

Dicyclohexylamides as Ionophores for Li-Selective Electrodes. Crystal Structures of a Triamide Ligand and Its Complex with Lithium Ion

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Abstract. The influence of structure and lipophilicity of dicyclohexylamides on the lithium selectivity in membrane electrodes is discussed. The crystal structures of the triamide podand **1** and its complex with LiBr **1b** has been determined by X-ray analysis. Crystal data for ligand **1**: $C_{48}H_{83}O_6N_3$, triclinic, $P1$, $a = 10.749(2)$, $b = 12.097(3)$, $c = 19.123(6)$ Å, $\alpha = 95.76(2)$, $\beta = 80.06(2)$, $\gamma = 100.27(2)^\circ$, $V = 2403(1)$ Å³, $Z = 2$. Crystal data for the lithium complex **1b**: $C_{48}H_{83}O_6N_3 \cdot LiBr \cdot x C_2H_5OH$, monoclinic, $P2_1/c$, $a = 21.297(6)$, $b = 16.316(8)$, $c = 19.450(4)$ Å, $\beta = 110.87(2)^\circ$, $V = 6315(3)$ Å³, $Z = 4$. In the complex the ligand adopts a conformation in which oxygen binding sites surrounding the Li^+ cation form a slightly distorted trigonal prism.

Supplementary Data relevant to this article have been deposited with the British Library as Supplementary Publication No. 82177 (20 pages).

Key words: Lithium ionophores, podand, dicyclohexylamides, Li-complex, crystal structure, X-ray analysis.

1. Introduction

The technical and medical applications of lithium [1–4] underlie the great interest in ligands showing high selectivity for the lithium ion. Over the last 15 years there have been many reports on this subject [4–16]. Some of the reported ligands have found application in the analytical field, acting as ionophores for electrochemical sensors, in lithium therapy (distribution of Li ion inside the body), in extractive metallurgy and in extraction of lithium from sea water as well as from waste waters.

Lithium is a cation with very specific characteristics. Its small size as a naked cation (the ion radius is 0.68 Å) and a very high hydration energy causes formation of stable hydrates of much larger size (the radius of the hydrated ion is 3.4 Å). The

best ligand for lithium ion would be one in which coordination centers substitute cation hydrating molecules and which is flexible enough to adjust its conformation to form a compact structure with the cation. The small radius of the lithium ion enables versatile coordination numbers (from 2 to 8) in different complexes.

In most known complexes with organic ligands the lithium cation, being a 'hard acid', is bonded to the ligands with oxygen donor atoms ('hard base') by ion-dipole ($\text{Li}^+ \text{---} \text{O}$) interactions. This interaction is strong and decreases as the ligand donors are changed from oxygen to nitrogen and sulfur: $\text{O} > \text{N} \gg \text{S}$. The coordination number of lithium in a complex is determined primarily by the number of binding sites in the ligand. Among many reported Li-complexing compounds are ethers, diamides, dicarboxylic acids and crown ethers [4–16]. The open chain amides seemed to act favorably as ionophores for Li-ion selective electrodes [12].

For podands it was found that a propylene bridge between the ether oxygen atoms is especially favorable in Li^+ complexation. The same rule applies to crown ethers; for instance 13-crown-4 or 14-crown-4 are more suitable for Li^+ than 12-crown-4. In the set of compounds **1**, **4** and **7** (see Figure 1) the selectivity determined by the separate solution method (SSM), expressed as $(-\log K_{\text{Li}/\text{Na}}^{\text{pot}})$ was greater for **1** than for **4** and **7** (respectively $2.05 > 1.61 > -0.5$) [10]. It was also pointed out that the high lipophilicity of dicyclohexylamides, and the appropriate number of binding sites of high polarizability are responsible for the good ionophoric behavior of these compounds. For instance, in the group of amides studied earlier the selectivity pattern was as follows: $-\log K_{\text{Li}/\text{Na}}^{\text{pot}}$ for **1** > **2** > **3** (2.05, 1.2 and 0.5, respectively), in favor of the dicyclohexylamides [10, 11].

In this paper we present further investigations and analysis of this problem, more examples of dicyclohexylamides **10–14** and their study in ion-selective electrodes. The structure and lipophilicity of the ionophores and the influence of these parameters on selectivity is discussed.

We also studied the crystal structure of compound **1** and its complex with lithium bromide **1b**. Our goal was to investigate whether all six oxygen binding sites of the ionophore take part in coordination of the lithium ion.

2. Experimental

The proton NMR spectra were obtained with a Varian 200 MHz spectrometer in CDCl_3 (Aldrich). Infrared (IR) spectra were recorded on a SPECORD M 80 spectrometer (Carl Zeiss-Jena). Mass spectra were taken on an AMD-604 Spectrometer (EI 70 eV, 8 kV, 5 kHz). The organic reagents and solvents used for the synthesis were of reagent grade.

2.1. SYNTHESIS OF THE COMPOUNDS

The synthesis and properties of compounds **1–9** were described in ref. [10]. The synthesis of ligands **10–14** was carried out in the same manner, starting from the

