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SYN-BISHYDROXYMETHYL-14-CROWN-4: A POSSIBLE PRE-ORGANIZED MOLECULE FOR SIMULTANEOUS LITHIUM COMPLEXATION AND ANION SOLVATION

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ABSTRACT

The synthesis and molecular structure of syn-6,13-bishydroxymethyl-14-crown-4 is reported. Conformational analysis reveals that the gauche arrangement between the ethereal oxygens (-O-CH_2CH_2-O- units) is the preferred conformation. The CH_2OH groups bonded to the ring, point away from the cavity and have a syn relationship. The synthetic route is elucidated by the crystal structure of 6,13-dimethylenyl-14-crown-4-LiSCN complex.

INTRODUCTION

From a large family of macrocyclic compounds,[1-5] macrocyclic diamides,[5-7] and linear related compounds,[5,8-12] 14-crown-4 derivatives have shown remarkable selectivity for lithium over sodium, potassium, calcium and magnesium ions.[1-3] For practical applications such as ion extraction and ion selective electrodes, it might be expected that the derivatives of 14-crown-4 would be favorable complexing agents for Li^+ because they are more stable than other ligands such as amides and organophosphates in acidic or basic conditions. The crown ethers 14-crown-4[1-3] and dibenzo-14-crown-4[4] exhibit the highest selectivity towards Li^+ among all the crown ethers which have been tested until now. The most favorable co-ordination geometry for Li^+-crown complexes is that of the square-pyramid[5] (see Figure 1). The macrocyclic ring provides the basis of a square pyramid, while the apical site is occupied by the anion[5,13-19] or solvent molecule.[5,19,20]

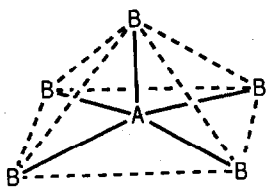

Figure 1. Square-pyramid

Recently, it was reported that hydroxy crown-ethers are bifunctional ligands for simultaneous cation complexation and anion solvation.[21] This research was focused on the hydroxy derivatives of dibenzo-14-crown-4.[22] No work has been conducted on similar derivatives of 14-crown-4. The ethereal oxygens of 14-crown-4 (aliphatic ether groups) are more basic than those of dibenzo-14-crown-4 (aromatic ether

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groups) because of the election withdrawing effect of the benzo groups.[23] With respect to the basicity of the ethereal oxygens, it might be expected that Li^+ will interact stronger with the former crown molecule.

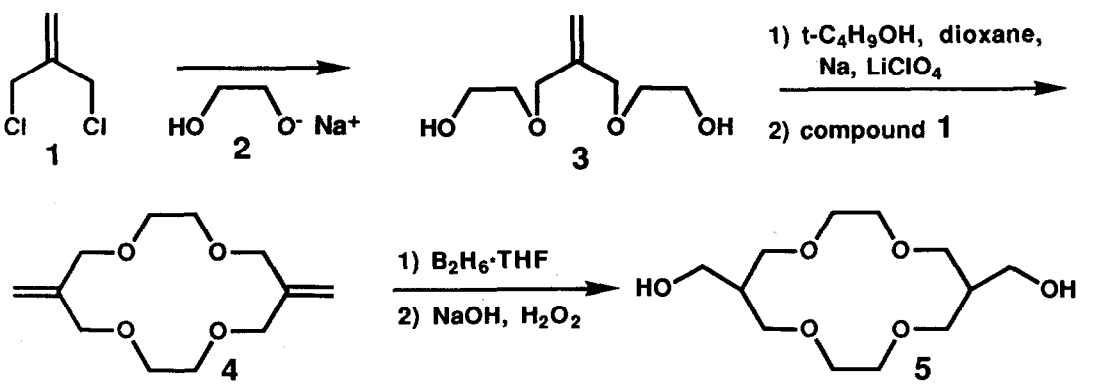
We now report the synthesis and molecular structure of syn-6,13-bishydroxymethyl-14-crown-4 (compound 5, Scheme I). This type of compound presents a potential bifunctional ligand for simultaneous Li^+ complexation by the ethereal oxygens and anion solvation via hydrogen bonds to the hydroxy groups.[24-28] The preparation and crystal structure of the LiSCN complex of 6,13-dimethylenyl-1,4,8,11-tetraoxacyclotetradecane (4), the intermediate for the synthesis of 5, is also reported.

