen bonded water molecule (O(15) $\bullet\bullet\bullet$ O(6) = 2.85(2)Å; O(15) $\bullet\bullet\bullet$ O(13) = 2.83(2)Å; O(6) $\bullet\bullet\bullet$ O(15) $\bullet\bullet\bullet$ O(13) = 128.4(7)°). Unfortunately the second crown molecule (O(8)-O(12)) is disordered such that the methylene substituent appears to reside either between O(8) and O(12) or between O(9) and O(10). As a result of this static disorder, all of the ethylene bridges are also disordered. Thus the esd's for the entire structure are high and details about the positioning of Na(2) within the crown cavity are obscured.

The crown ether conformation for the O(1)-O(5) ether is identical to that in 1 (Table 8). The conformation of the second crown molecule may be the same, but it is obscured by the disorder. It is, however, possible to tell that all of the C-O-C-C torsion angles are anti.

Each sodium cation in 2 is 7-coordinate with a geometry somewhere between a capped trigonal prism and a capped octahedron. Because of the higher coordination

Table 5 Final Fractional Coordinates for [Na_4I_4 (3,16-dimethylene-26-crown-8)] (4)

Atom	*x/a*	*y/b*	*z/c*	*B(eqv)*
Na(1)	0.4956(9)	0.4061(8)	0.7049(6)	3.83
Na(2)	0.0329(8)	0.3053(7)	0.6459(6)	3.79
I(1)	0.7303(2)	0.1954(2)	0.8591(1)	4.23
I(2)	0.2365(2)	0.6021(1)	0.5383(1)	3.26
O(1)	0.232(1)	0.140(1)	0.586(1)	3.28
O(2)	0.236(1)	0.231(1)	0.801(1)	3.72
O(3)	0.331(1)	0.458(1)	0.880(1)	3.30
O(4)	0.594(1)	0.626(1)	0.7208(9)	3.27
C(1)	0.329(2)	0.073(2)	0.675(2)	4.35
C(2)	0.254(2)	0.083(2)	0.803(2)	3.92
C(3)	0.186(2)	0.236(2)	0.924(1)	3.64
C(4)	0.165(2)	0.392(2)	0.917(2)	4.31
C(5)	0.336(2)	0.611(2)	0.866(2)	4.34
C(6)	0.520(2)	0.661(2)	0.830(2)	4.45
C(7)	0.770(2)	0.666(2)	0.682(1)	3.46
C(8)	0.800(2)	0.824(2)	0.627(2)	4.49
C(9)	0.705(2)	0.897(2)	0.526(2)	4.56
C(10)	0.896(3)	0.897(2)	0.672(2)	6.54

Table 6 Final Fractional Coordinates for [$Na_2(OH_2)_4$(3,16-dimethylene-26-crown-8)]I_2 (5)

Atom	*x/a*	*y/b*	*z/c*	*B(eqv)*
Na(1)	0.3652(9)	0.4482(7)	0.9094(7)	5.86
Na(2)	0.9269(9)	0.9353(7)	0.3948(7)	5.42
I(1)	0.2287(2)	0.8459(2)	0.9329(1)	6.65
I(2)	0.7309(2)	0.3045(2)	0.4387(1)	6.52
O(1)	0.588(2)	0.498(2)	0.804(1)	5.95
O(2)	0.428(2)	0.319(2)	0.778(1)	6.29
O(3)	0.249(2)	0.263(1)	0.926(1)	5.68
O(4)	0.174(2)	0.433(1)	1.037(1)	5.79
O(5)	0.245(2)	0.585(1)	0.814(1)	7.09
O(6)	0.556(2)	0.381(2)	1.000(1)	8.48
C(1)	0.586(3)	0.459(3)	0.718(2)	6.51
C(2)	0.555(2)	0.324(2)	0.738(2)	7.94
C(3)	0.400(3)	0.199(3)	0.814(2)	8.77
C(4)	0.258(3)	0.196(2)	0.848(2)	7.13
C(5)	0.113(3)	0.278(2)	0.955(2)	7.53
C(6)	0.106(3)	0.324(2)	1.047(2)	7.40
C(7)	0.152(2)	0.485(2)	1.124(2)	6.16
C(8)	0.192(3)	0.412(2)	1.217(2)	5.90
C(9)	0.337(3)	0.391(2)	1.207(2)	5.74
C(10)	0.116(3)	0.375(2)	1.292(2)	8.36
O(7)	1.101(1)	0.949(1)	0.276(1)	4.74
O(8)	0.961(2)	0.750(1)	0.337(1)	5.51
O(9)	0.770(2)	0.768(1)	0.476(1)	5.68
O(10)	0.686(2)	0.877(1)	0.639(1)	5.96
O(11)	0.761(2)	1.044(1)	0.319(1)	6.73
O(12)	0.986(2)	0.882(1)	0.561(1)	6.48
C(11)	1.113(2)	0.853(2)	0.230(2)	5.38
C(12)	1.089(2)	0.741(2)	0.296(2)	5.80
C(13)	0.924(3)	0.649(2)	0.407(2)	6.43
C(14)	0.786(2)	0.664(2)	0.434(2)	6.21
C(15)	0.637(3)	0.792(3)	0.501(2)	7.61
C(16)	0.621(2)	0.898(2)	0.554(2)	6.47
C(17)	0.646(3)	0.963(2)	0.699(2)	7.01
C(18)	0.708(3)	0.946(2)	0.789(2)	5.65
C(19)	0.856(3)	0.945(2)	0.784(2)	5.65
C(20)	0.640(3)	0.932(2)	0.875(2)	7.46

