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Crystal and Molecular Structure of Lithium Iodide Complex of 13-Membered Azoxycrown Ether

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The crystal structures of macrocyclic compounds with azo- or azoxybenzene unit and polyoxyethylene chain as constitutional parts of macrocycle, *i.e.* azo- and azoxycrown ethers of different ring size are known [1–5]. In exceptional structure of these compounds azo- (or azoxy) group brings about the existence of *cis* and *trans* isomers and redox activity. The macrocyclic unit, typical for crown ethers, extends properties of these compounds on well-recognized capability to form complexes. Stability of complexes differs for *cis* and *trans* isomers of azocrown ethers [6–10]. It was found that there are no essential differences in the mode of complex formation for azo- and azoxycrowns [6,7].

Recently, a remarkable correlation between the cation type, the size of macrocycle cavity and features of crystal structures of carrier complexes *versus* selectivity of membrane electrodes doped with the corresponding azo- or azoxycrowns has been found [11]. This paper supplements the correlation between structure of solid complex and the behavior of the respective membrane electrodes. Previously, structure of lithium bromide complex of 13-membered azocrown ($L13{\cdot}LiBr{\cdot}H_2O$) has been described, in which the $[L13{\cdot}Li{\cdot}H_2O]^+$ cation is present [12]. In NaI complex of 16-membered azoxycrown ether of 1:1 stoichiometry, there is an unusual coordination of oxygen atom of the azoxy group to sodium [11]. It pressed us additionally to investigate X-ray crystal and molecular structure of lithium iodide complex of 13-membered azoxycrown ether (L13–O).

^1H NMR spectra were recorded on Varian instrument at 500 MHz in acetone-d_6 solutions.

Azoxycrown ether L13–O was obtained according to [2]. ^1H NMR (δ [ppm]): 3.89 (4H, t, $J = 4.1$ Hz); 4.18 (2H, t, $J = 4.1$ Hz); 4.27 (2H, t, $J = 4.1$ Hz); 7.08 (1H, dt, $J_1 = 1$ Hz, $J_2 = 7.6$ Hz); 7.14–7.17 (2H, m); 7.29–7.32 (2H, m); 7.46 (1H, dd, $J_1 = 1.5$ Hz, $J_2 = 7.8$ Hz); 7.51 (1H, dt, $J_1 = 1.5$ Hz, $J_2 = 7.8$ Hz); 7.70 (1H, dd, $J_1 = 1.4$ Hz, $J_2 = 7.9$ Hz).

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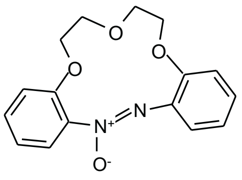
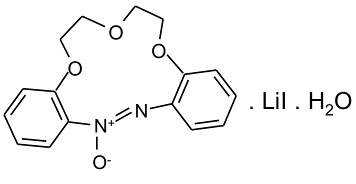
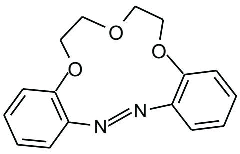