RESULTS AND DISCUSSION

Syn-6,13-bishydroxymethyl-14-crown-4 (5) was prepared as shown in Scheme I. Intermediate glycol 3 was prepared by first reacting sodium metal in an excess of ethylene glycol (2) and then slowly adding technical quality 3-chloro-2-chloromethylpropene (1) at 50°-60°C. The yield of 3 was 65-68%. Glycol 3 was reacted first with sodium metal or sodium *tert*-butoxide in a *tert*-butyl alcohol-dioxane mixture followed by addition of 1 to form 4.[29] The yield of macrocycle 4 was increased from 10% to 30% by the addition of lithium perchlorate since the product 14-crown-4 complexes best with lithium ions.[1-4] Lithium metal or lithium hydride, when used as the base, gave poor yields of the macrocycle, possibly because lithium alkoxides are not basic enough to deprotonate glycol 3. Good yields of macrocycle 4 were also obtained in other solvents such as THF. The macrocycle was purified by distillation or by alumina chromatography using isopropyl ether as eluant.

Dimethylenyl-substituted crown 4 was converted to diol 5 using diborane in THF followed by hydrogen peroxide. The hydroboration reaction is very selective resulting almost exclusively in the primary alcohol.[30] In our case, only a small amount of the tertiary

Scheme I. Preparation of Bishydroxymethyl-14-Crown-4



alcohol was observed by its methyl peak in the ^{1}H NMR spectrum. Recrystallization of this product from ethyl acetate did not completely remove the isomeric diol. Large reducing agents such as bis(3-methyl-2-butyl)borane (BMB) or 9-borohydro[3.3.1]nonane (9-BBN) could be used to produce a higher percent of the bisprimary alcohol. Our hydroboration reaction also gave macrocyclic diol **5** in the syn-form as shown in the X-ray structural analysis.

The structures of the lithium thiocyanate complex of **4** and uncomplexed **5** were determined by crystal structure analyses. Figure 2 is a computer drawing of the two molecules in the asymmetric unit of **4**. The atomic labels of molecule B are primed. A view of **5** perpendicular to the plane of its ring is shown in Figure 3 while a view of the same molecule approximately parallel to the plane of the ring is shown in Figure 4. Bond lengths and angles of **4** and **5** are contained in Tables I and II, respectively. The two molecules of **4** are similar extending even to the disorder of an oxygen in both molecules. The lattice parameters and the spacial relationship of the molecules in the unit cell indicate that the space group is close to $P2_1/n$. However some atoms, particularly in the disordered portion of the molecules along with the systematic absences and equivalent data clearly establish that the symmetry of this crystal is that of the triclinic space group $P\bar{1}$. In both molecules the coordination geometry about Li^+ is square pyramidal with the four ethereal oxygens of each molecule forming the base of the pyramid.

The lithium thiocyanate complex of **4** (Figure 2) elucidates, at least qualitatively,