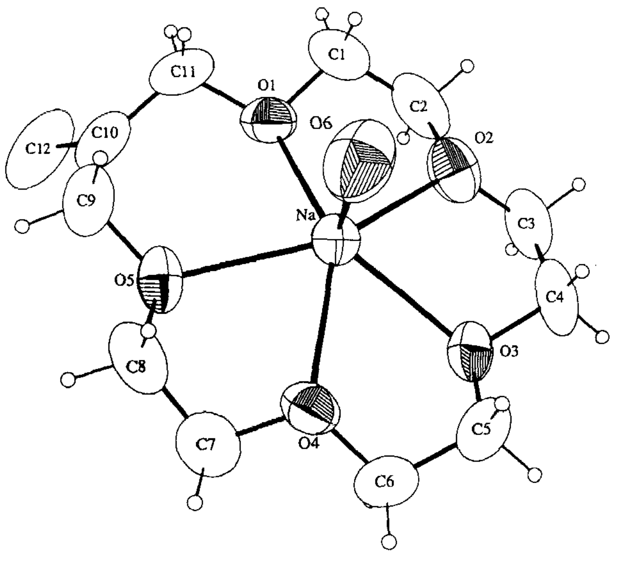

Figure 1 The cation environment in [Na(OH_2)(methylene-16-crown-5)]I (1). The nonhydrogen atoms are represented by their 50% probability ellipsoids. Hydrogen atom radii have been arbitrarily reduced. The two hydrogen atoms on C(12) were not located.

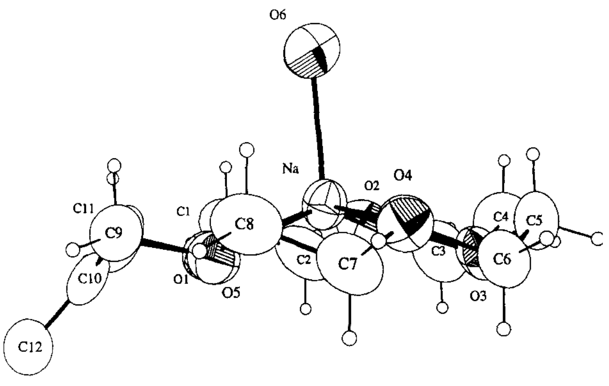

Figure 2 Side view of the cation in 1.

number than in 1, the Na-O(crown ether) distances are somewhat longer: 2.43(2)-2.53(1)Å range, 2.48(3)Å average. In the ordered molecule the Na(1)-O(2) (2.45(1)Å) and Na(1)-O(4) (2.43(2)Å) distances are the shortest (as observed in 1). The remaining three Na-O(crown ether) separations are nearly identical, however (2.51(1), 2.51(1), 2.53(1)Å). The bidentate nitrite anions are coordinated to Na(1) and Na(2) at an average Na-O distance of 2.45(3)Å.

