

X-Ray Structure and Proton NMR Study of a Hexacoordinated Lithium Complex

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Abstract. The structure of the lithium complex with 1,3,5-tris[oxymethylene(*N,N*-dicyclohexyl)carboxyamido]cyclohexane has been determined by the X-ray method. The compound is triclinic, space group $P\bar{1}$, $a = 15.623(3)$, $b = 19.279(4)$, $c = 19.295(4)\text{\AA}$, $\alpha = 102.32(3)$, $\beta = 92.45(3)$, $\gamma = 105.67(3)^\circ$, $V = 5436(2)\text{\AA}^3$, $Z = 4$. Its composition is represented by the formula $\text{C}_{48}\text{H}_{82}\text{N}_3\text{O}_6\text{Li}\cdot 0.5\text{H}_2\text{O}$. The lithium cation is encapsulated in a polar pseudo-cavity of six oxygen atoms of the ligand molecule and displays a distorted trigonal prism coordination. The conformation of the ligand in the solid state complex has been compared with the conformation of the complex in solution determined by $^1\text{H-NMR}$ measurements.

Key words: X-ray, crystal structure, Li-complex, triamides, $^1\text{H-NMR}$.

Supplementary data relevant to this publication have been deposited with the British Library, No. SUP 82224 (21 pages).

1. Introduction

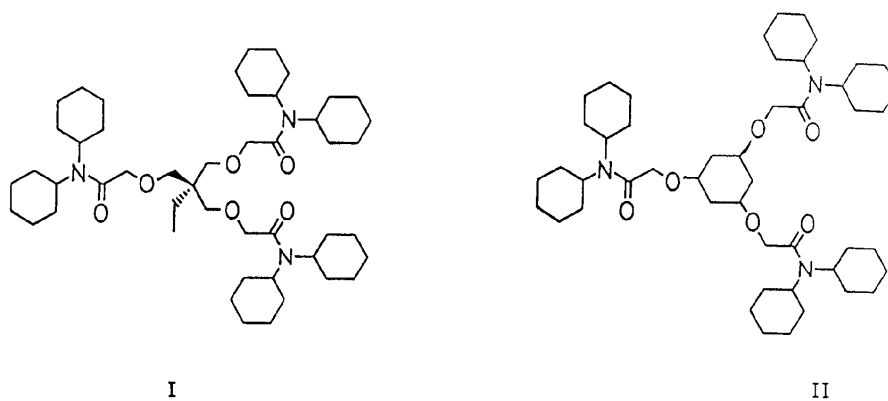
The coordination number of lithium varies from 2 to 8 in different complexes, depending on the number of binding sites in the ligand. However the most common numbers are 4, 5 and 6. The very high charge density of lithium is the reason for the high solvation energy and the tendency towards hydration. The lithium cation forms stable hydrates of much larger size than the calculated size of the naked ion. The difference in size causes a severe problem in choosing the right size ligands for Li complexation. The open chain ligands, the podands, are flexible and when complexing they wrap around the ion forming a pseudo-cavity, adjusting their conformation to the size of the cation.

The modification of the structure of carboxyamidopodands towards lipophilization seems to be more convenient than modification of the crown ethers [1, 2]. The high lipophilicity of dicyclohexylamides and the appropriate number of binding

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sites of high polarizability, such as amide carbonyls and ether oxygen atoms, is the reason for the good ionophoric behavior of such compounds as lithium ligands [2]. The spatial arrangement of the binding centers in amide podands is more flexible than in the small crown ethers; they can exchange the hydration shell of the Li cation slowly, stepwise. Among many amides of quite similar structure, tripodands – the octopus-like molecules with six coordinating centers shown below as compounds **I** and **II** – were found to have the best ionophoric properties [1–3].

In our previous paper [2] we described the crystal structure of the free ligand **I** and its LiBr-complex. Here we present the X-ray structure of the complex of lithium iodide with ligand **II**. The complexation of Li ion was also investigated by $^1\text{H-NMR}$ spectroscopy. The conformation of the complex in solution, revealed by $^1\text{H-NMR}$, has been compared with the conformation in the solid state obtained by X-ray analysis.



Formulas of **I** and **II**.

2. Experimental

2.1. SYNTHESIS OF COMPOUND **II**

A mixture of 1,3,5-*cis,cis*-cyclohexanetriol (Aldrich) 1 mM (168.19 mg) and 3 mM (150 mg) of NaH (50% in oil) in 15 mL of benzene was refluxed for about 0.5 h. A benzene solution of freshly prepared chloroacet-*N,N*-dicyclohexylamide (3 mM, 770 mg) was then added in portions. The mixture was refluxed for 24 h. After cooling the precipitate was filtered off and the filtrate was evaporated to dryness and then dissolved in 20 mL of methylene chloride. The solution was washed twice with water, dried with MgSO_4 and chromatographed on silicagel. The fraction eluted with CH_2Cl_2 /hexane (1 : 2) was collected. The yield of the product was 62%; m.p. 180–182 °C. The $^1\text{H-NMR}$ and mass spectra of the compound confirmed its structure and purity: NMR (CDCl_3): 4.12(s) 6H(O—CH₂—CO), 3.40(t), $J = 11.2$ Hz 6H (3H1'' and 3H1'), 2.91(broad singlet) (3H1), 2.54(d) $J = 11.2$ Hz 6H2' 2.47(broad singlet) 3H2, 1.05–1.9(m) others. MS (M^+) = 795.

2.2. SYNTHESIS OF THE LiI COMPLEX **IIIb**

Compound **II** (100 mg) and LiI (20 mg) were dissolved in 5 mL of methanol under reflux. After 48 h at room temperature single crystals suitable for X-ray analysis appeared; m.p. 248–50 °C, yield 70%. They were stable in the mother liquor, but when exposed to air they lost transparency.