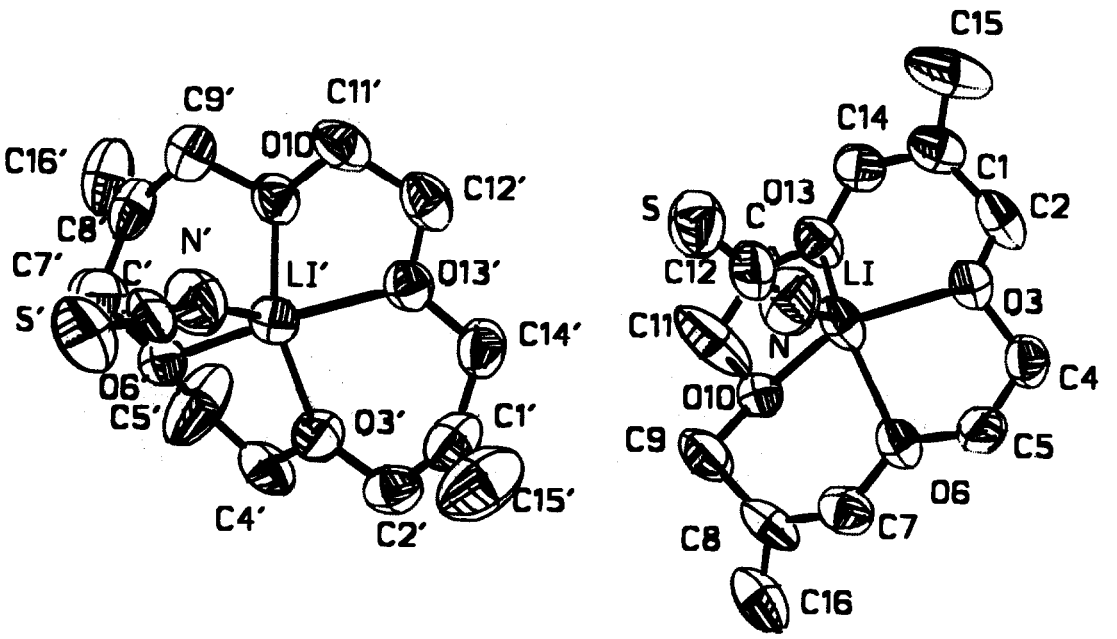


Figure 2. The two molecules of the Li complex of **4**. In each molecule the disordered oxygen with the smaller occupancy value and the hydrogen atoms are omitted for clarity.

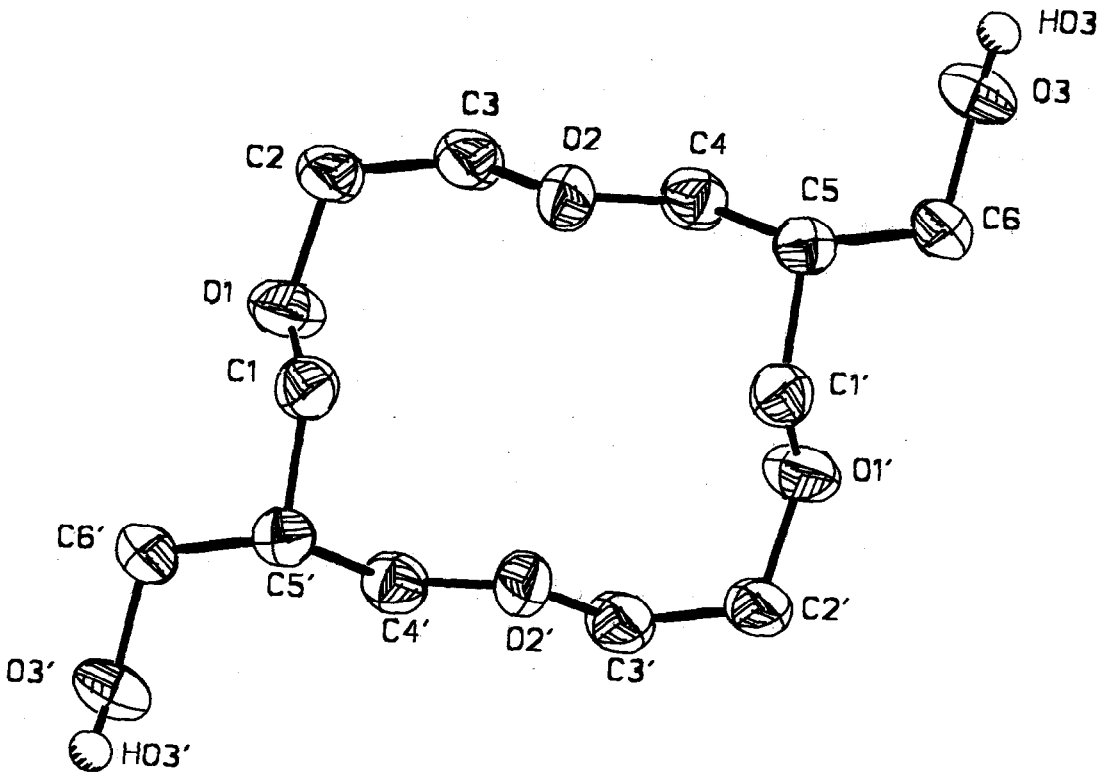


Figure 3. The conformation of 5 viewing the molecule in a direction perpendicular to the least-squares plane of the ring. All hydrogen atoms except the alcoholic hydrogens are omitted for clarity.