3,16-Dimethylene-26-crown-8 (3)

The rather elliptical cavity of uncomplexed 3 is depicted in Fig. 4. The macrocycle resides around a crystallographic center of inversion. Six of the eight oxygen atoms (O(1), O(2), O(3), O(1)^a, O(2)^a, O(3)^a) are planar to within 0.02Å, while O(4) is 0.80Å out of this mean plane. This plane and the plane of the methylene substituents meet at a dihedral angle of 37°. The elongation of the macrocycle's cavity is a manifestation of the conformation which has a series of six anti torsion angles in a row (Table 8: C(7)^a-C(8)^a-C(9)^a-O(1) through C(2)-O(2)-C(3)-C(4)). A true corner exists with two consecutive gauche angles of the same sign (C(6)-O(4)-C(7)-C(8) and O(4)-C(7)-C(8)-C(9)).

The bond distances and angles for 3 are given in Table 9. The average C-C and C-O distances, involving the ethylene linkages are 1.500(9) and 1.412(7)Å, respectively. The C-O-C angles average 112.5(7)°. The O(4)-C(7)-C(8) (114.1(3)°) and C(7)-C(8)-C(9) (114.6(4)°) angles are the largest interior angles at any carbon position. The remaining O-C-C angles average 108(1)°.

[Na_4I_4(3,16-dimethylene-26-crown-8)] (4)

Coordination of Na^+ to 3,16-dimethylene-26-crown-8 in 4 produces a much more square conformation (Fig. 5) of the macrocycle compared to 3. The macrocycle resides around a crystallographic center of inversion and is coordinated to four sodium cations. Two oxygen atoms (O(2) and O(2)^a) bridge two different cations. Each Na^+ coordination sphere is completed with coordination to bridging iodides (Fig. 6) which produces polymeric chains which propagate along unit cell direction a.

Na(1) is 6-coordinate, roughly octahedral, with coordination to O(2) (a μ_2 interaction), O(3), O(4), I(1) (μ_2), I(2) (μ_4), and I(2)^a (μ_4). The terminal Na(1)-O distances are shorter averaging 2.38(1)Å, than the bridging interaction (Na(1)-O(2) = 2.57(1)Å). Similarly the Na(1)-I(1) (μ_2) separation of 3.121(7)Å is shorter than the average Na(1)-I(2) (μ_4) distance of 3.25(2)Å.

Na(2) is only 5-coordinate and has two contacts with the macrocycle (Na(2)-O(1) = 2.40(1)Å; Na(2)-O(2) (μ_2) = 2.55(1)Å). The remaining coordination sites are filled by I(1) (μ_2, 3.067(6)Å) and two I(2) contacts (μ_4, 3.18(3)Å, average). The coordination geometry around Na(2) is trigonal bipyramidal (I(2)^a-Na(2)-O(2) = 177.3(3)°). I(2) has a see-saw coordination geometry.

As we have already noted, the coordination of 3,16-dimethylene-26-crown-8 has dramatically altered its conformation. The series of six anti torsion angles found for the uncomplexed crown ether is gone. Instead all of the torsion angles about C-C bonds are gauche and all but one of the remaining torsion angles are anti. The C(6)-O(4)-C(7)-C(8) torsion angle is -72.8° and starts a series of three–gauche angles in a row.

In our studies of unfunctionalized crown ethers such as 18-crown-6 or 15-crown-5, we generally find at least one of the C-O-C-C angles between O-C-C-O torsion angles of like sign (either both +g or both -g) forced away from anti toward gauche. In 4, the O(1)-C(1)-C(2)-O(2) and O(2)-C(3)-C(4)-O(3) torsion angles are both -g, yet both C(1)-C(2)-O(2)-C(3) and C(2)-O(2)-C(3)-C(4) are anti. This is most likely due to the additional coordination of O(2) to two metal centers and again demonstrates the flexibility of crown ethers.

[$Na_2(OH_2)_4$(3,16-dimethylene-26-crown-8)]I_2 (5)

5 crystallizes with two half molecules of the formula unit in the asymmetric unit, each residing around a crystallographic center of inversion. The major difference in the two molecules is a small conformational difference around O(10) which moves O(10) out of the Na(2) coordination sphere (Fig. 7).

Each macrocycle coordinates two sodium cations, but only six of eight oxygen donors are utilized in one of the macrocycles (O(7)-O(10)). Na(1) is 7-coordinate and nearly capped octahedral. The two Na(1) cations within the macrocycle are asymmetrically bridged by two water molecules (Na(1)-O(6) = 2.46(2)Å, Na(1)-O(6)^a = 2.65(2)Å) and there is one terminally coordinated water molecule (Na(1)-O(5) = 2.31(2)Å). The coordination sphere is completed with the four crown ether oxygen donors between methylene substituents.

