

13-Membered Azocrown Ether. Structure of the Lithium Bromide Complex and Membrane Properties

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Abstract. The lithium bromide hydrate complex of the 13-membered dibenzoazocrown ether of composition $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$ has been synthesized. Its structure has been determined by the X-ray method. The crystals are monoclinic, space group C2/c, $a = 12.720(6)$, $b = 19.969(9)$, $c = 13.963(6)$ Å; $\beta = 104.32(2)^\circ$. Selectivities of membrane electrodes based on 13-membered azocrown ethers are discussed in terms of complex stabilities and metal cation extractabilities as related to the structures of the respective complexes.

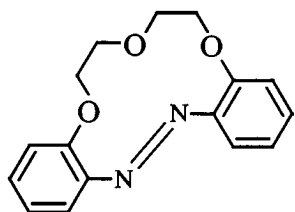
Key words: azocrown ether, lithium complex, X-ray structure, membrane electrodes

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1. Introduction

The 13-membered azocrown ether L13 obtained using different methods [1,2] presents an interesting compound capable of forming complexes with alkali metal cations. The stability constants of the sodium and potassium complexes of L13 are very small, whereas they are much higher for the lithium complex ($\log K_{\text{LLi}} = 4.10$; acetonitrile) [1]. On the other hand the crown ether and its lipophilic derivatives used as ionophores in ion-selective membrane electrodes show high sodium selectivity in the presence of lithium, potassium and other cations [2]. The sodium iodide complex of L13 is ionic and the complex cation consists of one sodium cation and two ligand molecules [3].

Inspection of the X-ray structures of crown ether complexes gives valuable information on the ligand's behavior as ionophores in ion-selective membrane electrodes. Their selectivities can correlate with some structural features of the respective complexes [4].

Ligand *E*-L13

The aim of this work was to examine why, in contrast to other 13-membered crown ethers, the azocrown ether L13 possesses poor lithium selectivity in an ion-selective membrane electrode as compared to other alkali metal cations.

2. Experimental

The azocrown ether was prepared according to [2]. All materials and solvents were of reagent grade. M.p. are uncorrected. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer of solutions in CDCl_3 .

2.1. SYNTHESIS OF THE LITHIUM BROMIDE COMPLEX OF AZOCROWN ETHER L13

Compound *E*-L13 (120 mg; 0.42 mmol) and lithium bromide dihydrate (123 mg; 1 mmol) were dissolved in methanol and the solvent was evaporated. The residue crystallized upon treatment with acetone. The crystals were collected and washed with acetone. Yield 150 mg (92%) of orange product. It darkened at 245° and decomposed at 260° . For X-ray analysis the compound was recrystallized from acetone containing traces of methanol. ^1H NMR, δ [ppm]: 1.63 (2H, s); 3.92–4.02 (4H, m); 4.40–4.54 (4H, m); 7.12–7.30 (4H, m); 7.40–7.50 (2H, m); 7.84–7.91 (2H, m).

Free ligand ^1H NMR, δ [ppm]: 3.90–3.98 (4H, m); 4.23–4.31 (4H, m); 7.08–7.22 (4H, m); 7.37 (2H, dt, $J_1 = 1.8$ Hz; $J_2 = 7.8$ Hz); 7.78 (2H, dd, $J_1 = 1.8$ Hz; $J_2 = 7.8$ Hz) [3].