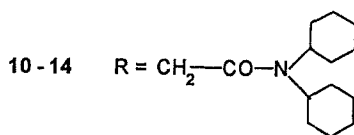
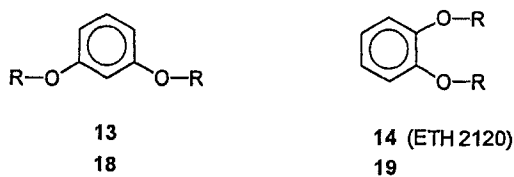
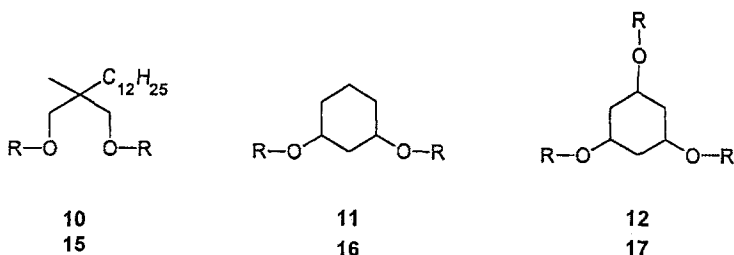
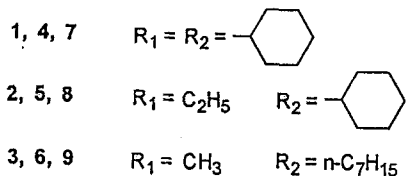
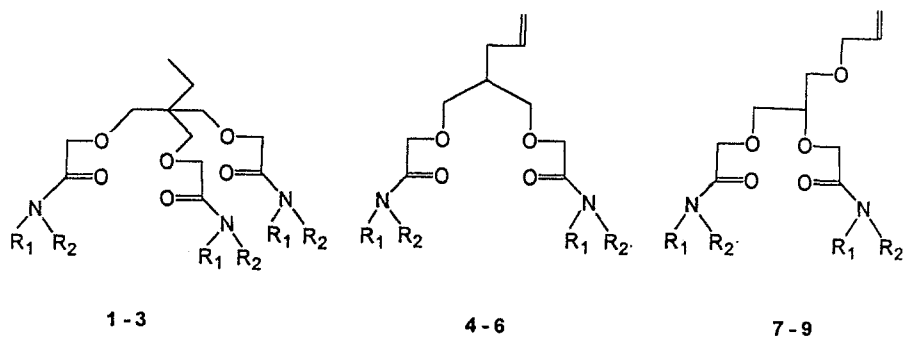


Fig. 1. Compounds used in this study.

corresponding diols **15**, **16**, triol **17** or 1,3- and 1,2-dihydroxybenzenes **18** and **19**. The properties and yields of the products are shown in Table I. The compounds used in this study are presented in Figure 1. The 1H -NMR spectra and mass spectra of the compounds confirmed their structure and purity.

TABLE Ia. The properties and yields of the compounds **10–14** and **1b**.

Comp.	Formula	MS (M ⁺)	m.p. °C	Yield %	IR (cm ⁻¹)		Log P*
					C=O	C—O—C	
10	C ₄₄ H ₈₀ N ₂ O ₄	700	oil	35	1645	1090	13.4
11	C ₃₄ H ₅₈ N ₂ O ₄	558	oil	58	1650	1100	8.05
12	C ₄₈ H ₈₁ N ₃ O ₆	795	180–82	62	1650	1050, 1100	9.44
13	C ₃₄ H ₅₂ N ₂ O ₄	552	150–52	42	1650	1080	8.16
14	C ₃₄ H ₅₂ N ₂ O ₄	552	169–73	36	1650	1050, 1120	8.27
1b	C ₄₈ H ₈₃ N ₃ O ₆ ·LiBr·C ₂ H ₅ OH	–	140–42	70	1660	1140	–

*Lipophilicity calculated by Hansch's method [22].

2.1.1. Synthesis of the Lithium Complex **1b**

A mixture of 0.25 mM of ligand **1** and 0.25 mM of LiBr·2H₂O in 8 mL of ethanol were refluxed and allowed to stand at room temperature. After crystallization, transparent white crystals of the complex **1b** were filtered off. The properties are presented in Table I.

2.2. MEMBRANE PREPARATION AND EMF MEASUREMENTS

The membrane components [2.5 wt.-% of ionophore, 33 wt.-% PVC, 65 wt.-% plasticizer and 15 mol.-% KTpCIPB (in respect to the ionophore)], 200 mg in total, were dissolved in 1.5 mL of freshly distilled THF. The solution was poured into a glass ring as described previously [11]. After solvent evaporation overnight the membranes were ready for making the electrodes. Four different plasticizers were used: NPOE (2-nitrophenyl octyl ether), TEHP [tris(2-ethylhexyl)phosphate], DOS [bis(2-ethylhexyl)sebacate] and BBPA [bis(1-butylpentyl)adipate]. The ionophores **10–14** were studied, with **1** and **4** for comparison.

The membranes were incorporated into Ag/AgCl electrode bodies 0.01 M LiCl was used as internal electrolyte. A double-junction reference Radelkis 0P0820P electrode was used with 1 M NH₄NO₃ solution in the bridge cell.

All potentials were measured at 20 °C using a METROHM 654 pH Meter. The selectivity coefficients (log $K_{Li/M}^{pot}$) were determined by the separate solution method (SSM) and were calculated by the matched potential method [19]. These are presented in diagrammatic form in Figure 2 only for selected membranes (containing ionophores, PVC, BBPA and no additives). In a few cases the selectivity coefficients (log $K_{Li/Na}^{pot}$) were also determined by FIM (Fixed Interference Method) at fixed 0.1 M concentration of sodium ion. The values are shown in Table II.

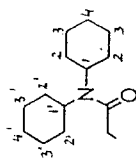


TABLE Ib. ¹H-NMR spectra of the compounds: δ (ppm) and J (Hz).

Comp.	O—CH ₂ —CO	C—CH ₂ —O or H _{gr}	H ₁ axial	H _{1'} axial	H _{2'} axial	Others
10	4.02 (s, 4H)	3.32 (2H, s)	3.48 (2H, m)	2.92 (2H, t J = 11)	2.45 (4H, m)	0.89 (3H, t J = 7); 1.2 (22H, s); 1-1.9 (41H, m)
11	4.08 (4H, s)	3.35 (2H, m)	3.48 (2H, m)	2.90 (2H, t J = 12)	2.45 (4H, m)	1-1.9 (42H, m); 2.05 (2H, m)
12	4.10 (6H, s)	3.39 (3H, m)	3.39 (3H, t J = 12)	2.92 (3H, t J = 12)	2.49 (6H, q J = 12)	1-1.9 (60H, m)
13	4.65 (4H, s)	6.57 (HC ₆ , s), 6.59 (2HC _{2,4} , d J = 8), 7.18 (HC ₃ , t J = 8)	3.54 (2H, m)	2.97 (2H, m)	2.5 (4H, m)	1-1.9 (36H, m)
14	4.64 (4H, s)	6.91 (4HC _{2,3,4,5} , s)	3.6 (2H, t J = 11)	2.94 (2H, t J = 12)	2.46 (4H, q J = 12)	1-1.9 (36H, m)
1b	4.14 (6H, s)	3.81 (6H, s)	3.0 (3H, t J = 11)	2.82 (3H, t J = 11)	2.54 (6H, q J = 11)	0.8 (3H, t); 1-1.8 (59H, m); 4.43 (s) OH