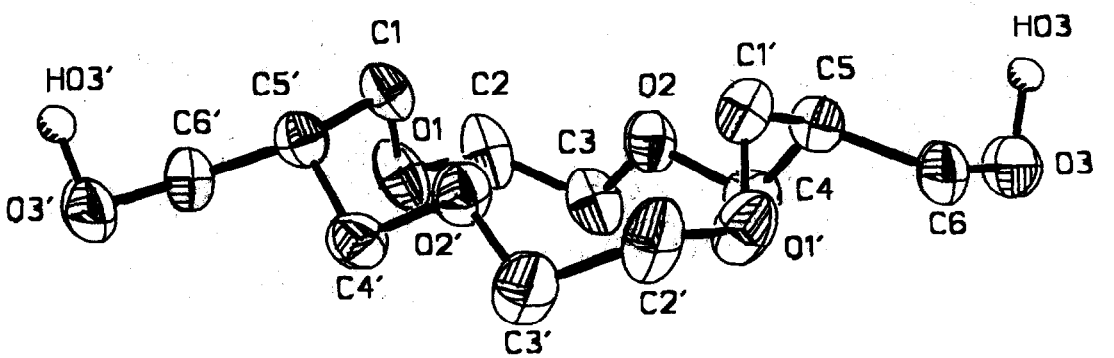


Figure 4. A view of 5 approximately perpendicular to that of figure 3 showing the relationship of the OH groups to the cavity.

Table I. Bond Lengths (Å) and Angles (deg) in the 4-LiSCN Complex With e.s.d. Values in Parenthesis.

			Molecule A	Molecule B	Molecule A	Molecule B
1	2	3	1 - 2(Å)	1 - 2(Å)	1-2-3(deg)	1-2-3-(deg)
C15	C1	C2	1.311(9)	1.325(10)	122.5(6)	119.7(6)
C14	C1	C15	1.509(8)	1.474(9)	120.7(6)	123.5(6)
C2	C1	C14	1.494(8)	1.498(8)	116.8(5)	116.8(5)
C1	C2	O3			110.5(5)	109.4(4)
C2	O3	C4	1.425(7)	1.419(7)	113.8(4)	114.6(4)
O3	C4	C5	1.446(7)	1.428(6)	107.1(5)	108.8(5)
C4	C5	O6	1.482(9)	1.474(10)	106.5(4)	112.2(6)
C4	C5	O6A	1.482(9)		106.5(4)	122.9(8)
C5	O6	C7	1.436(6)	1.372(10)	113(4)	110.2(6)
C5	O6A	C7		0.999(13)		119.2(10)
O6	C7	C8	1.422(7)	1.442(9)	108.6(4)	119.8(6)
O6A	C7	C8		1.650(14)		93.3(6)
C7	C8	C16	1.497(8)	1.494(9)	119.1(5)	122.0(6)
C7	C8	C9			118.7(5)	118.3(5)
C16	C8	C9	1.337(9)	1.317(9)	121.9(5)	119.4(6)
C8	C9	O10	1.482(9)	1.512(8)	99.8(6)	108.9(6)
C8	C9	O10A			125.06(6)	
C9	O10	C11	1.528(10)	1.438(7)	110.2(6)	112.7(4)
C9	O10A	C11	1.425(11)		113.7(7)	
O10	C11	C12	1.290(10)	1.430(6)	113.2(6)	106.2(4)
O10A	C11	C12	1.340(12)		119.7(6)	
C11	C12	O13	1.438(10)	1.488(9)	110.5(5)	108.4(5)
C12	O13	C14	1.433(6)	1.418(7)	115.0(4)	113.2(4)
O13	C14	C1	1.423(7)	1.407(7)	110.0(4)	110.0(5)
S	C	N	1.631(7)	1.614(7)	179.4(5)	179.1(6)
C	N		1.135(9)	1.143(9)		
Li	O3		2.057(10)	1.958(10)		
Li	O6		2.049(10)	2.055(10)		
Li	O6A			2.203(12)		
Li	O10		2.149(9)	2.051(10)		
Li	O10A		2.030(12)			
Li	O13		2.003(10)	2.052(10)		
Li	N		1.989(11)	2.018(11)		