2.3. NMR SPECTRA

The proton NMR spectra were recorded on Varian 200 MHz and/or 500 MHz spectrometers. The double resonance technique was used for determination of the H1, H1' and H1'', H3'', H5'' signals. Deuterated methanol, acetone and chloroform used as the solvents were purchased from Aldrich.

2.4. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR THE COMPLEX **IIIb**

A prismatic, colorless crystal was mounted in a sealed glass capillary. Preliminary examination and data collection were performed on a CAD-4 diffractometer (CuK α radiation). The cell constants and orientation matrices were calculated from the least-squares fitting of the setting angles for 25 reflections. Three control reflections were collected every hour. The crystals, stable in the capillary under normal conditions, were slowly destroyed under X-ray radiation. So, when the intensity of the control reflections decreased to about 80% of the initial value, the data collection sample was changed. Two samples were used for data collection. Crystal data and details of data collection together with structure refinement are summarized in Table I. Intensity data were corrected for Lorentz and polarization factors. The structure was solved by the heavy atom method. Non-H atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure based on F^2 . Hydrogen atoms were placed in idealized positions and their U values were fixed at 1.2 times U_{eq} of the corresponding C atoms. The highest peak on the difference electron density map, 5.2 e/Å³, was interpreted as the O-atom of the water molecule and was included in the refinement. The R index at this stage decreased from $R = 0.141$ to a final value $R_1 = 0.130$. The hydrogen atoms of the water molecule were not localized. The remaining highest four peaks in the final difference electron density map had values from 3.0–2.6 e/Å³ and were situated at distances of about 1 Å around the iodide atoms. The remaining peaks had values smaller than 1.4 e/Å³. The refinement of the structure in the non-centrosymmetric space group $P1$ did not decrease the R index and resulted in a similar difference electron density map. Neutral atom scattering factors with anomalous dispersion corrections were taken from Ref. [4]. All calculations were performed using the SHELXS-86 and SHELXS-93 program packages [5]. Atomic coordinates and equivalent isotropic thermal parameters are given in Table II. The large values of U_{eq}

Table I. Crystal data and structure refinement for Li complex **IIIb**.

Empirical formula	C ₄₈ H ₈₂ ILiN ₃ O ₆ 0.5H ₂ O
Formula weight	938.00
Temperature	293(2)K
Wavelength	1.54180 Å
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell	<i>a</i> = 15.623(3)Å <i>b</i> = 19.279(4)Å <i>c</i> = 19.295(4)Å α = 102.32(3)° β = 92.45(3)° γ = 105.67(3)°
Volume	5436(2)Å ³
<i>Z</i>	4
Density (calculated)	1.146 g/cm ³
Absorption coefficient	4.972 mm ⁻¹
<i>F</i> (000)	1992
Crystal size	0.40 × 0.25 × 0.20 mm
Theta range for data collection	2.36–55.24°
Index ranges	0 ≤ <i>h</i> ≤ 13, –20 ≤ <i>k</i> ≤ 19, –20 ≤ <i>l</i> ≤ 20
Reflections collected	7282
Independent reflections	7265 [<i>R</i> (int) = 0.0320]
Refinement method	Full-matrix-block least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.052
Final <i>R</i> indices for 7217 <i>F</i> ₀	<i>R</i> ₁ ^(a) = 0.1303
with <i>I</i> > 26(<i>I</i>)	<i>wR</i> ₂ ^(b) = 0.3211
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1316, <i>wR</i> ₂ = 0.3292
Largest diff. peak and hole	3.009 and –1.561 e Å ⁻³

$$^a R_1 = \frac{\sum[|F_0| - |F_c|]}{\sum|F_0|}$$

$$^b wR_2 = \frac{[\sum w(F_0^2 - F_c^2)^2]}{[\sum w(F_0^2)^2]^{0.5}}$$

$$w = 1/[\sigma^2(F_0^2) + (0.3102 \cdot P)^2 + 7.66 \cdot P] \text{ where } P = (\max(F_0^2, 0) + 2 \cdot F_0^2)/3.$$

might be explained by a slight disorder of bulky complexes in crystal packing. Bond distances, angles and selected torsion angles are listed in Table III.

3. Results and Discussion

3.1. X-RAY STRUCTURE

The crystal structure data show that two similar crystallographically independent complexes and one water molecule are present in the unit cell. The view of complex