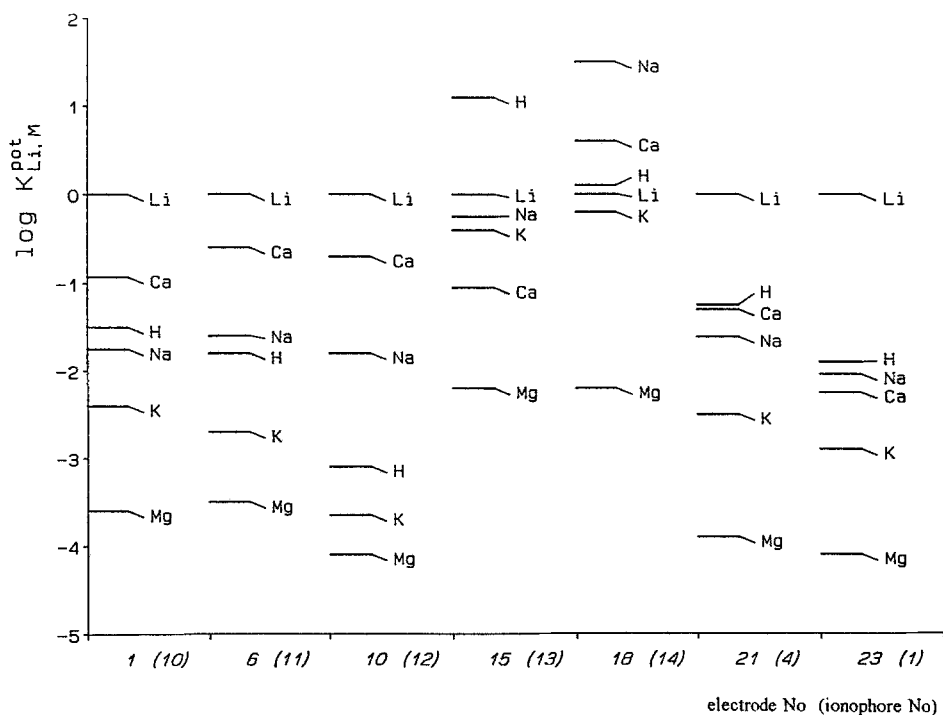


Fig. 2. Selectivity coefficients ($\log K$) for selected membranes with ionophores **10–14**, **1** and **4**.

2.3. CRYSTAL STRUCTURE DETERMINATION FOR COMPOUND **1** AND ITS COMPLEX WITH LiBr **1b**

Suitable crystals of **1** and **1b** were obtained by recrystallization from ethanol. Crystals of **1b** decomposed when removed from the mother liquor, therefore the crystal was measured in a sealed glass capillary.

Crystal data and details concerning data collection and structure refinement are given in Table III. Both structures have been solved and refined using the programs SHELXS86 [20] and SHELX-76 [21]. The positions of atoms in the complex ion of **1b** were located on the first E map, however the position of the Br^- ion was not clearly indicated. Further refinement of the structure has shown that the Br^- ion, located in a large cage, was disordered. The electron density had a 'banana' shape and therefore the Br^- ion was placed in several positions with partial occupancies. The occupancy of the Br^- ion in the middle of the 'banana-shaped' electron density was 25%. There are also several (4–5) ethanol molecules included in the crystal lattice of **1b**; their position was not clearly indicated by the ΔF map. The highest peaks in the solvent region were chosen and refined with fractional occupancies. The residual electron density in the final ΔF map was $\pm 0.30e \text{ \AA}^{-3}$. Final atomic coordinates for **1** and for **1b** are given in Tables VII and VIII, respectively; bond

TABLE II. The composition and characteristics of the electrode membranes.

Electrode No.	PVC-membrane composition			Membrane characteristic			
	Ionophore	KTpCIPB	Plasticizer	S_{Li} [mV]	Linear range [-log c_{Li}]	Selectivity $\log K_{Li/Na}^{pot}$ SSM	FIM
1	10	-	BBPA	59	4.8-1	-1.75	
2	10	+	<i>o</i> -NPOE	60	5.1-1	-1.47	
3	10	-	TEHP	58	4.5-1	-1.76	
4	10	+	TEHP	60	4.9-1	-1.4	
5	10	+	DOS	59	4.5-1	-1.75	
6	11	-	BBPA	56	4.8-1	-1.6	
7	11	+	BBPA	55	5.0-1	-1.6	-1.8
8	11	+	<i>o</i> -NPOE	55	4.8-1	-1.4	
9	11	+	DOS	59	5.0-1	-1.65	
10	12	-	BBPA	55	5.2-1	-1.80	-2.0
11	12	+	BBPA	58	5.1-1	-1.75	-1.95
12	12	+	<i>o</i> -NPOE	60	5.5-1	-1.2	-1.6
13	12	+	DOs	58	5.0-1	-1.45	-1.6
14	12	+	TEHP	55	5.0-1	-1.6	-1.9
15	13	-	BBPA	45	3.8-1	-0.25	
16	13	+	BBPA	51	4-1	-0.1	
17	13	+	<i>o</i> -NPOE	51	4-1	-0.75	
18	14	-	BBPA	50	3.5-1	1.5	
19	14	+	BBPA	50	4-1	1.23	
20	14	+	DOS	51	4-1	1.4	
21	4	-	BBPA	58	5.0-1	-1.6	
22	4	+	BBPA	59	5.0-1	-1.5	
23	1	-	BBPA	59	5.1-1	-2.04	
24	1	+	BBPA	59	5.1-1	-2.05	-2.4
25	1	+	TEHP	58	5.0-1	-1.96	
26	1	+	DOS	59	5.0-1	-1.86	
27	1	+	<i>o</i> -NPOE	59	5.0-1	-1.85	

length and bond angles are in Tables V and VI. The lists of fractional coordinates for disordered atoms in **1b**, anisotropic thermal parameters, H-atom coordinates and lists of structure factors have been deposited with the British Library Lending Division and copies may be ordered quoting Sup. No 82177.