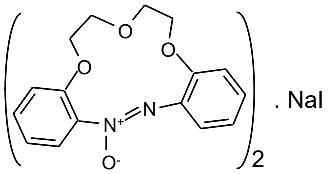
1. L13-O



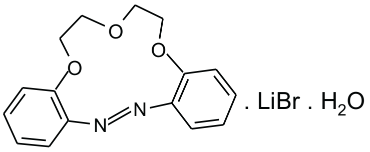
2. L13-O . LiI . H$_2$O



3. L13



4. (L13-O)$_2$. NaI



5. L13 . LiBr . H$_2$O

Lithium iodide complex of azoxycrown L13–O (complex **2**): Azoxycrown ether (300 mg; 1 mmol) and lithium iodide (300 mg; 2 mmol) were dissolved in methanol and the solvent was evaporated. The crystalline residue was dissolved in small amount of acetone and left at room temperature for slow evaporation. Yellow monocrystals were collected (yield quantitative). M.p. 255°C (decomp.). ^{1}H NMR (δ [ppm]): 3.46 (2H, s); 3.90 (4H, t, $J = 3.9$ Hz); 4.19 (2H, t, $J = 4.1$ Hz); 4.28 (2H, t, $J = 4.1$ Hz); 7.08 (1H, dt, $J_1 = 1$ Hz, $J_2 = 7.6$ Hz); 7.14–7.18 (2H, m); 7.29–7.33 (2H, m); 7.48 (1H, dd, $J_1 = 1.9$ Hz, $J_2 = 7.8$ Hz); 7.52 (1H, dt, $J_1 = 1.4$ Hz, $J_2 = 7.8$ Hz); 7.72 (1H, dd, $J_1 = 1.4$ Hz, $J_2 = 7.8$ Hz).

Properties of membrane electrode doped with compound **1** are described in [13].

X-ray studies. *Crystal data of* $\{[Li(L13\text{–}O)H_2O]^+ I^-\}$ *(complex* ***2****)*: $C_{16}H_{18}ILiN_2O_5$; $M_t = 452.16$; monoclinic; $P2_1/n$; $a = 7.6383(4)$; $b = 11.6231(6)$; $c = 20.1976(11)$ Å; $\beta = 99.596(1)°$; $V = 1768.1(2)$ Å^3; $Z = 4$; $D_x = 1.699$ g/cm^3; T = 293(2) K; $\lambda = 0.71073$ Å; $\mu = 1.839$ mm^{-1}; $F(000) = 896$; final $R1 = 0.0266$, $wR2 = 0.0564$ for 3001 reflections with $I > 2\sigma(I)$ and $R1 = 0.0459$, $wR2 = 0.0597$ for all data (collected 10339 and unique 4081 reflections, $R(int) = 0.0202$). The intensity data were collected and the unit cell parameters were determined using SMART Program package on SMART CCD diffractometer.

The structure was solved by direct method within the program SHELXS-86 [14] and refined by full-matrix least squares on F^2 with SHELXL-97 [15]. The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of water molecule were localized on a difference Fourier map and refined isotropically. The remaining hydrogen atoms were placed in calculated positions and were refined as riding on the corresponding carbon atoms with individual isotropic displacement parameters. The selected geometrical parameters are collected in Table 1 and 2.

Table 1. Selected bond lengths [Å] and angles [°] for lithium coordination polyhedron of complex **2**.

Li(1)–O(1W)	1.917(5)	O(1W)–Li(1)–O(1)	124.0(2)	O(7)–Li(1)–O(4)	80.5(2)
Li(1)–O(1)	2.015(4)	O(1W)–Li(1)–O(4)	99. 6(2)	O(7)–Li(1)–N(11)	79.4(2)
Li(1)–O(4)	2.090(4)	O(1W)–Li(1)–O(7)	115.2(2)	O(11)–Li(1)–O(1W)	91.2(4)
Li(1)–O(7)	2.014(4)	O(1W)–Li(1)–N(11)	124.0(2)	O(11)–Li(1)–O(1)	98.9(4)
Li(1)–N(11)	2.248(4)	O(1)–Li(1)–O(4)	81.4(2)	O(11)–Li(1)–O(4)	166.8(4)
Li(1)–O(11)	1.715(11)	O(1)–Li(1)–N(11)	76.0(2)	O(11)–Li(1)–O(7)	88.0(4)
		O(4)–Li(1)–N(11)	136.4(2)	O(11)–Li(1)–N(11)	33.3(4)
		O(7)–Li(1)–O(1)	120.1(2)		

Table 2. Selected torsion angles [°] for complex **2** and complex **5**.