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **IIb**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
I(1)	7834(1)	3545(1)	574(1)	90(1)
I(2)	12112(1)	4035(1)	3996(1)	102(1)
OW1	8492(12)	4251(12)	6125(12)	258(9)
<i>Molecule 1</i>				
Li(1)	7759(8)	2758(8)	3800(5)	70(6)
C(1)	9403(8)	4254(6)	4047(5)	67(4)
C(2)	9581(9)	4063(7)	3288(5)	79(4)
C(3)	8734(8)	3816(5)	2774(5)	71(4)
C(4)	8147(9)	4319(7)	2913(6)	81(4)
C(5)	7964(8)	4522(6)	3677(5)	70(4)
C(6)	8808(8)	4744(6)	4187(5)	75(4)
O(2A)	9014(6)	3586(4)	4292(4)	84(3)
C(3A)	9665(8)	3277(7)	4546(8)	90(5)
C(4A)	9175(9)	2512(6)	4609(6)	74(4)
O(5A)	8415(6)	2214(4)	4320(4)	81(3)
N(6A)	9630(7)	2190(5)	5004(5)	77(3)
C(7A)	10550(10)	2553(7)	5308(6)	97(5)
C(8A)	10626(12)	2903(10)	6111(7)	139(7)
C(9A)	11594(12)	3329(11)	6375(11)	185(13)
C(10A)	12213(13)	2855(11)	6216(10)	176(12)
C(11A)	12128(11)	2498(12)	5427(10)	181(11)
C(12A)	11165(9)	2071(11)	5157(10)	146(8)
C(13A)	9185(9)	1474(6)	5136(7)	86(5)
C(14A)	8397(10)	1468(8)	5564(9)	109(6)
C(15A)	8003(15)	751(9)	5762(10)	153(8)
C(16A)	7823(12)	111(10)	5143(11)	169(11)
C(17A)	8591(13)	100(7)	4699(11)	143(8)
C(18A)	8964(11)	833(7)	4507(8)	115(6)
O(2B)	8268(5)	3066(4)	2816(3)	74(3)
C(3B)	7630(9)	2667(6)	2212(5)	77(4)
C(4B)	7023(8)	2010(5)	2400(5)	68(4)
O(5B)	7077(7)	1937(4)	3017(3)	92(3)
N(6B)	6411(7)	1509(4)	1884(4)	80(4)
C(7B)	6302(10)	1632(6)	1150(5)	83(5)
C(8B)	6514(14)	1031(7)	595(5)	123(7)
C(9B)	6450(13)	1180(9)	-144(6)	132(8)
C(10B)	5519(12)	1281(7)	-329(7)	121(7)
C(11B)	5346(11)	1893(7)	226(7)	108(6)
C(12B)	5391(9)	1723(8)	958(6)	97(5)
C(13B)	5794(10)	870(6)	2044(7)	124(8)
C(14B)	6272(14)	359(6)	2284(8)	166(11)
C(15B)	5635(20)	-333(10)	2422(13)	266(23)
C(16B)	4960(21)	-133(12)	2899(15)	398(48)
C(17B)	4485(17)	377(14)	2675(13)	270(22)
C(18B)	5154(12)	1062(9)	2565(8)	150(9)
O(2C)	7359(5)	3839(3)	3830(4)	75(3)
C(3C)	6856(9)	3991(6)	4409(6)	79(4)
C(4C)	6531(8)	3289(5)	4655(5)	61(4)

Table II. Continued.

Atom	x	y	z	U_{eq}
<i>Molecule 1 continued</i>				
O(5C)	6841(6)	2772(4)	4440(4)	81(3)
N(6C)	5940(6)	3253(4)	5151(4)	64(3)
C(7C)	5609(8)	3884(6)	5471(5)	75(4)
C(8C)	4611(8)	3752(7)	5247(6)	86(4)
C(9C)	4283(11)	4406(8)	5592(6)	107(5)
C(10C)	4477(10)	4611(7)	6391(6)	98(5)
C(11C)	5469(10)	4758(7)	6614(8)	103(5)
C(12C)	5814(11)	4104(7)	6286(6)	104(5)
C(13C)	5548(8)	2543(5)	5349(5)	69(4)
C(14C)	5051(10)	1929(6)	4728(6)	99(5)
C(15C)	4596(11)	1243(7)	4979(8)	131(8)
C(16C)	5250(14)	997(7)	5403(8)	143(9)
C(17C)	5778(13)	1629(6)	6004(7)	124(7)
C(18C)	6237(9)	2316(7)	5753(7)	88(5)
<i>Molecule 2</i>				
Li(2)	2022(7)	3418(8)	10269(7)	204(21)
C(1')	1892(9)	4466(7)	11845(6)	92(5)
C(2')	2394(10)	5163(6)	11656(7)	92(5)
C(3')	2123(11)	5158(7)	10900(6)	101(6)
C(4')	1140(10)	5032(8)	10751(7)	97(5)
C(5')	605(10)	4327(7)	10930(6)	94(5)
C(6')	898(9)	4291(8)	11688(6)	90(5)
O(2D)	2185(7)	3841(4)	11469(4)	101(3)
C(3D)	2142(11)	3287(6)	11844(6)	94(5)
C(4D)	2145(9)	2603(5)	11304(6)	81(4)
O(5D)	2210(7)	2623(4)	10683(4)	97(3)
N(6D)	2140(8)	1990(5)	11531(5)	87(4)
C(7D)	2125(10)	1965(8)	12292(7)	108(6)
C(8D)	1257(15)	1430(10)	12407(8)	202(14)
C(9D)	1241(22)	1429(12)	13206(9)	258(22)
C(10D)	2054(22)	1231(14)	13459(13)	279(27)
C(11D)	2901(21)	1814(18)	13368(11)	312(28)
C(12D)	2974(16)	1840(14)	12576(9)	204(13)
C(13D)	2112(10)	1320(6)	11018(7)	112(6)
C(14D)	1291(10)	1022(7)	10491(7)	105(5)
C(15D)	1254(11)	298(8)	9983(9)	127(7)
C(16D)	2061(11)	385(9)	9587(10)	136(7)
C(17D)	2876(13)	646(10)	10124(11)	154(8)
C(18D)	2925(11)	1377(7)	10612(10)	125(7)
O(2E)	2447(8)	4615(4)	10415(5)	117(4)
C(3E)	2958(8)	4872(5)	9908(6)	65(4)
C(4E)	3246(7)	4257(5)	9481(5)	51(3)
O(5E)	2977(5)	3628(3)	9606(4)	65(2)
N(6E)	3806(6)	4415(4)	8980(4)	55(3)
C(7E)	4144(7)	5161(5)	8876(5)	57(3)
C(8E)	5144(7)	5486(5)	9035(6)	69(4)
C(9E)	5421(9)	6282(6)	8982(7)	84(4)