3. Results and Discussion

Membranes were prepared of different composition, containing ionophores **10-14**. The properties of the electrodes obtained are shown in Table II. The selectivity for lithium over sodium ions differ depending on the plasticizer used. Of all the

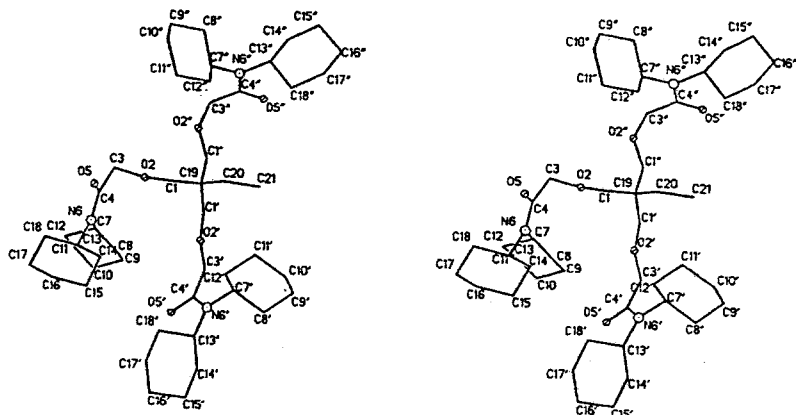


Fig. 3. Stereoview of ionophore 1.

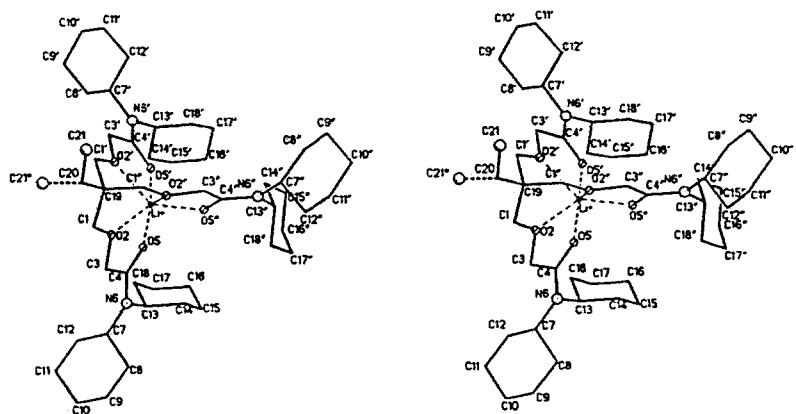


Fig. 4. Stereoview of complex 1b.

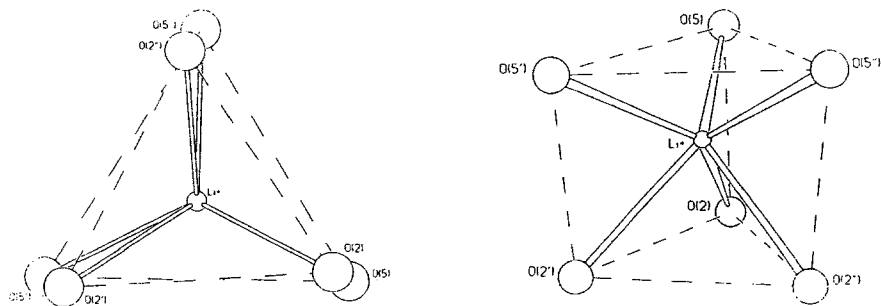


Fig. 5. Coordination of lithium ion in complex 1b.

TABLE III. Crystal data and details of data collection and structure refinement.

Crystal data	1	1b
Empirical formula	C ₄₈ H ₈₃ N ₃ O ₆	C ₄₈ H ₈₃ N ₃ O ₆ ·LiBr·C ₂ H ₅ OH
Color, habit	Colorless, plate	Colorless, plate
Crystal size (mm)	0.15 × 0.4 × 0.6	0.8 × 0.7 × 0.2
<i>Z</i>	2	4
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 10.748(2) Å <i>b</i> = 12.097(3) Å <i>c</i> = 19.122(6) Å <i>α</i> = 95.76(2)° <i>β</i> = 80.06(2)° <i>γ</i> = 100.27(2)°	<i>A</i> = 21.297(6) Å <i>b</i> = 16.316(8) Å <i>c</i> = 19.450(4) Å <i>β</i> = 110.87(3)°
Volume	2403(1) Å ³	6315(4) Å ³
Diffractometer used	KM-4	SYNTEX <i>P</i> 2 ₁
Radiation	CuK _α (λ = 1.54178 Å)	CuK _α (λ = 1.54178 Å)
Temperature (K)	292	292
2θ Range	3.0 to 120.0°	0.0 to 115.0°
Scan type	θ/2θ	θ/2θ
Standard reflections	2 measured every 100 reflections	2 measured every 100 reflections
Index ranges	-11 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 21	0 ≤ <i>h</i> ≤ 23, 0 ≤ <i>k</i> ≤ 17 -21 ≤ <i>l</i> ≤ 19
Reflections collected	6621	8173
Independent reflections	6599 (<i>R</i> _{int} = 3.20%)	7934 (<i>R</i> _{int} = 9.26%)
Observed reflections	4689 (<i>F</i> > 4.0σ(<i>F</i>))	4628 (<i>F</i> > 4.0σ(<i>F</i>))
Absorption correction	N/A	N/A
Quality minimized	Σ <i>w</i> (<i>F</i> _o - <i>F</i> _c) ²	Σ <i>w</i> (<i>F</i> _o - <i>F</i> _c) ²
Weighting scheme	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0001 <i>F</i> ²	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0001 <i>F</i> ²
Number of parameters refined	847	644
<i>R</i> , <i>wR</i>	3.86%, 4.93%	9.75%, 11.26%

plasticizers studied here BBPA generally gives the best electrode characteristic and selectivities for lithium. The second plasticizer of choice would be TEHP.

The ionophores presented here are di- and triamides with four or six oxygen (carbonyl and ethereal) coordinating centers. The newly studied compounds **10–14** are dicyclohexylamides. They are presented in Figure 1.