Table 7 Comparison of Bonding Parameters

Compound	*CN*	*IR*[a]	*Na-O(crown ether), Å*			*Na-OH$_2$, Å*	*Na-O$_2$N, Å*	*Na-I, Å*	*Ref.*
			Avg.	*Range*	*Δ*	*Avg.*	*Avg.*	*Avg.*	
[Na(OH$_2$)(methylene-16-crown-5)]I	6	1.02	2.43(6)	2.364(6) - 2.511(6)	0.147	2.311(7)			This study
[Na(NO$_2$)(methylene-16-crown-5)]•0.5(H$_2$O)	7	1.12	2.48(3)	2.43(2) - 2.53(1)	0.10		2.45(3)		This study
[Na$_4$I$_4$(3,16-dimethylene-26-crown-8)]	6	1.02	2.38(1) 2.57(1) (μ_2)	2.37(1) - 2.38(1)	0.01			3.121(7) (μ_2) 3.25(2) (μ_4)	
	5	1.00	2.40(1) 2.55(1) (μ_2)					3.067(6) (μ_2) 3.18(3) (μ_4)	This study
[Na$_2$(OH$_2$)$_4$(3,16-dimethylene-26-crown-8)]I$_2$	7	1.12	2.58(9)	2.45(2) - 2.69(2)	0.24	2.31(2) 2.46(2), 2.65(2) (μ_2)			
	6	1.02	2.5(1)	2.38(2) - 2.65(2)	0.27	2.32(2) 2.44(2), 2.47(2) (μ_2)			This study
[Na(NCS)(15,15-bis(dodecyloxy-methyl)16-crown-5)]	6	1.02	2.44(6)	2.356 - 2.538	0.182				11
[Na(C$_{14}$H$_{24}$O$_8$)][B(C$_6$H$_5$)$_4$][b]	6	1.02	2.45(3)	2.407(4) - 2.495(4)	0.088				13
[Na(ClO$_4$)(15-crown-5)]	7	1.12	2.415(7)	2.406(3) - 2.423(3)	0.017				14
[Na(NO$_3$)(15-crown-5)]	7	1.12	2.45(3)	2.415(4) - 2.477(4)	0.062				15

[a] Effective ionic radius for Na$^+$ and coordination number indicated from reference 16.

[b] C$_{14}$H$_{24}$O$_8$ is a 16-crown-5 macrocycle with an integrated 1,6-anhydro sugar.