Table II. Bond Lengths (Å) and Angles (deg) in 5 with e.s.d. Values in Parenthesis

1	2	3	1-2 (Å)	1-2-3 (deg)
C5A	C1	O1	1.517(5)	108.2(4)
C1	O1	C2	1.415(6)	114.0(4)
O1	C2	C3	1.427(4)	112.8(3)
C2	C3	O2	1.500(6)	110.8(4)
C3	O2	C4	1.399(5)	111.6(3)
O2	C4	C5	1.432(4)	109.0(4)
C4	C5	C6	1.510(6)	111.4(4)
C4	C5	C1A		111.8(3)
C6	C5	C1A	1.509(5)	111.1(3)
O3	C6	C5	1.424(4)	113.6(3)
HO3	O3	C6	1.116[a]	107.7[a]

[a]Positional parameters of HO3 were not refined

the cyclization route from the linear molecules **1** and **3** to the cyclic 14-crown-4 (**4**). Presumably, cyclization is driven by the "template effect".[31] A molecule of **3** interacts with Li^+ to form a preorganized dienolate-Li^+ complex. The four oxygen atoms probably provide the base of the square pyramid Li^+ complex. Such conformations are common in Li^+ complexes.[5] This dienolate-Li^+ complex is available for cyclization with **1** to form the desired cyclic product **4**.

The free ligand **5** lies about a 2-fold axis with the axis passing through the cavity. The cavity is ellipical in shape (see Figure 3) as indicated by the diagonal O-O distances which are O1-O1', 5.428Å and O2-O2', 3.847Å. A least-squares plane was calculated for the four ring oxygen atoms. Each oxygen atom deviates 0.19Å from the plane in an alternating manner with one atom above and the next below the plane. In contrast to the dibenzo derivative[32] this ligand is not preorganized for complexation of a metal ion. The CH_2OH groups bonded to the ring are in equatorial positions and point away from the cavity (see Figure 4) and, since the molecule lies about a two-fold axis, have a syn relationship. Table III contains the torsion angles in the ring and these indicate a considerable deviation from expected low energy values about the O1-C2 bond. O1 does not point into the ring but rather has a vertical deviation to the plane of the ring tending towards an exo conformation.

Table III. Torsion Angles (deg) For Atoms of 5 With e.s.d. Values in Parenthesis

Atoms	Torsion Angle
C5A-C1-O1-C2	168.3(3)
C1-O1-C2-C3	91.3(6)
O1-C2-C3-O2	-76.9(6)
C2-C3-O2-C4	173.1(3)
C3-O2-C4-C5	-179.4(3)
O2-C4-C5-C6	-172.1(3)
O2-C4-C5-C1A	62.9(4)
C4-C5-C6-O3	64.1(6)
C1A-C5-C6-O3	-170.4(5)

As far as we know, this is the first crystal structure of a 14-crown-4 derivative. The torsion angle O1-C2-C3-O2 (see Table III) demonstrates that the gauche arrangement between oxygens O1 and O2 is the preferred conformation in **5**. This conformation is typical for linear [33-36] and cyclic [31,37,38] polyoxyethylenes. In order to provide a base of a square pyramid, which is favored for Li^+ binding,[5] the 14-crown-4 macrocyclic ring must undergo a significant conformational change, even though 14-crown-4 and its derivatives are the most selective Li^+ ionophores among the crown-ethers.[1-3] This

indicates the relative ease of this conformational change, which is attributed to the -O-$CH_2CH_2CH_2$-O- unit.[38] The conformation arrangement of the CH_2OH groups with respect to the polyether ring suggests that the hydroxyl groups might be involved in solvation of two types of anions, (i) those of separate ion pairs, in which the anion is located far enough from the cation, so the hydroxyl groups can solvate them, and (ii) anions of neighboring contact ion-pair complexes.[21] We have not been able to grow suitable crystals of a Li^+ complex with 5 to verify the role of the OH functions on complexation.