The selectivity coefficients (log $K_{Li/M}^{pot}$) for the lithium cations against sodium, potassium, magnesium, calcium and hydronium ions for selected electrodes, with BBPA as plasticizer, are presented in diagrammatic form in Figure 2. They were determined by the SSM method and were calculated by the match potential method.

TABLE IV. Coordination of Li⁺. Bond lengths (Å) and bond angles (°).

Li ⁺ —O(2)	2.144(11)	Li ⁺ —O(5)	2.007(12)
Li ⁺ —O(2')	2.190(12)	Li ⁺ —O(5')	2.006(12)
Li ⁺ —O(2'')	2.138(10)	Li ⁺ —O(5'')	2.026(10)
O(2)—Li ⁺ —O(5)	74.5 (4)	O(2)—Li ⁺ —O(2')	77.7(4)
O(5)—Li ⁺ —O(2')	130.2(5)	O(2)—Li ⁺ —O(5')	135.1(5)
O(5)—Li ⁺ —O(5')	99.4(4)	O(2')—Li ⁺ —O(5')	73.3(4)
O(2)—Li ⁺ —OO(2'')	78.2(3)	O(5)—Li ⁺ —OO(2'')	133.2(6)
O(2')—Li ⁺ —OO(2'')	77.9(4)	O(5')—Li ⁺ —OO(2'')	126.4(6)
O(2)—Li ⁺ —OO(5'')	128.8(6)	O(5)—Li ⁺ —OO(5'')	94.5(5)
O(2')—Li ⁺ —OO(5'')	134.8(6)	O(5')—Li ⁺ —OO(5'')	95.7(5)
O(2'')—Li ⁺ —OO(5'')	74.3(3)		
Li ⁺ —O(2)—C(1)	128.8(5)	Li ⁺ —O(5)—C(4)	121.5(4)
Li ⁺ —O(2')—C(1')	127.9(5)	Li ⁺ —O(2')—C(3')	117.7(4)
Li ⁺ —O(2'')—C(1'')	128.7(4)	Li ⁺ —O(5')—C(4')	125.2(5)
		Li ⁺ —O(2'')—C(3'')	116.8(4)
		Li ⁺ —O(5'')—C(4'')	120.0(5)

The biggest differences in the behavior of the studied membranes are observed for the aromatic ionophores **13** and **14**. The aliphatic compounds **1–6** and **10–12** are lithium selective. Ligands **1** and **12**, with six oxygen electron donors and of high lipophilicity, show the highest selectivity for lithium over sodium ions (–2.04 and –1.80, for the electrodes 23 and 10, respectively). The increase in lipophilicity of ligand **10**, which possesses four coordinating oxygen atoms does not lead to greater selectivity when compared with ligands **1** and **12**.

The aromatic isomeric compounds **13** (lithium selective) and **14** (ETH 2120, sodium selective) are much less selective for lithium ions when compared to aliphatic compounds. The arrangement of coordination centers attached to the planar benzene ring is probably less suitable for lithium, and favors sodium ions. Comparison of the ionophoric properties of ligands **13** ($\log K_{\text{Li}/\text{Na}} = -0.25$, electrode No. 15) and **14** ($\log K_{\text{Li}/\text{Na}} = +1.5$, electrode No. 18) leads to the conclusion that the three-carbon-bridge between ether oxygen atoms, even in an aromatic structure, favors lithium complexation.

The membranes with more lipophilic ionophores **10**, **12** and **1** ($\log P > 9$) are very good, considering the stability of the potentiometric signal, the lifetime characteristic and the selectivity for lithium over sodium. The electrode characteristics of these membranes do not change after several weeks of use. Certainly, the lipophilicity is not the only factor to be considered, however the optimal value of $\log P$ would be about 8–13. Probably more lipophilic molecules are not sufficiently mobile in the membrane. The conformation of the ligand, its flexibility and the number of coordinating centers need to be considered in choosing a ligand for lithium ions.

TABLE V. Bond lengths (Å) for compounds **1** and **1b**.

	1	1b
C(1)—O(2)	1.436(3)	1.416(7)
O(2)—C(3)	1.419(2)	1.392(9)
C(4)—O(5)	1.228(2)	1.238(9)
N(6)—C(7)	1.480(3)	1.481(9)
C(7)—C(8)	1.513(3)	1.516(11)
C(8)—C(9)	1.518(4)	1.518(12)
C(10)—C(11)	1.518(5)	1.505(14)
C(13)—C(14)	1.520(4)	1.535(8)
C(14)—C(15)	1.515(3)	1.528(10)
C(16)—C(17)	1.511(5)	1.530(14)
C(1')—O(2')	1.423(2)	1.408(7)
O(2')—C(3')	1.424(2)	1.405(8)
C(4')—O(5')	1.224(3)	1.245(9)
N(6')—C(7')	1.476(3)	1.486(9)
C(7')—C(8')	1.533(3)	1.506(9)
C(8')—C(9')	1.518(4)	1.522(14)
C(10')—C(11')	1.520(4)	1.488(13)
C(13')—C(14')	1.523(3)	1.486(11)
C(14')—C(15')	1.519(4)	1.513(12)
C(16')—C(17')	1.517(5)	1.489(17)
C(1'')—O(2'')	1.420(2)	1.420(7)
O(2'')—C(3'')	1.431(2)	1.422(8)
C(4'')—O(5'')	1.226(2)	1.216(7)
N(6'')—C(7'')	1.480(3)	1.467(8)
C(7'')—C(8'')	1.512(3)	1.525(12)
C(8'')—C(9'')	1.529(4)	1.517(12)
C(10'')—C(11'')	1.505(4)	1.503(20)
C(13'')—C(14'')	1.516(3)	1.519(9)
C(14'')—C(15'')	1.523(5)	1.519(11)
C(16'')—C(17'')	1.509(5)	1.470(13)
C(19)—C(20)	1.540(3)	1.547(9)
C(20)—C(21')	1.390(19)	
C(1)—C(19)	1.519(3)	1.518(10)
C(3)—C(4)	1.528(3)	1.515(8)
C(4)—N(6)	1.342(2)	1.339(9)
N(6)—C(13)	1.481(2)	1.481(7)
C(7)—C(12)	1.523(4)	1.516(8)
C(9)—C(10)	1.510(6)	1.502(12)
C(11)—C(12)	1.518(4)	1.535(12)
C(13)—C(18)	1.518(3)	1.496(10)
C(15)—C(16)	1.517(4)	1.488(16)
C(17)—C(18)	1.514(3)	1.536(10)

TABLE V. Continued.