Table II. Continued.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(10E)	5156(9)	6333(6)	8226(6)	83(4)
C(11E)	4157(8)	6013(6)	8059(7)	79(4)
C(12E)	3824(9)	5213(6)	8134(5)	80(4)
C(13E)	4142(7)	3831(5)	8565(5)	59(3)
C(14E)	4753(9)	3545(7)	9005(6)	81(4)
C(15E)	5155(10)	3035(7)	8532(8)	104(5)
C(16E)	4469(11)	2397(7)	8045(8)	125(7)
C(17E)	3856(10)	2676(7)	7613(7)	106(6)
C(18E)	3444(8)	3190(6)	8091(6)	77(4)
O(2F)	731(6)	3649(5)	10472(4)	96(3)
C(3F)	131(10)	3429(9)	9822(7)	113(6)
C(4F)	384(9)	2816(7)	9331(6)	88(5)
O(5F)	1100(6)	2720(5)	9479(4)	86(3)
N(6F)	-174(8)	2404(6)	8742(5)	101(4)
C(7F)	-1031(12)	2537(9)	8538(8)	132(8)
C(8F)	-1033(13)	2747(10)	7813(8)	148(8)
C(9F)	-1938(16)	2911(15)	7688(13)	249(21)
C(10F)	-2727(18)	2240(16)	7678(10)	249(20)
C(11F)	-2713(14)	2015(19)	8388(11)	239(17)
C(12F)	-1824(12)	1881(12)	8555(9)	158(9)
C(13F)	51(9)	1798(6)	8273(6)	77(4)
C(14F)	875(10)	2038(6)	7900(7)	92(5)
C(15F)	1026(13)	1403(8)	7342(8)	129(7)
C(16F)	1104(17)	795(11)	7683(10)	177(11)
C(17F)	291(14)	539(7)	8069(9)	148(9)
C(18F)	147(11)	1179(7)	8610(8)	116(6)

IIb (molecule 1 and molecule 2) are shown in Figures 1a and b. They are in different orientations.

The Li cations in both complex molecules are completely encapsulated in a polar pseudo-cavity of three ether oxygen and three carbonyl oxygen atoms and display a distorted trigonal prism coordination. The bases of the prism determined by the three oxygen atoms lay in nearly parallel planes; the angles between both planes in molecule 1 is $1.7(4)^\circ$ and $1.5(4)^\circ$ in molecule 2. The Li atom does not occupy the center of the prism. The deviation of the lithium atom from the plane determined by three ether oxygen atoms are $1.50(2)$ and $1.52(2)$ Å in molecule 1 and 2, respectively, while the deviation from the plane of the three carbonyl oxygen atoms are only $0.96(2)$ and $0.97(2)$ Å, respectively.

Each arm of the ligand molecule coordinates to lithium in an *O, O*-bidentate fashion and forms a five membered metallocycle. Chelate fragments determined by O(2), C(3), C(4), O(5) atoms are almost planar, the torsion angles O(2)—C(3)—

Table III. Selected bond lengths [\AA] and angles [$^\circ$] for **IIIb**.

Molecule 1		Molecule 2	
<i>Coordination polyhedron of Li</i>			
O(2A)—Li(1)	2.19(1)	O(2D)—Li(2)	2.26(1)
O(5A)—Li(1)	2.03(1)	O(5D)—Li(2)	1.95(1)
O(2B)—Li(1)	2.22(1)	O(2E)—Li(2)	2.17(2)
O(5B)—Li(1)	1.96(1)	O(5E)—Li(2)	2.02(1)
O(2C)—Li(1)	2.32(1)	O(2F)—Li(2)	2.21(2)
O(5C)—Li(1)	1.93(1)	O(5F)—Li(2)	2.03(1)
O(5C)—Li(1)—O(5B)	99.0(6)	O(5D)—Li(2)—O(5E)	106.8(8)
O(5C)—Li(1)—O(5A)	95.7(6)	O(5D)—Li(2)—O(5F)	93.9(6)
O(5B)—Li(1)—O(5A)	100.1(6)	O(5E)—Li(2)—O(5F)	93.6(6)
O(5C)—Li(1)—O(2A)	110.2(4)	O(5D)—Li(2)—O(2E)	142.2(6)
O(5B)—Li(1)—O(2A)	150.6(6)	O(5E)—Li(2)—O(2E)	74.3(3)
O(5A)—Li(1)—O(2A)	75.0(3)	O(5F)—Li(2)—O(2E)	123.9(5)
O(5C)—Li(1)—O(2B)	145.7(5)	O(5D)—Li(2)—O(2F)	113.4(5)
O(5B)—Li(1)—O(2B)	75.3(3)	O(5E)—Li(2)—O(2F)	138.2(5)
O(5A)—Li(1)—O(2B)	118.6(5)	O(5F)—Li(2)—O(2F)	73.1(4)
O(2A)—Li(1)—O(2B)	81.7(5)	O(2E)—Li(2)—O(2F)	80.8(6)
O(5C)—Li(1)—O(2C)	72.9(3)	O(5D)—Li(2)—O(2D)	73.0(3)
O(5B)—Li(1)—O(2C)	112.4(4)	O(5E)—Li(2)—O(2D)	126.5(5)
O(5A)—Li(1)—O(2C)	146.7(5)	O(5F)—Li(2)—O(2D)	139.7(5)
O(2A)—Li(1)—O(2C)	79.8(5)	O(2E)—Li(2)—O(2D)	76.6(5)
O(2B)—Li(1)—O(2C)	78.1(5)	O(2F)—Li(2)—O(2D)	77.6(5)
<i>Ligands</i>			
C(1)—O(2A)	1.45(1)	C(1')—O(2D)	1.46(1)
C(3)—O(2B)	1.45(1)	C(3')—O(2E)	1.46(1)
C(5)—O(2C)	1.49(1)	C(5')—O(2F)	1.48(1)
O(2A)—C(3A)	1.43(1)	O(2D)—C(3D)	1.40(1)
C(3A)—C(4A)	1.50(1)	C(3D)—C(4D)	1.49(1)
C(4A)—O(5A)	1.22(1)	C(4D)—O(5D)	1.21(1)
C(4A)—N(6A)	1.37(1)	C(4D)—N(6D)	1.34(1)
N(6A)—C(13A)	1.45(1)	N(6D)—C(13D)	1.44(1)
N(6A)—C(7A)	1.45(2)	N(6D)—C(7D)	1.48(2)
O(2B)—C(3B)	1.43(1)	O(2E)—C(3E)	1.38(1)
C(3B)—C(4B)	1.49(1)	C(3E)—C(4E)	1.48(1)
C(4B)—O(5B)	1.23(1)	C(4E)—O(5E)	1.25(1)
C(4B)—N(6B)	1.36(1)	C(4E)—N(6E)	1.36(1)
N(6B)—C(13B)	1.45(1)	N(6E)—C(7E)	1.45(1)
N(6B)—C(7B)	1.50(1)	N(6E)—C(13E)	1.47(1)
O(2C)—C(3C)	1.42(1)	O(2F)—C(3F)	1.45(1)
C(3C)—C(4C)	1.50(1)	C(3F)—C(4F)	1.50(2)
C(4C)—O(5C)	1.23(1)	C(4F)—O(5F)	1.21(1)
C(4C)—N(6C)	1.36(1)	C(4F)—N(6F)	1.36(1)
N(6C)—C(7C)	1.48(1)	N(6F)—C(13F)	1.45(1)
N(6C)—C(13C)	1.49(1)	N(6F)—C(7F)	1.48(2)