Atoms	Present study	c.f. ref. [12]	Atoms	Present study	c.f. ref. [12]
O(1)–C(2)–C(3)–O(4)	50.2(3)	54(1)	C(8)–C(9)–N(10)–N(11)	–46.5(3)	–24(1)
C(2)–C(3)–O(4)–C(5)	78.8(2)	93(1)	C(9)–N(10)–N(11)–C(12)	178.2 (2)	178(1)
C(3)–O(4)–C(5)–C(6)	–163.1(2)	–162(1)	N(10)–N(11)–C(12)–C(13)	–138.0(2)	–162(1)
O(4)–C(5)–C(6)–O(7)	58.6(2)	57(1)	N(11)–C(12)–C(13)–O(1)	–3.0(3)	–6(1)
C(5)–C(6)–O(7)–C(8)	164.7(2)	161(1)	C(12)–C(13)–O(1)–C(2)	133.4(2)	116(1)
C(6)–O(7)–C(8)–C(9)	–157.4(2)	–169(1)	C(13)–O(1)–C(2)–C(3)	179.9(2)	–173(1)
O(7)–C(8)–C(9)–N(10)	2.1(3)	0(1)			

The contents of asymmetric part of the unit cell with the atoms numbering scheme is shown in Figure 1.

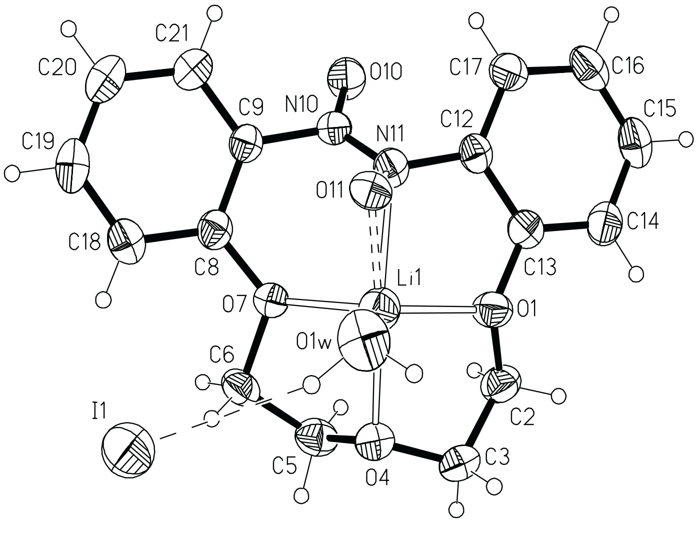


Figure 1. Molecular structure of $\{[Li(L13–O)H_2O]^+I^-\}$complex with atom numbering scheme showing the 50% probability displacement ellipsoids.

The crystal is build of complex cations of $[Li(L13-O)H_2O]^+$ composition and iodide counter anions. The specific feature of L13–O in this structure is a statistical disorder of azoxygroup over two positions. The positions of both nitrogen atoms coincide within the resolution of data, but oxygen atoms are bonded to the N(10) or N(11) atoms with 0.866(4) probability for O(10) and 0.134(4) for O(11). In the higher abundant form of complex cation the lithium atom is coordinated by three oxygen atoms of the ligand oxyethylene fragment and by nitrogen N(11) of the azoxy group. The oxygen atom of this group points away from the macrocycle cavity. The heteroatoms N(11), O(1), O(4) and O(7) coordinated to metal ion deviate from their mean plane not more than ±0.1 Å and form the base of tetragonal pyramid of lithium coordination polyhedron. The Li–O distances (Table 1) are in the range 2.014–2.090, the Li(1)–N(11) distance equals 2.248(4) Å. The latter is essentially longer than the corresponding Li–N distance (2.11 Å) in the relative complex **5** [12] with azo macrocycle. Water molecule occupies the apical position of the tetragonal pyramid. The Li–O(1w) distance is 1.917 Å. The Li ion stands aside from the base mean plane of the pyramid by 0.904(4) Å in the direction of the water molecule.