2.2. X-RAY STUDIES OF $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$

A preliminary examination showed that the crystals of $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$ slowly decompose under X-ray radiation. A few orange colored crystals of prismatic habitus of approximately the same size ($0.1 \times 0.2 \times 0.4$ mm) were selected for the experiment and three of them were used for data collection. The lattice constants were invariably refined by the least squares fits of 24 reflections in the θ range 12.4 – 16.7° in all cases. After the intensity of the standard reflection decayed more than 10% the crystal sample was changed. All intensity data were obtained on a DAR-UMB diffractometer ($\text{CuK}\alpha$ radiation, graphite monochromator) applying the combinational $\omega - \theta/2\theta$ scanning method. Diffractive data from three crystals

were standardized on the basis of the standard reflection and then were scaled to the overall level. Only the reflections with $I > 2\sigma(I)$ were measured and used in all calculations. The absorption corrections were not applied to avoid the additional systematic errors in data obtained from three different crystal samples. For most reflections in the case of the equiinclined scheme applied for data collection the μR values was < 1 . The structure was solved by a direct method [5] and refined by full matrix least squares [6] in the anisotropic approach. The lithium was refined isotropically. The positions of the hydrogen atoms were calculated from geometrical considerations and were refined as constrained to bonding atoms in a 'ride' mode, whereas the hydrogen atoms of water molecules were found objectively from a differential Fourier syntheses and were refined isotropically. Two Br^- anions reside principally on the two-fold axis. However the position of one of them was not clearly indicated. Further refinement of the structure showed that this Br^- was disordered. The electron density had a 'banana' shape and refinement indicated elevated anisotropy. Many attempts were made to clarify the model of disorder for this Br(2) atom. Its location was split into two positions with half occupancy off the two-fold axis. Their isotropic refinements led to a higher R -factor. Anisotropic refinement also did not improve the R -factor in comparison with bromine location on the two-fold axis. Further splitting of the disordered atom on possible multiple locations led to similar results without improving the R -factor and caused instability of the refinement process.

An alternative structure refinement in the acentric Cc space group starting from an asymmetric location of Br(2) results essentially in the same representation of electron density distribution without decreasing the R -factor.

One can conclude that these bromide anions are strongly disordered in the crystal structure by an infinite sequence of positions near the two-fold axis; the main axis of the corresponding formal ellipsoid of thermal motion roughly indicate its possible location. High anisotropy also indicates a potential pathway for crystal decomposition during irradiation. The two highest residual peaks on ΔF (1.23 and $0.83 \text{ e}/\text{\AA}^3$) located close to this atom support our assumption. The other residual peaks on the differential synthesis are smaller than $0.52 \text{ e}/\text{\AA}^3$. The experimental and model refinement data are given in Table I. The final coordinates and geometrical parameters are collected in Tables II and III, respectively.

3. Description of the Structure

As a consequence of the interaction of LiBr with L13 a complex of 1:1:1 (crown:LiBr:H₂O) stoichiometry is formed. In the crystals complex cations of composition $[\text{L13.Li.H}_2\text{O}]^+$ are present (Figure 1) enabling its formulation as ionic. The complex cation $[\text{LiL13.H}_2\text{O}]^+$ occupies a general position in the elementary cell, whereas two bromide anions reside on special positions on a twofold crystallographic axis. The bromine atoms (Figure 2) unite the complex cations to form a dimeric entity by means of hydrogen bonds $\text{O}(1\text{w}) \cdots \text{Br}(1) = 3.272(9)$,

Table I. Crystal data and structure refinement for $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$

Empirical formula	$\text{C}_{16}\text{H}_{18}\text{BrLiN}_2\text{O}_4$
Formula weight	389.17
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	$a = 12.720(6)$ Å $\alpha = 90^\circ$ $b = 19.969(9)$ Å $\beta = 104.32(2)^\circ$ $c = 13.963(6)$ Å $\gamma = 90^\circ$
Volume	3437(3) Å ³
<i>Z</i>	8
Density (calculated)	1.504 Mg/m ³
Absorption coefficient	3.450 mm ⁻¹
<i>F</i> (000)	1584
Crystal size	0.1 × 0.2 × 0.4 mm
Theta range for data collection	4.22 to 67.63°
Index ranges	$-11 \leq h \leq 13$; $0 \leq k \leq 23$; $0 \leq l \leq 15$
Reflections collected	1352
Independent reflections	1312 [<i>R</i> (int) = 0.0170]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1312/0/216
Goodness-of-fit on <i>F</i> ²	1.060
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0743, <i>wR</i> 2 = 0.1958
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0757, <i>wR</i> 2 = 0.2009
Largest diff. peak and hole	1.231 and -0.879 e.Å ⁻³