Table III. Continued.

Molecule 1		Molecule 2	
<i>Ligands continued</i>			
O(2A)—C(1)—C(2)	110.5(9)	O(2D)—C(1')—C(2')	110.4(10)
O(2A)—C(1)—C(6)	108.4(9)	O(2D)—C(1')—C(6')	109.1(10)
O(2B)—C(3)—C(4)	111.6(10)	O(2E)—C(3')—C(4')	112.2(11)
O(2B)—C(3)—C(2)	106.7(8)	O(2E)—C(3')—C(2')	109.5(11)
O(2C)—C(5)—C(4)	106.6(8)	O(2F)—C(5')—C(4')	113.4(10)
O(2C)—C(5)—C(6)	107.2(9)	O(2F)—C(5')—C(6')	103.9(10)
C(3A)—O(2A)—C(1)	113.4(8)	C(3D)—O(2D)—C(1')	114.2(9)
C(3A)—O(2A)—Li(1)	113.6(6)	C(3D)—O(2D)—Li(2)	113.7(6)
C(1)—O(2A)—Li(1)	123.8(6)	C(1')—O(2D)—Li(2)	124.7(6)
O(2A)—C(3A)—C(4A)	106.9(9)	O(2D)—C(3D)—C(4D)	106.4(9)
O(5A)—C(4A)—N(6A)	123.8(10)	O(5D)—C(4D)—N(6D)	121.3(11)
O(5A)—C(4A)—C(3A)	120.3(10)	O(5D)—C(4D)—C(3D)	120.0(10)
N(6A)—C(4A)—C(3A)	115.9(10)	N(6D)—C(4D)—C(3D)	118.5(10)
C(4A)—O(5A)—Li(1)	121.1(7)	C(4D)—O(5D)—Li(2)	124.2(8)
C(4A)—N(6A)—C(13A)	119.5(10)	C(4D)—N(6D)—C(13D)	119.3(10)
C(4A)—N(6A)—C(7A)	121.7(9)	C(4D)—N(6D)—C(7D)	122.5(11)
C(13A)—N(6A)—C(7A)	118.8(10)	C(13D)—N(6D)—C(7D)	118.1(10)
N(6A)—C(7A)—C(12A)	114.2(11)	N(6D)—C(7D)—C(12D)	110.9(12)
N(6A)—C(7A)—C(8A)	112.4(12)	N(6D)—C(7D)—C(8D)	110.6(11)
O(2C)—C(3C)—C(4C)	107.0(8)	O(2F)—C(3F)—C(4F)	107.3(11)
O(5C)—C(4C)—N(6C)	120.8(8)	O(5F)—C(4F)—N(6F)	122.6(12)
O(5C)—C(4C)—C(3C)	119.7(10)	O(5F)—C(4F)—C(3F)	117.6(11)
N(6C)—C(4C)—C(3C)	119.3(9)	N(6F)—C(4F)—C(3F)	119.9(12)
C(4C)—O(5C)—Li(1)	126.4(7)	C(4F)—O(5F)—Li(2)	123.3(8)
C(4C)—N(6C)—C(7C)	122.8(8)	C(4F)—N(6F)—C(13F)	120.5(11)
C(4C)—N(6C)—C(13C)	119.9(8)	C(4F)—N(6F)—C(7F)	123.1(11)
C(7C)—N(6C)—C(13C)	117.2(8)	C(13F)—N(6F)—C(7F)	116.4(10)
N(6C)—C(7C)—C(12C)	111.7(10)	N(6F)—C(7F)—C(12F)	111.3(14)
N(6C)—C(7C)—C(8C)	113.0(8)	N(6F)—C(7F)—C(8F)	111.5(14)
N(6C)—C(13C)—C(14C)	113.5(8)	N(6F)—C(13F)—C(14F)	114.2(10)
N(6C)—C(13C)—C(18C)	111.8(9)	N(6F)—C(13F)—C(18F)	115.6(10)
<i>Selected torsion angles</i>			
O(2A)—C(3A)—C(4A)—O(5A)	15(2)	O(2D)—C(3D)—C(4D)—O(5D)	2(2)
O(2B)—C(3B)—C(4B)—O(5B)	7(2)	O(2E)—C(3E)—C(4E)—O(5E)	3(1)
O(2C)—C(3C)—C(4C)—C(5C)	12(2)	O(2F)—C(3F)—C(4F)—O(5F)	-14(2)

C(4)—O(5) are shown in Table III. It shows a *cis*-conformation. The maximum deviation of these atoms from the best planes determined by them is 0.073(8) for the fragment O(2a)—C(3a)—C(4a)—O(5a). In molecule 1 the values of the dihedral angles between the chelate moieties a : b : c : a are 128.6(8), 106.4(6) and 109.7(5)^o. The corresponding values d : e : f : d for molecule 2 are 148.7(6), 95.4(6)