EXPERIMENTAL SECTION

Proton magnetic resonance (^1H NMR) spectra were obtained on a Varian Gemini 200 MHz spectrometer using $CDCl_3$ as the solvent. Molecular weights were obtained by the electron impact method on a Finnegan 8430 High Resolution Mass Spectrometer. Infrared (IR) spectra were obtained in a Perkin-Elmer FT 1600 spectrometer. Elemental analyses were determined by MHW Laboratories, Phoenix, Arizona. Starting materials were used as purchased from Aldrich Chemical Company.

5-Methylenyl-3,7-dioxa-1,9-nonanediol (3). Sodium metal (10 g) was added to 250 ml of stirred ethylene glycol at room temperature (CAUTION: this reaction is rapid and exothermic). After 1 h, 27.5 g (0.22 mol) of 1 was added to the solution by means of a dropping funnel and the resulting mixture was stirred at 80 °C for 6 h. The mixture was filtered and the excess ethylene glycol was distilled under reduced pressure. Methylene chloride (100 ml) was added to the cooled residue and the resulting mixture was filtered and evaporated under reduced pressure. The residue was distilled to give 26g (67%) of 3; bp 110-114 °C; ^1H NMR (δ): 2.75 (b, 2 H), 3.55 (m, 4 H), 3.75 (m, 4 H), 4.2 (s, 4 H), 5.2 (s, 2 H).

6,13-Dimethylenyl-1,4,8,11-tetraoxacyclotetradecane(4).[29] **Compound 3** (7.04 g, 0.04 mol) was dissolved in 250 ml of t-butyl alcohol in which 2.0 g of sodium had been reacted. Dichloride 1 (5.0 g, 0.04 mol) in 125 ml of dioxane was slowly added over a 2 h period. Solid lithium perchlorate (0.8 g) was added and the mixture was stirred under nitrogen at reflux temperature for 16 h. The solvents were then removed under reduced pressure. The bath temperature was kept below 50 °C and the solvent was not completely removed since dry lithium perchlorate is explosive when heated. The residue was added to 25 ml of water and the aqueous phase was extracted three times with 50 ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The solvent was then evaporated and the residue distilled to give 3 g (30%) of 4, bp 80-83 °C/0.15 mm; ^1H NMR (δ): 3.70 (s, 8 H), 4.15 (s, 8 H), 5.20 (s, 4 H). This product could also be purified by alumina chromatography using isopropyl ether as eluant. This material was used to prepare 5 without further purification. A LiSCN complex with 4 was prepared by dissolving the salt and 4 in acetonitrile and allowing the acetonitrile to slowly evaporate.

Syn-6,13-bishydroxymethyl-1,4,8,11-tetraoxacyclotetradecane(5). A 1 M solution of borane-THF complex (35 ml) was added dropwise to 1.14 g (5 mmol) of 4 in 10 ml of THF at

0 °C under nitrogen. The mixture was stirred at 0 °C for 2 h and then at 25 °C for 2 h. Water (6 ml) was carefully added and the solvents were evaporated under reduced pressure. Aqueous 3 N sodium hydroxide (35 ml) and 2.5 ml of 30% aqueous hydrogen peroxide were successively added to the residue. The resulting mixture was stirred at 50 °C for 2 h and the organic layer was separated. The aqueous layer was saturated with salt and extracted with 25 ml of chloroform. The combined organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure and the residue recrystallized from ethyl acetate to give 0.65 g (49%) of **5**, mp 141-143 °C; ^{1}H NMR (δ): 0.85 and 0.87 (two s, CH_3 of isomer impurity), 1.90 (m, 2 H), 2.50 (m, 2 H, exchanged with D_2O), 3.65 (s, 8 H), 3.80 (two s, 12 H); MS (*m/e*) 265. Anal. Calcd for $C_{12}H_{24}O_6$: C, 54.53; H, 9.15. Found: C, 54.68; H, 9.18.