H(1w)··Br(1) = 2.57(6), O(1w)—H(1w) = 0.74, and O(1w)··Br(2) = 3.114(10), H(2w)··Br(2) = 2.44(10), O(1w)—H(2w) = 1.03 Å; O(1w)—H(2w)··Br(2) = 122(9)°, O(1w)—H((1w)··Br((1) = 157(15)°. This way the composition and structure of the complex could be formulated as $\{[\text{Li.H}_2\text{O.L13}]\text{Br}\}_2$.

The dimeric associates form chains directed along the *c* axis of the crystal. The chains are formed due to π - π stacking interactions between antiparallel molecules of L13. Two neighboring L13 molecules, related by a symmetry center (0.5 - *x*, 0.5 - *y*, 1 - *z*) are placed in the crystal lattice in such a way that the ligands partially overlap; the distance between the mean planes [$2.502x - 0.807y + 12.574z = 8.466$ for C(8), C(9), C(18—C(21), N(10), N(11) and C(12)—C(17); rms = 0.116] of the flat aryl containing fragments of the neighboring ligands equals 3.51 Å.

In the complex cation the lithium atom is coordinated by three oxygen atoms of the ligand oxyethylene fragment and by nitrogen N(11) of the azo group. The ligand heteroatoms are nearly coplanar in the range of ± 0.04 Å and form the base of a tetragonal pyramid of Li coordinational polyhedron. The Li—O distances

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
Br(1)	5000	3657(1)	2500	62(1)
Br(2)	5000	1153(1)	2500	245(3)
Li(1)	5043(17)	2147(10)	5103(16)	62(5)
O(1w)	4609(7)	2354(5)	3791(6)	66(2)
O(1)	5043(4)	1127(3)	5548(5)	37(2)
C(2)	6032(8)	987(7)	6217(9)	63(4)
C(3)	6931(8)	1288(6)	5785(11)	64(4)
O(4)	6723(5)	1977(4)	5574(5)	46(2)
C(5)	7229(7)	2435(5)	6343(8)	42(3)
C(6)	6619(7)	3078(6)	6092(9)	52(3)
O(7)	5499(5)	2937(3)	6033(5)	45(2)
C(8)	4773(8)	3441(5)	6096(7)	44(3)
C(9)	3760(8)	3255(6)	6207(7)	48(3)
N(10)	3388(6)	2585(4)	6269(6)	38(2)
N(11)	3829(6)	2137(4)	5896(6)	36(2)
C(12)	3451(7)	1492(5)	6017(7)	37(3)
C(13)	4126(7)	959(5)	5882(7)	37(2)
C(14)	3884(8)	306(5)	6038(8)	46(3)
C(15)	2933(10)	159(7)	6300(9)	65(3)
C(16)	2230(8)	667(8)	6410(8)	63(4)
C(17)	2509(8)	1323(6)	6273(7)	47(3)
C(18)	5074(10)	4119(6)	6068(8)	55(3)
C(19)	4317(11)	4605(7)	6200(8)	63(4)
C(20)	3325(12)	4428(7)	6323(9)	74(4)
C(21)	3043(9)	3761(6)	6340(8)	52(3)

(Table III) are in the range 2.034–2.130, Li—N = 2.11(2) Å. The apical position of the tetragonal pyramid is occupied by a water molecule with the Li—O(1w) distance = 1.82(5) Å. The Li atom stands aside from the basic plane [$1.233x - 3.755y + 12.888z = 7.309$ for O(1), O(4), O(7) and N(11); rms = 0.040] of the pyramid by 0.92 Å in the direction of the oxygen atom of the water molecule. The interatomic distances and deviation of the lithium atom from the mean plane are typical for lithium complexes of 12-14 membered Pedersen type crown ethers with 1:1 stoichiometry. The Li—O distances are 2.012–2.163 Å and deviations of the metal ion from the mean plane are in the range 0.77–0.89 Å [7–10].