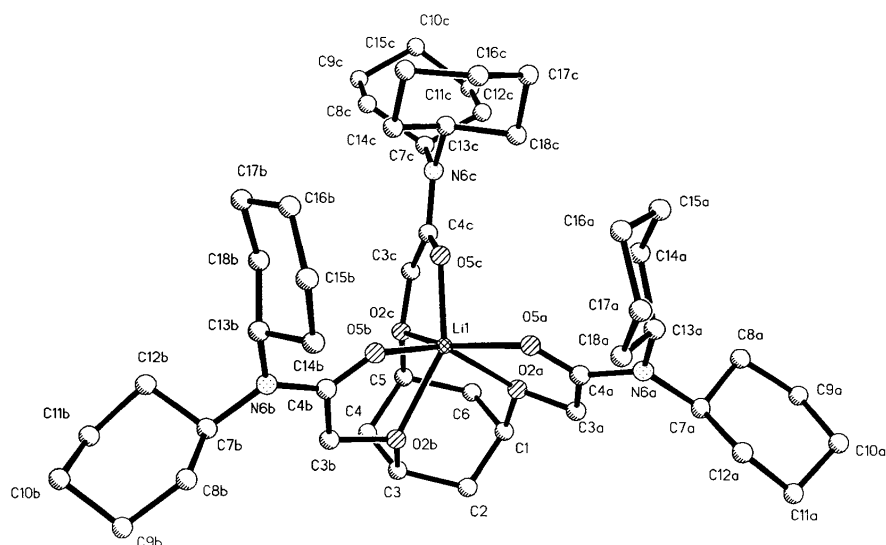


Figure 1a. The structure of LiI complex **IIIb** (molecule 1).

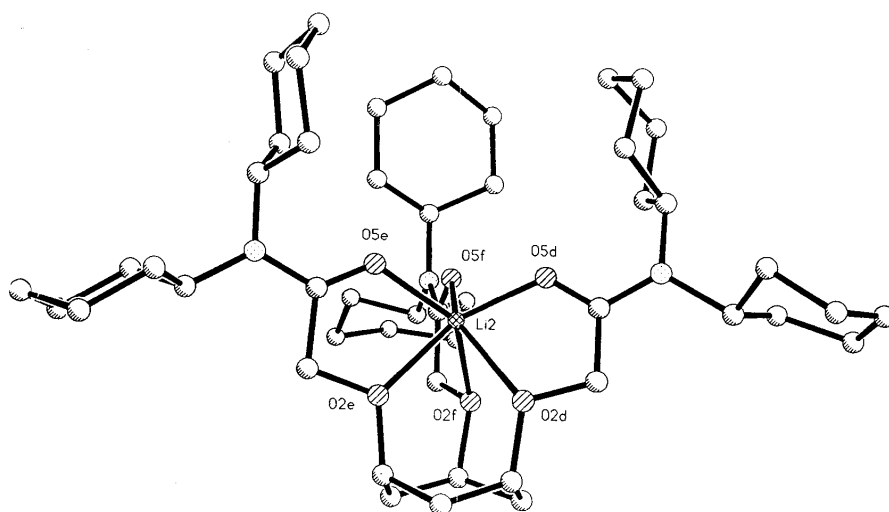


Figure 1b. The structure of LiI complex **IIIb** (molecule 2).

and $119.2(6)^\circ$. The deviation of the lithium atom from these planes is in the region: $0.31(2)$ – $0.56(2)$ Å for molecule 1 and $0.35(2)$ – $0.63(2)$ Å for molecule 2.

The complex does not have the expected three-fold C_{3v} or even C_3 symmetry. This might be due to the inexact correspondence of the pseudocavity size and the Li diameter dimension and self organization of the complex. The second reason for a distorted symmetry of the complex is the intermolecular interaction of the bulky

amide substituents and in this case the symmetry of complexes in solution might be higher.

The distances between the Li ion and carbonyl and ether oxygen atoms differ significantly (Table III). The mean values for Li—O(2) and Li—O(5) are 2.246 and 1.974 Å respectively for molecule 1 and 2.214 and 2.000 Å for molecule 2. These distances are also typical of similar lithium complexes [6], there are some differences between values of distances (Li—ether oxygen atoms) of the complex with ligand **I** [2] and in our complex **IIb**. In the case of complex **IIb** they are larger, because of the rigidity of the central cyclohexyl fragment which determines the distance between the ether oxygen atoms. This makes the ligand less flexible and it might be the reason for a slightly worse selectivity for Li/Na ions when compared to compound **I** [2]. It is interesting to note that in the case of the similar potassium complexes [7], in which the potassium atom is encapsulated in a polar environment of eight oxygen atoms (four ether O-atoms connected with the flexible 16-membered ring of calixarene, and four carboxamide oxygens) all oxygen—potassium distances are almost equal.

Bond distances and angles are summarized in Table III, showing no significant differences for both molecules 1 and 2.

The bond distances C(4)—N(6) varies between 1.34—1.36 Å and is shorter than other bonds N(6)—C(7) and N(6)—C(13) (1.44—1.50 Å), which is typical of the amide group.

Figure 2 shows the packing of the molecules. In the crystal structure one water molecule for every two molecules of complexed cation was found to exist as a solvent entrapped in the crystal. The iodide atoms do not form short contacts (less than the sum of the van der Waals radii for the corresponding atom) with the complexes. The closest intermolecular distance is between I(2) and water molecule OW1 ($2 - x, 1 - y, 1 - z$) and equals 3.72(2) Å showing the possibility of H-bond formation.

3.2. COMPLEXATION STUDIES IN SOLUTION

The complexation of the hexadentate amidoether **II** with lithium ions was also studied by the ¹H-NMR technique in solution. Deuterated chloroform, methanol and acetone were used as the solvents. The electron donating properties of the ethereal and amide groups responsible for the complexing properties of the ligand are larger than those of the chosen solvents and the complex is quite stable in solution.