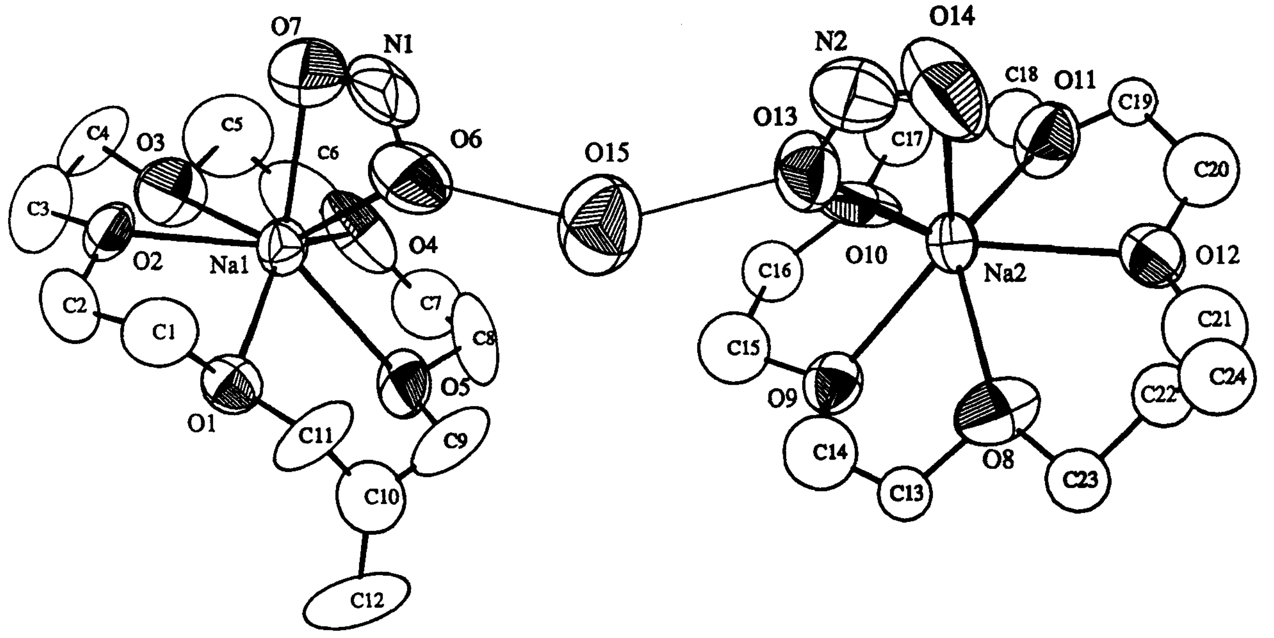

Figure 3 The asymmetric unit in [Na(NO$_2$)(methylene-16-crown-5)]•0.5(H$_2$O) (2). Only one conformation of the disordered crown molecule (O(8)–O(12)) is depicted.

The Na(2) cation is only 6-coordinate and is nearer to trigonal prismatic than octahedral. The two Na(2) cations within the second macrocycle are also bridged by two water molecules, however, the bridging interactions are symmetrical (Na(2)-O(12) = 2.44(2)Å, Na(2)-O(12)^a = 2.47(2)Å). There is again a terminal water interaction, but only three of the four crown donors between the methylene substituents coordinate Na(2). O(10) is 4.11(2)Å from Na(2), well outside the primary coordination sphere.

The conformational differences resulting in the different structures are actually limited to only two torsion angles. O(9)-C(15)-C(16)-O(10) is -gauche vs. O(3)-C(5)-C(6)-O(4) (+g) and C(16)-O(10)-C(17)-C(18) is anti vs. C(6)-O(4)-C(7)-C(8) (+g). Neither conformation is the same as observed in 4.

The water molecules participate in a polymeric network of hydrogen bonds with the iodide anions. The O • • • I contacts range from 3.46(2) to 3.63(2)Å.

DISCUSSION

In the two title complexes containing methylene-16-crown-5 (1 and 2) an identical conformation of the crown ether was observed. This same conformation was observed for the derivatized 16-crown-5 molecule in [Na(NCS)(15,15-bis(dodecyloxymethyl)16-crown-5)].[11] Each of these structures exhibit similar crown coordination of Na$^+$: five oxygen donors roughly forming the base of a pentagonal pyramid and one apical solvent or anion coordination site (assuming the bidendate nitrite occupies a single coordination site in 2).

The larger, more flexible, 3,16-dimethylene-26-crown-8 macrocycle does not seem to have a preferred conformation when coordinated to Na$^+$. Not only were different conformations observed in 4 and 5, two different conformations were observed in 5 itself, where both crown ethers complexed [Na$_2$(OH$_2$)$_4$]$^{2+}$. It is interesting to note that in both 4 and 5, two metal ions are coordinated to the ether despite the fact that it should be flexible enough to wrap around a single cation as observed in the asymmetric dibenzo-24-crown-8 complex, [Na(dibenzo-24-crown-8)] [ClO$_4$].[12]

An interesting facet of each Na$^+$ complex involves coordination of the Na$^+$ ion to the oxygen bridged by the

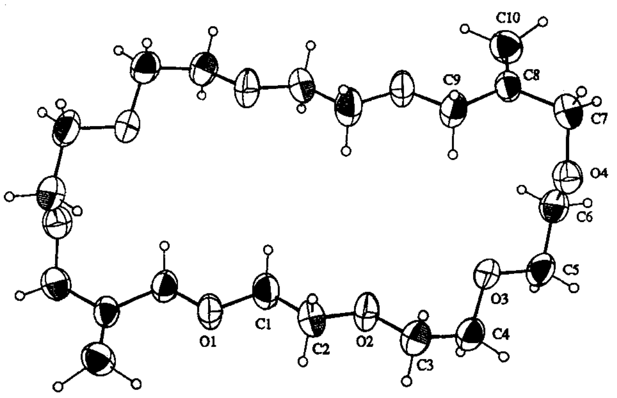

Figure 4 3,16-dimethylene-26-crown-8 (3).