The title compound differs from all the above mentioned complexes where the lithium forms tight ionic pairs with NCS^- or NO_3^- [7–10]. This illustrates the general rule that in all of these pentacoordinated lithium complexes, the ligand

Table III. Selected bond lengths [\AA] and angles [$^\circ$] for $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$.

Coordination polyhedron of Li	
O(1w)—Li(1)	1.82(2)
O(1)—Li(1)	2.13(2)
O(4)—Li(1)	2.10(2)
O(7)—Li(1)	2.03(2)
N(11)—Li(1)	2.11(2)
O(1w)—Li(1)—O(7)	115.6(11)
O(1w)—Li(1)—O(4)	112.5(11)
O(7)—Li(1)—O(4)	79.6(8)
O(1w)—Li(1)—N(11)	116.7(11)
O(7)—Li(1)—N(11)	78.6(8)
O(4)—Li(1)—N(11)	130.8(11)
O(1w)—Li(1)—O(1)	119.2(11)
O(7)—Li(1)—O(1)	125.2(11)
O(4)—Li(1)—O(1)	80.1(8)
N(11)—Li(1)—O(1)	77.6(8)
Ligand	
O(1)—C(2)	1.397(12)
O(1)—C(13)	1.399(10)
C(2)—C(3)	1.54(2)
C(3)—O(4)	1.417(13)
O(4)—C(5)	1.437(12)
C(5)—C(6)	1.497(14)
C(6)—O(7)	1.434(11)
O(7)—C(8)	1.383(12)
C(8)—C(9)	1.39(2)
C(8)—C(18)	1.41(2)
C(9)—C(21)	1.40(2)
C(9)—N(10)	1.428(14)
N(10)—N(11)	1.236(11)
N(11)—C(12)	1.400(13)
C(12)—C(17)	1.374(14)
C(12)—C(13)	1.411(14)
C(13)—C(14)	1.370(14)
C(14)—C(15)	1.38(2)
C(15)—C(16)	1.39(2)
C(16)—C(17)	1.38(2)
C(18)—C(19)	1.41(2)
C(19)—C(20)	1.36(2)
C(20)—C(21)	1.38(2)

Table III. Continued.

Ligand (continued)	
C(2)—O(1)—C(13)	114.6(8)
C(2)—O(1)—Li(1)	108.7(9)
C(13)—O(1)—Li(1)	112.7(8)
O(1)—C(2)—C(3)	107.1(9)
O(4)—C(3)—C(2)	110.1(8)
C(3)—O(4)—C(5)	115.9(8)
C(3)—O(4)—Li(1)	110.2(8)
C(5)—O(4)—Li(1)	111.3(8)
O(4)—C(5)—C(6)	105.2(8)
O(7)—C(6)—C(5)	107.1(8)
C(8)—O(7)—C(6)	121.5(8)
C(8)—O(7)—Li(1)	121.0(8)
C(6)—O(7)—Li(1)	108.2(8)
O(7)—C(8)—C(9)	117.8(10)
O(7)—C(8)—C(18)	120.4(10)
C(9)—C(8)—C(18)	121.8(10)
C(8)—C(9)—C(21)	118.3(12)
C(8)—C(9)—N(10)	126.1(10)
C(21)—C(9)—N(10)	115.4(10)
N(11)—N(10)—C(9)	117.3(9)
N(10)—N(11)—C(12)	114.2(8)
N(10)—N(11)—Li(1)	132.9(9)
C(12)—N(11)—Li(1)	112.9(8)
C(17)—C(12)—N(11)	127.2(10)
C(17)—C(12)—C(13)	116.6(10)
N(11)—C(12)—C(13)	116.1(9)
C(14)—C(13)—O(1)	121.4(9)
C(14)—C(13)—C(12)	121.9(9)
O(1)—C(13)—C(12)	116.7(9)
C(13)—C(14)—C(15)	119.4(11)
C(14)—C(15)—C(16)	120.4(12)
C(17)—C(16)—C(15)	118.9(10)
C(12)—C(17)—C(16)	122.6(11)
C(8)—C(18)—C(19)	117.2(11)
C(20)—C(19)—C(18)	121.5(12)
C(19)—C(20)—C(21)	120.3(12)
C(20)—C(21)—C(9)	120.8(12)