	1	1b
C(1')—C(19)	1.524(3)	1.503(9)
C(3')—C(4')	1.512(3)	1.531(8)
C(4')—N(6')	1.360(3)	1.319(9)
N(6')—C(13')	1.479(3)	1.485(7)
C(7')—C(12')	1.512(3)	1.529(12)
C(9')—C(10')	1.506(4)	1.497(18)
C(11')—C(12')	1.522(4)	1.523(14)
C(13')—C(18')	1.523(3)	1.518(9)
C(15')—C(16')	1.511(4)	1.496(16)
C(17')—C(18')	1.518(5)	1.491(10)
C(1'')—C(19)	1.525(3)	1.508(9)
C(3'')—C(4'')	1.516(3)	1.492(9)
C(4'')—N(6'')	1.349(3)	1.376(8)
N(6'')—C(13'')	1.483(3)	1.466(7)
C(7'')—C(12'')	1.519(3)	1.505(11)
C(9'')—C(10'')	1.509(4)	1.482(20)
C(11'')—C(12'')	1.526(4)	1.520(12)
C(13'')—C(18'')	1.515(4)	1.516(12)
C(15'')—C(16'')	1.517(5)	1.524(16)
C(17'')—C(18'')	1.527(6)	1.520(10)
C(20)—C(21)	1.512(4)	1.368(27)

The purpose of the X-ray structure analysis was to clarify whether all six oxygen binding sites of the ionophore (three ether oxygen atoms and three carboxamide oxygens) take part in coordination of the lithium ion. In structures of lithium complexes so far known, with a similar type of amide ligands the lithium coordination numbers are: four (tetrahedron) [13], five (slightly distorted quadratic pyramid) [5] or six (distorted octahedral–tetragonal) [17].

The atom labeling and conformation of the free ligand **1** and its complex with lithium ion **1b** as determined by X-ray analyses are presented in Figures 3 and 4, respectively.

The conformation adopted in the crystal by ligand **1** differs significantly from that observed in the lithium complex **1b**. An *all-trans* arrangement of atoms along the chains O(2')—C(1')—C(19)—C(1'')—O(2'') and O(2)—C(1)—C(19)—C(20)—C(21) minimizes repulsion forces between the atoms C(21), O(2), O(2') and O(2''), i.e. atoms situated in the β position to the pivot C(19) atom.

The conformation of the ligand in the complex is such that six oxygen atoms surround the lithium cation forming a slightly distorted trigonal prism, as shown in Figure 5. This is the first case of such a coordination polyhedron to be observed for the hexacoordinated lithium cation [18]. The geometry of the coordination around Li ion is given in Table IV.

TABLE VI. Bond angles ($^{\circ}$) in ligand **1** and complex **1b**.

	1	1b
C(1)—O(2)—C(3)	111.3(1)	113.1(5)
C(3)—C(4)—O(5)	117.6(2)	118.0(6)
O(5)—C(4)—N(6)	123.6(2)	122.7(5)
C(4)—N(6)—C(7)	123.7(2)	122.1(5)
C(7)—N(6)—C(13)	117.0(1)	118.2(5)
N(6)—C(7)—C(12)	111.9(2)	111.2(5)
C(7)—C(8)—C(9)	110.7(2)	110.8(6)
C(9)—C(10)—C(11)	111.1(3)	110.8(8)
C(7)—C(12)—C(11)	110.8(2)	110.6(5)
N(6)—C(13)—C(18)	112.7(2)	113.1(5)
C(13)—C(14)—C(15)	110.4(2)	109.7(5)
C(15)—C(16)—C(17)	111.7(2)	112.4(9)
C(13)—C(18)—C(17)	110.8(1)	111.2(7)
C(1')—O(2')—C(3')	110.9(1)	114.4(5)
C(3')—C(4')—O(5')	118.5(2)	116.7(6)
O(5')—C(4')—N(6')	122.1(2)	123.6(5)
C(4')—N(6')—C(7')	122.9(2)	122.3(5)
C(7')—N(6')—C(13')	117.2(2)	118.2(5)
N(6')—C(7')—C(12')	112.3(2)	111.2(5)
C(7')—C(8')—C(9')	110.2(2)	110.2(7)
C(9')—C(10')—C(11')	111.5(3)	110.9(9)
C(7')—C(12')—C(11')	111.3(2)	108.2(6)
N(6')—C(13')—C(18')	112.6(2)	112.8(5)
C(13')—C(14')—C(15')	110.1(2)	112.1(7)
C(15')—C(16')—C(17')	110.7(2)	111.8(9)
C(13')—C(18')—C(17')	110.9(2)	111.7(5)
C(1'')—O(2'')—C(3'')	113.1(1)	113.4(4)
C(3'')—C(4'')—O(5'')	118.0(2)	121.0(6)
O(5'')—C(4'')—N(6'')	122.9(2)	120.9(5)
C(4'')—N(6'')—C(7'')	122.3(2)	121.7(5)
C(7'')—N(6'')—C(13'')	117.6(2)	118.3(5)
N(6'')—C(7'')—C(12'')	113.0(2)	112.5(7)
C(7'')—C(8'')—C(9'')	111.2(2)	110.9(7)
C(9'')—C(10'')—C(11'')	111.9(2)	111.6(10)
C(7'')—C(12'')—C(11'')	110.4(2)	110.4(8)
N(6'')—C(13'')—C(18'')	113.2(2)	114.1(6)
C(13'')—C(14'')—C(15'')	111.2(3)	110.4(6)
C(15'')—C(16'')—C(17'')	110.9(3)	111.7(7)
C(13'')—C(18'')—C(173'')	110.4(3)	110.0(6)

TABLE VI. Continued.