Table 8 Torsion Angles (degrees)

	Compound					
Atoms	1	2	3	4	5	
O(1)-C(1)-C(2)-O(2)	61.6	-66.2	165.2	-57.7	66.5	(59.1)[a]
C(1)-C(2)-O(2)-C(3)	-179.2	-173.3	-179.2	-173.0	-169.9	(-176.8)
C(2)-O(2)-C(3)-C(4)	176.1	-178.3	175.2	-179.2	-174.7	(-173.2)
O(2)-C(3)-C(4)-O(3)	-55.4	62.9	66.0	-68.9	-64.6	(-61.1)
C(3)-C(4)-O(3)-C(5)	175.6	-177.1	172.7	178.8	172.6	(177.8)
C(4)-O(3)-C(5)-C(6)	-178.3	178.9	179.6	178.1	167.7	(174.6)
O(3)-C(5)-C(6)-O(4)	60.3	-61.2	64.4	56.0	58.4	(-61.2)
C(5)-C(6)-O(4)-C(7)	-174.4	173.7	-167.5	-178.2	172.6	(-166.5)
C(6)-O(4)-C(7)-C(8)	176.7	-172.7	63.8	-72.8	57.5	(179.2)
O(4)-C(7)-C(8)-O(5)	-61.7	63.0				
C(7)-C(8)-O(5)-C(9)	-173.9	168.3				
C(8)-O(5)-C(9)-C(10)	169.6	-177.1				
O(5)-C(9)-C(10)-C(11)	79.1	-81.4				
C(9)-C(10)-C(11)-O(1)	-74.5	85.9				
C(10)-C(11)-O(1)-C(1)	-177.7	171.3				
C(11)-O(1)-C(1)-C(2)	170.6	-166.7				
O(4)-C(7)-C(8)-C(9)			46.3	-52.4	61.7	(57.9)
C(7)-C(8)-C(9)-O(1)[b]			-173.3	-70.1	63.5	(52.9)
C(8)-C(9)-O(1)[b]-C(1)[b]			-177.4	177.9	74.6	(76.9)
C(9)-O(1)[b]-C(1)[b]-C(2)[b]			-176.1	169.7	-158.8	(-171.1)

[a] The values in parens are for the O(7)-O(10), C(11)-C(20) crown molecule in 5.
[b] Symmetry code 1-x, -y, 1-z.

methylene substituted propyl linkage. In the smaller crown ether in 1 and 2, each Na^+ is coordinated to all five oxygen atoms of the crown ether. The O • • • O contacts are similar in both structures. The O • • • O separation involving the substituent is 3.15(2)Å in 1 (for the ordered crown ether) and 3.099(8)Å in 2. The remaining O • • • O contacts are a much shorter 2.73(2)Å (1) and 2.72(4)Å (2) on average.

In the larger dimethylene-26-crown-8 complexes 4 and 5, no single Na^+ ion coordinates to two oxygens bridged by a methylene substituted propyl linkage. The resulting O • • • O contacts involving these propyl bridged atoms are thus a much longer 3.58(2)Å, 3.38(2)Å (4), and 3.63(1)Å (5). The ethyl bridged O • • • O contacts in these complexes are nearly the same as observed in 1 and 2 (2.74(1)Å, 2.77(5)Å (4), and 2.80(6)Å (5)).

Table 7 provides a comparison of the Na-O(methylene-16-crown-5) separations with those observed in two similar 15-crown-5 adducts. The average Na-O separa-

Table 9 Bond Distances (Å) and Angles (deg) for 3,16-dimethylene-26-crown-8 (3)

Atoms	*Distance*	*Atoms*	*Distance*
O(1) – C(1)	1.411(5)	O(1) – C(9)[a]	1.423(5)
O(2) – C(2)	1.405(4)	O(2) – C(3)	1.413(4)
O(3) – C(4)	1.403(4)	O(3) – C(5)	1.422(5)
O(4) – C(6)	1.420(5)	O(4) – C(7)	1.424(5)
C(1) – C(2)	1.512(5)	C(3) – C(4)	1.489(5)
C(5) – C(6)	1.498(5)	C(7) – C(8)	1.510(5)
C(8) – C(9)	1.501(5)	C(8) – C(10)	1.309(5)