provides four binding sites, the fifth site is occupied by either the anion or a solvent molecule [11].

In all complexes of azo and azocrown ethers of known structure [3] where the metal cation is coordinated to the nitrogen atom the —N=N— and —N(O)=N—

Table III. Continued.

Ligand (continued)

O(1)—C(2)—C(3)—O(4)	54 (1)
C(2)—C(3)—O(4)—C(5)	93 (1)
C(3)—O(4)—C(5)—C(6)	-162 (1)
O(4)—C(5)—C(6)—O(7)	57 (1)
C(5)—C(6)—O(7)—C(8)	161 (1)
C(6)—O(7)—C(8)—C(9)	-169 (1)
O(7)—C(8)—C(9)—N(10)	0 (1)
C(8)—C(9)—N(10)—N(11)	-24 (1)
C(9)—N(10)—N(11)—C(12)	178 (1)
N(10)—N(11)—C(12)—C(13)	-162 (1)
N(11)—C(12)—C(13)—O(1)	-6 (1)
C(12)—C(13)—O(1)—C(2)	116 (1)
C(13)—O(1)—C(2)—C(3)	-173 (1)

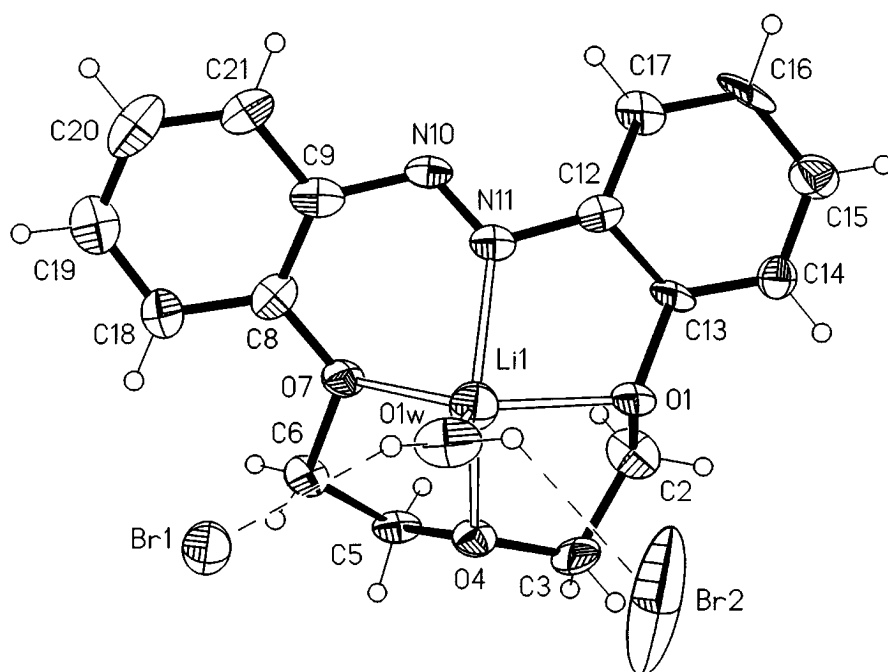


Figure 1. Molecular structure of $\{[\text{LiL13}(\text{H}_2\text{O})]\text{Br}\}_2$ showing 30% probability displacement ellipsoids.

fragments are *trans* with respect to the aromatic substituents. In the case of our LiBr complex the torsion angles for the —N=N— bond equal 178° .