	1	1b
C(1)—C(19)—C(1'')	110.3(2)	112.3(6)
C(1)—C(19)—C(20)	106.8(2)	106.4(6)
C(1'')—C(19)—C(20)	111.6(2)	105.3(7)
C(19)—C(20)—C(21')	—	118.9(7)
O(2)—C(1)—C(19)	110.1(1)	111.4(5)
O(2)—C(3)—C(4)	113.3(2)	106.9(5)
C(3)—C(4)—N(6)	118.8(2)	119.2(6)
C(4)—N(6)—C(13)	119.3(2)	119.7(5)
N(6)—C(7)—C(8)	112.4(2)	112.7(5)
C(8)—C(7)—C(12)	112.1(2)	111.3(6)
C(8)—C(9)—C(10)	112.1(3)	111.7(6)
C(10)—C(11)—C(12)	11.5(3)	110.9(6)
N(6)—C(13)—C(14)	113.3(2)	112.2(4)
C(14)—C(13)—C(18)	111.6(2)	111.7(6)
C(14)—C(51)—C(16)	110.9(2)	111.6(8)
C(16)—C(17)—C(18)	111.7(2)	1009.6(6)
O(2')—C(1')—C(19)	110.5(1)	111.7(6)
O(2')—C(3')—C(4)	111.3(2)	106.9(6)
C(3')—C(4')—N(6')	119.6(2)	119.6(6)
C(4')—N(6')—C(13')	119.8(2)	119.4(6)
N(6')—C(7')—C(8')	111.9(2)	112.3(6)
C(8')—C(7')—C(12')	111.5(2)	112.2(6)
C(8')—C(9')—C(10')	112.0(2)	110.9(8)
C(10')—C(11')—C(12')	111.2(2)	112.2(9)
N(6')—C(13')—C(14')	113.7(2)	114.2(6)
C(14')—C(13')—C(18')	111.9(2)	111.2(6)
C(14')—C(14')—C(16')	111.4(3)	111.6(7)
C(16')—C(17')—C(18')	111.6(3)	112.4(8)
O(2'')—C(1'')—C(19)	110.1(1)	111.6(5)
O(2'')—C(3'')—C(4'')	110.1(2)	105.4(5)
C(3'')—C(4'')—N(6'')	119.0(2)	118.1(5)
C(4'')—N(6'')—C(13'')	119.9(2)	119.9(5)
N(6'')—C(7'')—C(8'')	113.0(2)	112.9(5)
C(8'')—C(7'')—C(12'')	111.1(2)	110.4(6)
C(8'')—C(9'')—C(10'')	111.8(3)	111.1(10)
C(10'')—C(11'')—C(12'')	111.6(2)	111.7(8)
N(6'')—C(13'')—C(14'')	113.0(2)	113.4(6)
C(14'')—C(13'')—C(18'')	111.5(2)	111.4(5)
C(14'')—C(15'')—C(16'')	111.6(2)	111.1(7)
C(16'')—C(17'')—C(18'')	112.0(3)	111.9(7)
C(1)—C(19)—C(1')	110.3(2)	112.0(5)
C(1')—C(19)—C(1'')	110.3(2)	111.8(6)
C(1'')—C(19'')—C(20)	111.6(2)	108.5(6)
C(19)—C(20)—C(21)	116.0(1)	121.3(11)
C(21)—C(20)—C(21')	—	98.8(13)

TABLE VII. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for ligand 1.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(1)	7615(2)	6824(2)	6237(1)	38(1)
O(2)	8371(1)	6295(1)	6612(1)	40(1)
C(3)	7701(2)	5241(2)	6843(1)	43(1)
C(4)	6493(2)	5340(2)	7383(1)	38(1)
O(5)	5458(1)	4920(1)	7204(1)	52(1)
N(6)	6613(2)	5886(2)	8021(1)	38(1)
C(7)	7861(2)	6355(2)	8249(1)	40(1)
C(8)	8071(2)	7627(2)	8349(2)	53(1)
C(9)	9375(3)	8075(3)	8562(2)	76(1)
C(10)	9564(3)	7556(3)	9214(2)	85(1)
C(11)	9352(3)	6280(3)	9108(2)	73(1)
C(12)	8044(2)	5819(3)	8903(1)	56(1)
C(13)	5448(2)	6047(2)	8533(1)	40(1)
C(14)	4623(2)	6762(2)	8267(1)	50(1)
C(15)	3516(2)	6981(2)	8842(2)	62(1)
C(16)	2728(2)	5882(3)	9093(2)	67(1)
C(17)	3542(2)	5153(2)	9346(1)	60(1)
C(18)	4668(2)	4944(2)	8783(1)	50(1)
C(1')	8924(2)	8730(2)	6398(1)	39(1)
O(2')	7877(1)	9168(1)	6826(1)	42(1)
C(3')	8317(2)	10094(2)	7291(1)	46(1)
C(4')	7255(2)	10358(2)	7881(1)	48(1)
O(5')	7365(2)	10243(2)	8495(1)	71(1)
N(6')	6235(2)	10745(1)	7718(1)	45(1)
C(7')	6104(2)	10921(2)	6983(1)	43(1)
C(8')	6013(3)	12149(2)	6897(1)	49(1)
C(9')	5932(3)	12302(2)	6129(1)	60(1)
C(10')	4838(3)	11505(2)	5866(1)	58(1)
C(11')	4916(3)	10287(2)	5958(1)	58(1)
C(12')	5001(3)	10118(2)	6726(1)	53(1)
C(13')	5164(2)	10953(2)	8287(1)	48(1)
C(14')	5536(3)	11897(2)	8839(1)	63(1)
C(15')	4361(3)	12112(2)	9368(1)	71(1)
C(16')	3699(4)	11056(3)	9723(2)	90(1)
C(17')	3325(4)	10117(3)	9173(2)	83(1)
C(18')	4475(3)	9882(2)	8632(1)	64(1)
C(1'')	9638(2)	7435(2)	5410(1)	38(1)
O(2'')	9293(1)	6413(1)	5004(1)	44(1)
C(3'')	10274(2)	6181(2)	4427(1)	40(1)
C(4'')	10055(2)	6624(2)	3751(1)	39(1)
O(5'')	10738(2)	7494(2)	3549(1)	56(1)
N(6'')	9125(2)	6051(1)	3401(1)	44(1)