Atoms	*Angle*	*Atoms*	*Angle*
C(1) – O(1) – C(9)[a]	112.2(3)	C(2) – O(2) – C(3)	112.1(3)
C(4) – O(3) – C(5)	112.0(3)	C(6) – O(4) – C(7)	113.7(3)
O(1) – C(1) – C(2)	106.1(3)	O(2) – C(2) – C(1)	107.9(3)
O(2) – C(3) – C(4)	110.2(3)	O(3) – C(4) – C(3)	110.2(3)
O(3) – C(5) – C(6)	108.5(3)	O(4) – C(6) – C(5)	107.7(4)
O(4) – C(7) – C(8)	114.1(3)	C(7) – C(8) – C(9)	114.6(4)
C(7) – C(8) – C(10)	121.1(4)	C(9) – C(8) – C(10)	124.3(4)
O(1)[a] - C(9) - C(8)	109.3(3)		

[a] Symmetry code: 1-x, -y, 1-z

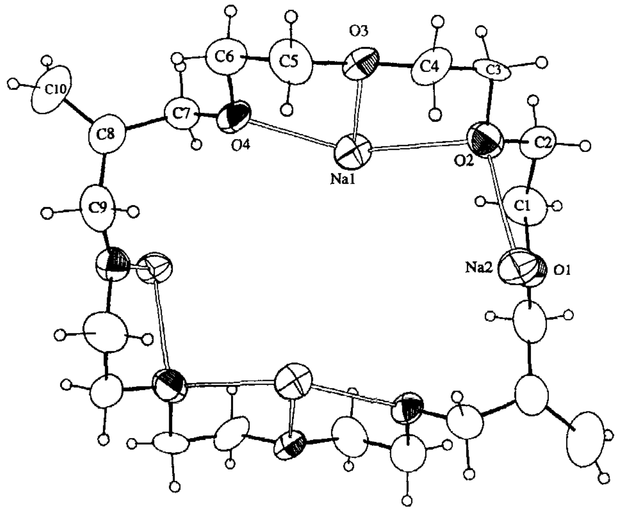

Figure 5 The macrocycle environment in $[Na_4I_4(3,16\text{-dimethylene-}26\text{-crown-}8)]$ (4).