Table III shows geometric parameters and torsion angles in coordinated *E*-L13. The average distances $\text{C}_{\text{sp}^2}\text{—O} = 1.39$, $\text{C}_{\text{sp}^3}\text{—O} = 1.43$, $\text{C}_{\text{sp}^2}\text{—C}_{\text{sp}^2} = 1.39$ and

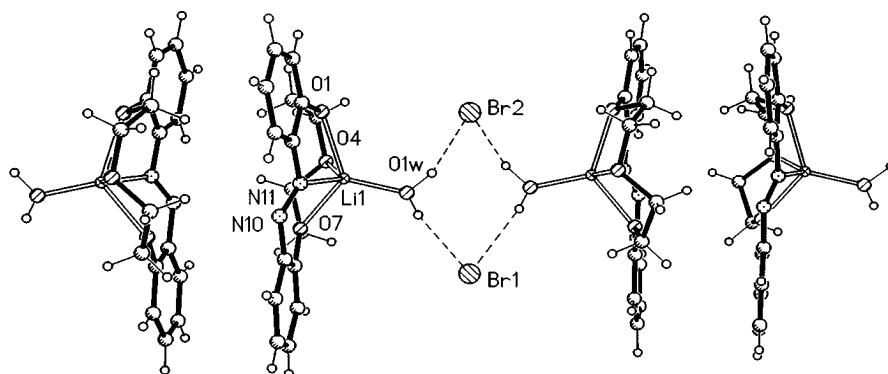


Figure 2. Packing diagram of $\{[LiL13(H_2O)]Br\}_2$ along the c axis. Note the dimer in the center.

$C_{sp^3}-C_{sp^3} = 1.52 \text{ \AA}$. The $C-N$ distances equal 1.43 and 1.40 \AA , $N=N = 1.24 \text{ \AA}$. In the polyoxyethylene fragment the conformation around two $C-C$ bonds is *gauche*, around $C-O$ there are three *anti* and one *gauche* conformations at $C(3)-C(4)$. At $C(3)$ it is a so called angular fragment [12].

4. Discussion

The 13-membered ligand L13 resembles small 12–14 membered crown ethers in its susceptibility to form complexes with Li^+ . The shape of the ligand in the lithium complex is similar to that in the sodium complex [3].

Studies of ionophores for ion-selective membrane electrodes show that the properties of the electrode depend on the stability constants of the complexes formed, their lipophilicities [13,14] (considering ligand to cation ratio) and susceptibility to form ionic species or ionic pairs. The role of solvent molecules frequently present in the solid state was not elucidated. Experimental data show that complex stabilities are less important for electrode selectivities as compared with structural features of the complexes [4].

The stability constant for the L13 lithium complex is high. It presupposes good behavior as an ionophore for lithium-selective membrane electrodes. As mentioned above, in the solid state the lithium cation complexed by the 13-membered azocrown ether is additionally coordinated by water molecules. This water molecule bonded directly to lithium in the complex cation presumably decreases its lipophilicity. The hydrate of the sodium iodide complex of L13 is ionic and the complex cation has a sandwich like structure. However, in this case the water molecule is bonded to the anion [3]. The lipophilicity of the complex cation is much higher as compared with the lithium complex; water bonded to the counterion does not decrease it. This rationalizes the high sodium selectivity ($\log K_{Na,Li}^{Pot} = -2.1$) of the respective membrane electrode [2,3].

It was demonstrated [15], that lithium ionophores showing very good electrode properties ($\log K_{\text{Na,Li}}^{\text{Pot}}$ up to -2.05) form solid complexes in which the lithium cation is six coordinated to the ligand molecule and the lithium cation is not coordinated to the solvent or anion.

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