The proton NMR spectra of ligand **II** and of its complex with lithium iodide **IIb**, both in CDCl₃ solutions are presented in Figure 3. Both spectra differ in chemical shifts of the hydrogen atoms, especially those in positions close to the electrondonating oxygen atoms taking part in complexation. The largest downfield shift was expected for the methylene hydrogens located in between ethereal and carbonyl oxygens: —O—CH₂—CO—. However the observed changes in chemical

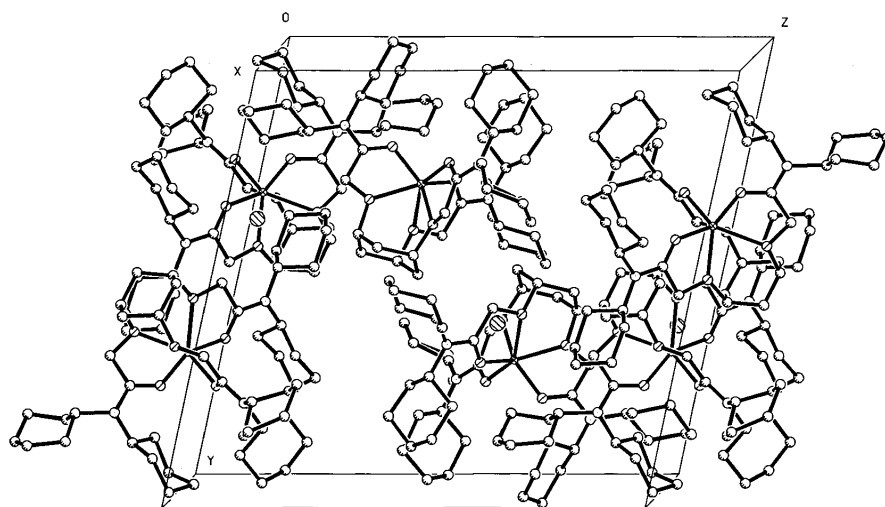


Figure 2. The crystal packing of two independent molecules 1 and 2 in the unit cell.

shifts were different; they are listed in Table IV. In the chloroform solution the downfield shift of $-\text{O}-\text{CH}_2-\text{CO}-$ hydrogens is only 0.14 ppm, whereas the downfield shift of $\text{H}1''$, $\text{H}3''$, $\text{H}5''$, next to the ethereal oxygen, is much larger: 0.69 ppm. This has been attributed to the conformational changes in the ligand molecule due to complexation. The protons $\text{H}1''$, $\text{H}3''$, $\text{H}5''$, of the central cyclohexyl ring are in axial positions in the free ligand, but in the complex they are equatorial, which is observed as a typical downfield shift. Considerably restricted rotation around the C—N bond in the ligand molecule differentiate both amide-cyclohexyls and thus the hydrogens $\text{H}1'$ (*trans*) and $\text{H}1$ (*cis* to the carbonyl group). The chemical shifts of these hydrogens in the free ligand are 3.40 ppm for $\text{H}1'$ and 2.91 ppm for $\text{H}1$. In the complex these signals are shifted; the $\text{H}1$ signal is shifted slightly downfield and a high field shift is observed for $\text{H}1'$. Similar shifts were observed in all three solvents (as shown in Table IV), and also for other dicyclohexyl ligands, as for example the complex with ligand **I** [8]. The quite large shift of the amide protons can be explained in terms of conformational changes within the molecule due to complexation, resulting in a different arrangement of the cyclohexyl rings. A similar observation was made by others [9].

^1H -NMR measurements of the chemical shifts were performed also in the solutions prepared by mixing 0.01 M acetone- d_6 solutions of ligand **II** with variable amounts of lithium iodide. As the result of the different $[\text{LiI}]/[\text{ligand}]$ molar ratio different spectra were obtained. As seen in Table V, when the ratio was less than 1 (0.15 or 0.60) the ^1H -NMR spectra consisted of signals characteristic of the complexed and uncomplexed host in the same ratio (0.15 and 0.60, respectively). This indicates that, at room temperature, the exchange rate between the two species is slow on the NMR time scale and that the lithium cation is tightly encapsulated in

Table IV. The most characteristic fragments of the ¹H-NMR spectra of ligand **II** and its Li-complex **IIb** [ppm], *J* [Hz].

Compound	Solvent	O—CH ₂ —CO 6H	H1'', H3'', H5''	3 H1' (<i>trans</i>)	3 H1 (<i>cis</i>)	3 H2; 6 H2'
II	CDCl ₃	4.12 (s)	3.40 (t), <i>J</i> = 11.2	3.40 (t), <i>J</i> = 11.2	2.91 (m)	2.53 (d), <i>J</i> = 11.2, 2.47 (m)
IIb	CDCl ₃	4.26 (s)	4.09 (s)	3.12(t), <i>J</i> = 11.2	2.92 (m)	2.49 (d), <i>J</i> = 16, 3H 2.63 (q), <i>J</i> = 11.5
II	Methanol- <i>d</i>	4.15 (s)	3.37 (t), <i>J</i> = 11.5	3.58 (t), <i>J</i> = 11.5	3.03 (t), <i>J</i> = 11.5	2.3–2.55 (m)
IIb	Methanol- <i>d</i>	4.19 (s)	3.91 (m)	3.25 (m)	3.05 (t), <i>J</i> = 11.5	2.35–2.6 (m)
II	Acetone- <i>d</i>	4.16 (s)	3.39 (t), <i>J</i> = 11.2	3.66 (t), <i>J</i> = 11.2	2.98 (t), <i>J</i> = 11.5	2.38–2.6 (m)
IIb	Acetone- <i>d</i>	4.38 (s)	4.01 (s)	3.31 (m)	3.08 (m)	2.43 (d), <i>J</i> = 16, 3H 2.75 (q), <i>J</i> = 12, 6H

Table V. The most characteristic fragments of the $^1\text{H-NMR}$ spectra of 0.01 M solution of ligand **II** in acetone-*d* in the presence of variable amounts of LiI. **1**: free ligand; **2**: ratio of [LiI]/[ligand] = 0.15; **3**: 0.6; **4**: 1.0; **5**: 1.25; **6**: 2; **7**: 10.