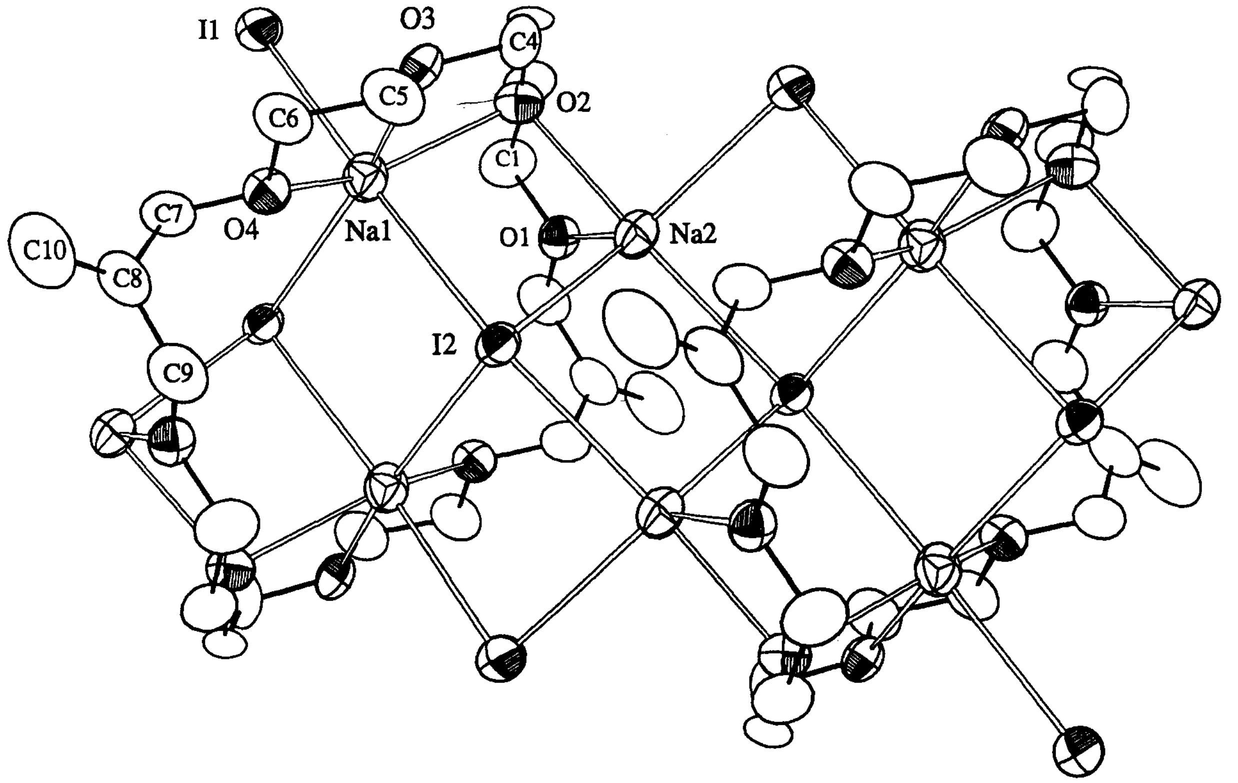

Figure 6 The polymeric nature of 4.

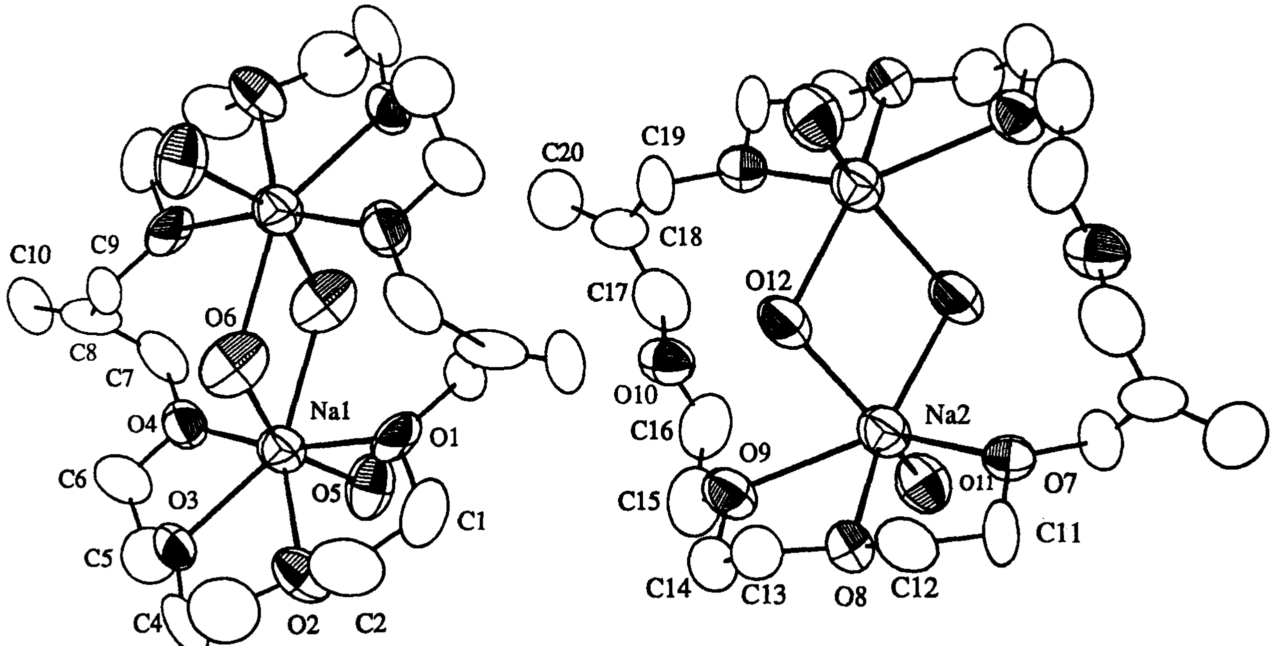

Figure 7 The two unique crown ethers in $[Na_2(OH_2)_4(3,16\text{-dimethylene-26-crown-8})]I_2$ (5).

tions are all similar (including those in the 3,16-dimethylene-26-crown-8 structures) and fall within 3σ of being equal. The differences in the ranges of Na-O distances are noteworthy, however. The sodium cations are more symmetrical with respect to 15-crown-5 and the ranges in Na-O separations are small. Much larger ranges are observed for 1, 2, 4, 5, and [Na(NCS)(15,15-bis(dodecyloxymethyl)16-crown-5)]. This too, may be a result of the optimization of Na • • • O contacts involving five vs. six-membered chelate rings.

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