TABLE VII. Continued.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(7'')	8235(2)	5058(2)	3683(1)	48(1)
C(8'')	8316(3)	3999(2)	3198(1)	64(1)
C(9'')	7452(3)	2980(3)	3534(2)	78(1)
C(10'')	6090(3)	3183(3)	4229(2)	69(1)
C(11'')	6015(3)	4249(3)	4229(2)	78(1)
C(12'')	6860(2)	5264(2)	3883(2)	64(1)
C(13'')	8901(2)	6467(2)	2737(1)	50(1)
C(14'')	10046(3)	6492(3)	2148(1)	62(1)
C(15'')	9739(4)	6836(3)	1460(2)	82(1)
C(16'')	9246(3)	7950(3)	1570(2)	81(1)
C(17'')	8112(4)	7915(4)	2161(2)	90(1)
C(18'')	8417(3)	7584(3)	2855(2)	66(1)
C(19)	8446(2)	7808(2)	5858(1)	35(1)
C(20)	7613(2)	8230(2)	5395(1)	44(1)
C(21)	8219(3)	9271(3)	5009(2)	67(1)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

The amide carbonyls are better electron donors than ether oxygens and therefore the complexed lithium ion interacts more strongly with the carbonyl than with the ether oxygens. It is reflected in the observed Li—O distances of the complex studied. The amide oxygen atoms give shorter contacts with Li ion (2.006, 2.007 and 2.026 Å) than the ether oxygen atoms (2.138, 2.144 and 2.190 Å). These distances are typical, and are in agreement with the finding that the average Li—O distance increases slightly with the increase of the lithium coordination number [18].

The complex ion has an approximate C_3 symmetry. This symmetry, however, is broken by the presence of the methyl group attached to C(20). In crystals this group is disordered and adopts two different orientations along the C(19)—C(20) bond.

A knowledge of the crystal structures of Li complexes will hopefully lead to a better understanding of the biological activity of the lithium ion and to the synthesis of better, more selective lithium ionophores. However, it should be emphasized that the structure of the complex in the solid state may differ from that in solution.

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TABLE VIII. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) in complex **1b**.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Li ⁺	7699(5)	-259(6)	7790(6)	80(4)
C(1)	8434(3)	1150(4)	8965(4)	96(3)
O(2)	7845(2)	694(3)	8591(2)	95(2)
C(3)	7344(3)	798(3)	8888(4)	87(3)
C(4)	6765(3)	247(4)	8458(4)	78(3)
O(5)	6815(2)	-146(3)	7935(3)	91(2)
N(6)	6220(2)	212(3)	8647(3)	79(2)
C(7)	6161(3)	700(3)	9263(3)	82(3)
C(8)	6023(4)	176(4)	9836(4)	106(4)
C(9)	5977(4)	701(5)	10461(4)	123(4)
C(10)	5457(4)	1363(5)	10186(5)	124(4)
C(11)	5601(4)	1891(4)	9625(5)	120(3)
C(12)	5640(3)	1371(4)	8983(4)	98(3)
C(13)	5646(3)	-313(3)	8222(4)	83(3)
C(14)	5829(3)	-1227(4)	8299(4)	106(3)
C(15)	5205(4)	-1740(5)	7897(7)	136(5)
C(16)	4888(5)	-1489(7)	7114(7)	155(6)
C(17)	4705(4)	-578(6)	7031(5)	138(4)
C(18)	5332(3)	-63(4)	7433(4)	115(4)
C(1')	8811(3)	1141(4)	7883(3)	101(3)
O(2')	8281(2)	647(3)	7438(2)	94(2)
C(3')	8119(3)	760(4)	6678(3)	86(3)
C(4')	7558(3)	152(4)	6288(4)	83(3)
O(5')	7368(2)	-305(3)	6688(2)	97(2)
N(6')	7322(2)	113(3)	5563(3)	81(2)
C(7')	7541(3)	1189(4)	4597(4)	118(4)
C(8')	6968(4)	1185(4)	4597(4)	118(4)
C(9')	7225(5)	1794(5)	4163(6)	142(5)
C(10')	7598(6)	1361(7)	3747(6)	153(6)
C(11')	8163(5)	870(5)	4253(5)	137(5)
C(12')	7925(4)	238(4)	4682(4)	108(3)
C(13')	6800(3)	-505(4)	5188(4)	90(3)
C(14')	6155(3)	-390(5)	5310(5)	123(4)
C(15')	5630(4)	-1009(7)	4887(5)	151(5)
C(16')	5884(5)	-1869(7)	5052(6)	154(6)
C(17')	6532(5)	-1985(5)	4935(4)	127(4)
C(18')	7052(3)	-1379(4)	5353(4)	98(3)
C(1'')	9230(3)	66(4)	8851(4)	109(3)
O(2'')	8700(2)	-498(3)	8524(3)	101(2)
C(3'')	8914(3)	-1330(4)	8601(4)	101(3)
C(4'')	8297(3)	-1820(4)	8218(3)	84(3)
O(5'')	7753(2)	-1489(2)	7942(3)	101(2)
N(6'')	8359(2)	-2658(3)	8193(3)	88(2)

TABLE VIII. Continued.

	x	y	z	$U(\text{eq})$
C(7'')	9014(3)	-3066(4)	8500(4)	97(3)
C(8'')	9172(4)	-3601(7)	7940(5)	123(4)
C(9'')	9871(5)	-3965(7)	8268(8)	164(7)
C(10'')	9948(5)	-4436(8)	8945(8)	179(7)
C(11'')	9787(5)	-3922(7)	9502(6)	166(6)
C(12'')	9087(4)	-3552(4)	9183(4)	118(4)
C(13'')	7760(3)	-3167(4)	7857(4)	89(3)
C(14'')	7420(4)	-3028(4)	7035(4)	110(4)
C(15'')	6854(4)	-3640(5)	6711(52)	130(4)
C(16'')	6360(4)	-3614(5)	7116(62)	136(5)
C(17'')	6697(4)	-3743(5)	7911(5)	118(4)
C(18'')	7258(3)	-3126(4)	8247(4)	102(3)
C(19)	8996(3)	941(4)	8685(3)	86(3)
C(20)	9605(3)	1474(5)	9132(3)	117(4)
C(21A)	10207(11)	1412(13)	9032(12)	117(10)
C(21B)	9538(7)	2322(10)	9100(8)	145(7)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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