	O—CH ₂ —CO 6H	H1a (<i>trans</i>)	3H1e'' 3H1a''	3H1a' (<i>cis</i>)	6H2a' 3H2e''
1	—	3.66 (t)	—	2.98 (t)	2.4–2.60 (m)
2	4.37 (s) 15%	3.66 (t)	4.0 (s) 15%	2.98 (t)	2.38–2.58 (m); 2.73 (broad s)
3	4.38 (s) 60%	3.66 (t) 40%	4.0 (s) 60%	3.34 (m) 40%	2.35–2.58 (m) 2.73 (s)
4	4.37 (s)	—	4.0 (s)	3.08 (m)	2.36–2.5 (m) 3H
5	4.37 (s)	—	4.0 (s)	3.09 (m)	2.73 (q), <i>J</i> = 12, 6H 2.42 (d), <i>J</i> = 16, 3H
6	4.38 (s)	—	4.02 (s)	3.09 (t)	2.73 (q), <i>J</i> = 12, 6H 2.44 (d), <i>J</i> = 16, 3H
7	4.38 (s)	—	4.03 (s)	3.09 (m)	2.73 (q), <i>J</i> = 12, 6H 2.44 (d), <i>J</i> = 16; 3H 2.74 (q), <i>J</i> = 12, 6H

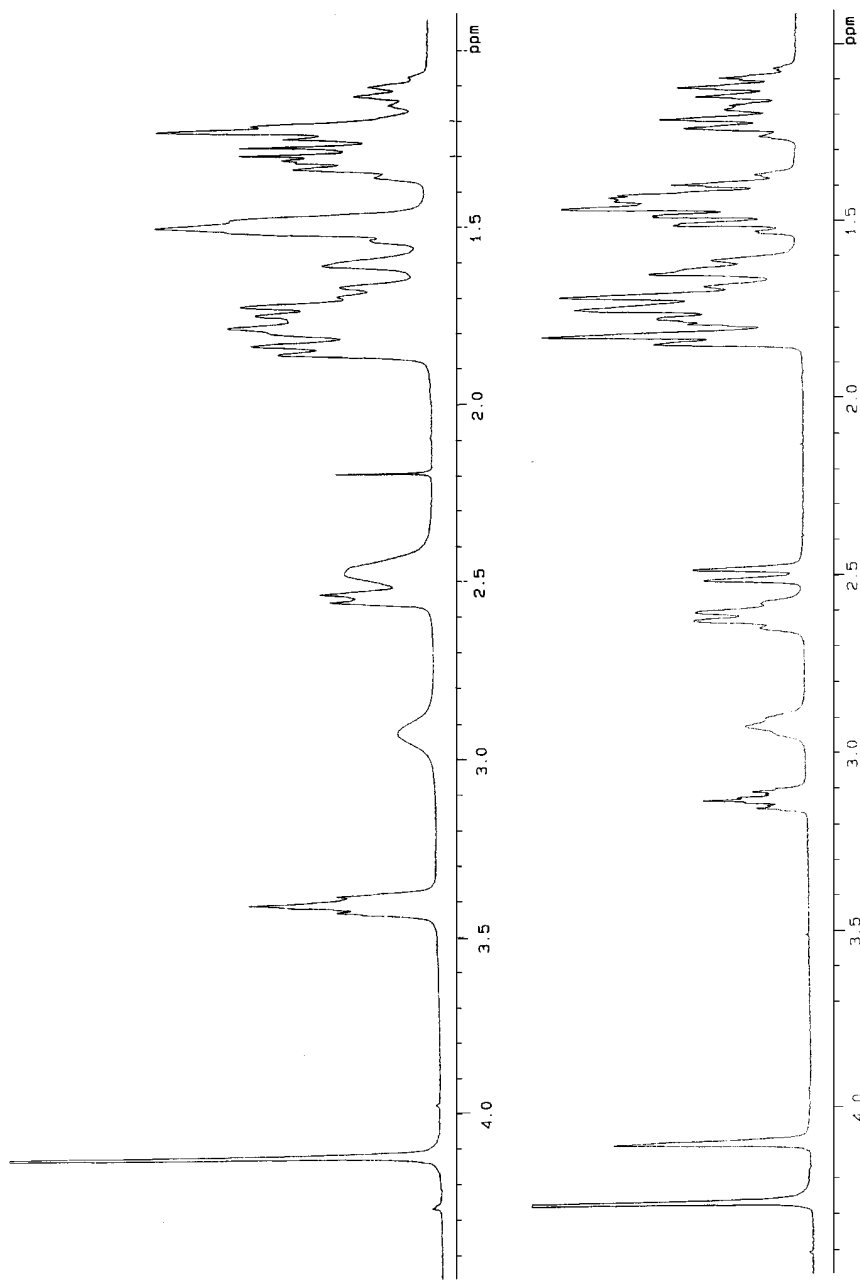


Figure 3. The $^1\text{H-NMR}$ spectra of the free ligand **II** (upper trace) and its LiI complex **IIb** (lower trace) in CDCl_3 (500 MHz).

the hydrophilic pseudocavity of the ligand. When the [LiI]/[ligand] ratio was >1 (1.25, 2 and 10) the spectra remained unchanged. This observation indicates that the formed complex is of 1 : 1 stoichiometry. There is no evidence of the formation of bislithiated complexes.

The structure of the complex in the solid state, revealed by X-ray analysis corresponds well with the geometry of the complex in solution defined by the proton NMR spectra. This finding suggests that the structure of the complex is quite stable in solution and a complex of similar structure and conformation is formed. The symmetry of the molecule is probably higher in solution as the protons of each bidentate arm are not differentiated in NMR.

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