For the second position of azoxy group with minor abundance the O(11) atom coordinates to lithium at a short distance = 1.715(11) Å and the lone electron pair of N(10) points away from the macrocyclic cavity. The first example of such coordination of NNO group was recently found in the [(L16–O)·NaI] complex [11], where the corresponding Na–O (azoxy) distance is also the shortest among the Na–O distances in coordination polyhedron, but the azoxy group is fully ordered in that structure.

The azoxy group has *trans* geometry with respect to the aromatic rings placed in almost parallel planes (dihedral angle 3.76(9)°). Atoms of the azoxy group for the higher abundant complex are close to the mean plane within ±0.02 Å and form dihedral angles 43.04(7) and 42.55(7)° with aromatic residues linked to N(10) and N(11), respectively. The corresponding deviations of atoms from the best plane and the respective dihedral angles for azoxy group with minor site occupation factor are ±0.11 Å, and 58.0(3) and 57.1(3)°. In the structure of free ligand L13–O [2] the dihedral angles between the plane of azoxy group and aromatic rings bonded to it are 86.5 and 47.7°, and 78.4 and 86.3° for two crystallographically independent molecules, respectively. In the sandwich complex 3 these angles for two crown ether ligands equal 39.6 and 24.3°, and 43.4 and 28.2°, respectively. This comparison shows some mobility in mutual orientation of these flat π-delocalized fragment(s) and, in consequence, variation in the degree of π-π conjugation.

The torsion angles along macroring (Table 2) show a close similarity of conformation of this ligand in the complex to that found for the relative lithium bromide complex **5**. The major differences concern the torsion angles around C(9)–N(10) and N(11)-C(12) bonds and indicate increased π-π conjugation in the case of azo-group in complex **5** as compared to complex **2**.

Compounds L13 and L13–O form sandwich-like complexes with sodium of 1:2 metal-ligand stoichiometry [6], whereas the stoichiometry with lithium cation is 1:1. The explanation is the difference in cation sizes. The Na–O and Na–N distances in sandwich azo- and azoxycrown complexes are in the standard range of 2.31–2.55 and 2.50–2.59 Å, and the sodium cation stands 1.52–1.56 Å apart from the mean planes of coordinating heteroatoms. Thus two ligands can approach to the cation. The size of lithium cation is smaller, and the Li - macrocycle heteroatom distances are essentially shorter (Table 1). The cation is closer to the coordinating plane of macrocycle and deviate from it by about 0.9 Å. Thus, due to steric reasons only one macrocyclic ligand can approach lithium cation.

Summarizing, in a solid state azoxycrown **1** forms lipophilic complex cation $[(L13\text{–}O)_2\cdot Na]^+$ with sodium ions, and a "hydrated" complex cation with lithium ions of 1:1 stoichiometry. Membrane electrode doped with the azoxycrown 1 is highly sodium selective in the presence of lithium ($\log K^{Pot}_{Na,Li} = -2.3$) [13]. This behavior is adequate to structures of complexes and membrane electrode properties of membrane doped with azocrown ether [6,12,13].

In the crystal structure the water molecule forms two hydrogen bonds with the neighboring iodide anions (related by two-fold screw axis) resulting in chain formation along the *b* axis of the unit cell (Figure 2). Parameters of the O(1W)–H(1W)...I(1) hydrogen bonds are: O(1W)...I(1) 3.613(2), O(1W)–H(1W) 0.97(2) and H(1W)...I(1) 2.69(2) Å; the O(1W)–H(1W)...I(1) angle equals 160(2)°, the distances in O(1W)–H(2W)...I(1) $(-x + 1/2, y - 1/2, -z + 1/2)$ are O(1W)...I(1) 3.568(2), O(1W)–H(2W) 0.91(2), H(2W)...I(1) 2.67(2) Å and the O(1W)–H(2W)...I(1) angle is 171(3)°.