X-Ray Determinations. Suitable crystals of the LiSCN complex of **4** and uncomplexed **5** were grown from acetonitrile and mounted in a Nicolet R3 automated diffractometer which utilized graphite monochromated Mo Kα radiation (λ = 0.71073Å). Crystal data and the orientation matrix for each crystal were obtained using a least-squares procedure involving 25 carefully centered reflections from each crystal. Crystal data along with a summary of experimental conditions for each study are given in Table IV. Intensity data for each compound were obtained using a variable scan rate (3.91-58.59 degree/minute) θ-2θ scan procedure. Standard reflections measured every 100 data (approximately 2h) indicated that the crystals did not decompose and that the electronics were stable.

Trial structures for both compounds were obtained using direct methods. The two molecules in the asymmetric unit of **4**-LiSCN are similar including disorder of an oxygen in each ligand. The population parameters of these fractional oxygens are O10, 0.60; O10A, 0.40; O6′, 0.60 and O6A′, 0.40. While it was possible to resolve the disorder for these oxygens, the lack of precision in bond lengths and angles associated with the disordered atoms was disappointing and can be attributed to the inability to resolve the disorder of the neighboring carbon atoms. Compound **5** has a 2-fold axis perpendicular to and passing through the cavity of the ring with the result that the asymmetric unit consists of half of the molecule. Both structures were refined using a cascading blocked least-squares refinement procedure. In compound **4**-LiSCN, all non-hydrogen atoms were refined anisotropically with the exception of the disordered oxygen of each molecule which were refined isotropically. The positions of the hydrogen atoms except those bonded to the carbons next to disordered oxygens were calculated based on known chemical geometry. The hydrogens were allowed to ride on their neighboring carbon atom during the refinement process. The isotropic thermal parameters for the hydrogens were set equal to 1.2 times the initial equivalent isotropic thermal parameter of the neighboring carbon atom and were not refined.

A similar refinement procedure was used for **5** except that the position for the alcoholic hydrogen was obtained from a difference map. This hydrogen was allowed to ride on its neighboring oxygen and the isotropic thermal parameter of that hydrogen was refined. There was no disorder in **5** so positions for all hydrogens bonded to carbons were calculated

Table IV. Crystal and Experimental Data

	4-LiSCN	5
Formula	$[Li(C_{12}H_{20}O_4)SCN]$	$C_{12}H_{24}O_6$
Formula Weight	93.4	264.3
F(000)	624	576
Crystal size, (mm)	0.15 x 0.30 x 0.55	0.05 x 0.25 x 0.50
, cm^{-1}	2.03	0.96
space group	P1	Aba2
a, Å	9.372(2)	15.242(7)
b, Å	12.553(2)	18.519(6)
c, Å	13.802(3)	4.829(2)
α, deg	90.02(2)	90
ß, deg	90.49(2)	90
γ, deg	101.68(1)	90
V, $Å^3$	1590.1(5)	1363.0(7)
Z	4	4
Dx, g/cc	1.23	0.59
Sin θ/λ	1.23	1.29
Observed Data	2665	565
Unobserved Data	1502(4) F < 4σ (F)	114 F < 3σ (F)
R	0.067	0.046
R_w	0.083	0.051
G (weighting scheme)	7.5×10^{-4}	7.4×10^{-4}
Goodness of Fit	1.87	1.212
largest peaks in difference map ($eÅ^{-3}$)	0.40, - 0.25	0.19, -0.15

and were treated in the same manner as the hydrogens in 4-LiSCN. The resulting R values were R = 0.067 and Rw = 0.083 for 4-LiSCN and R = 0.046 and Rw = 0.051 for 5. Weights were based on counting statistics. The rather high R values for 4-LiSCN likely result from unresolved disorder for the carbon atoms bonded to the disordered oxygen atoms. Their large highly anisotropic thermal parameters suggest such disorder. Atomic scattering factors for the atoms in both structures were obtained from the International Tables of X-ray Crystallography[39]. All computer programs used in this study are contained in the SHELXTL[40] program package.

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