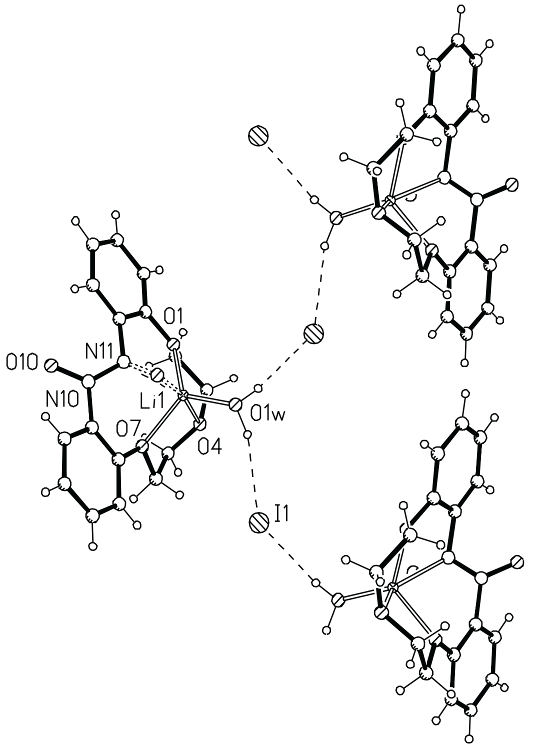


Figure 2. Fragment of crystal structure showing chain formation *via* O(1w)–H···I(1) hydrogen bonds along *b* axis.

The complex cations (related by symmetry center) form dimeric entity by means of C(2)–H...O(10) (–x + 2,–y + 1,–z + 1) hydrogen bonds with the following parameters: C(2)...O(10) 3.253(3), C(2)–H(2B) 0.97, H(2B)...O(10) 2.45; C(2)–H(2B)...O(10) angle = 140.4°. Furthermore, the dimers associate to form column directed along the *a* axis of the crystal (Figure 3) due to π–π stacking interaction between antiparallel aromatic moieties. Two neighboring molecules related by symmetry center (*1 – x, 1 – y, 1 – z*) are placed in the crystal in such a way that the benzene units partially overlap; the distances between the mean planes of overlapping fragments to the corresponding atoms of neighboring fragment are in the range 3.398(4)–3.655(4) Å.

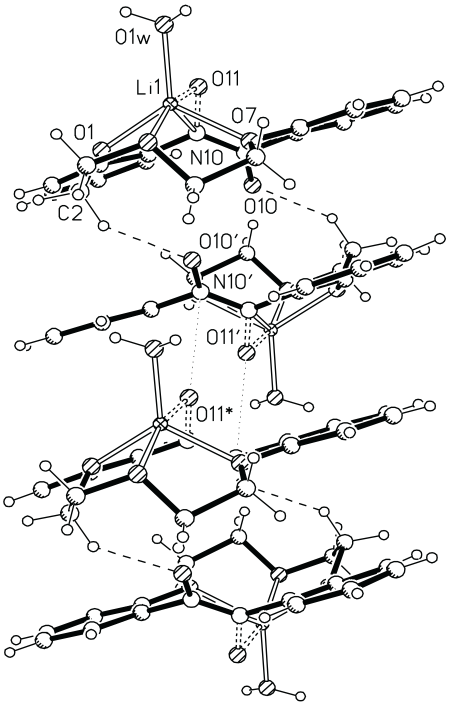


Figure 3. Infinite column in the structure along *a* axis. Atoms related by symmetry center (*2 – x, 1 – y, 1 – z*) and (*1 – x, 1 – y, 1 – z*) are marked by apostrophes and stars, respectively.

As the mutual arrangement of benzene fragments in the dimers is similar to that found in associates of the dimers, one may speculate that the π–π stacking interaction also takes place within the dimer; the characteristic distances in this case are in the range of 3.524(3)–3.763(3) Å. The short intermolecular contact N10…O11 equal 2.86 Å appears between the molecules coupled by stacking interaction.

Supplementary data are deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no CCDC 171891 (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail deposit@ccdc.cam.ac.uk).

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