

Inclusion Compounds of NaI with 13-Membered Azo- and Azoxycrown Ethers

YU. A. SIMONOV*

Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev, Moldova.

E. LUBOCH and J. F. BIERNAT

Department of Chemical Technology, Technical University, 80-952 Gdańsk, Poland.

N. V. BOLOTINA

Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia.

V. E. ZAVODNIK

Karpov's Physico-Chemical Institute, Russian Academy of Sciences, Moscow, Russia.

(Received: 16 April 1996; in final form: 22 October 1996)

Abstract. Sodium iodide complexes of 13-membered azo-(**I**) and azoxycrown ethers (**II**) have been synthesized. Compound **I** [Na(L1*trans*)₂].I·H₂O is triclinic with $a = 11.53(2)$, $b = 15.74(2)$, $c = 19.17(2)$ Å, $\alpha = 98.93(9)$, $\beta = 105.51(9)$, $\gamma = 89.20(9)$ deg.; $Z = 4$, space group $P\bar{1}$. Compound **II** [Na(L2)₂].I is orthorhombic with $a = 12.451(2)$, $b = 13.796(3)$, $c = 18.667(4)$ Å; $Z = 4$, space group $P2_12_12_1$. In both complexes the cation is coordinated to chain oxygen atoms and to one nitrogen atom of the azo or azoxy unit. The ability of both ligands to form complexes in relation to the geometry of the azo or azoxy subunit of the macrocycle is discussed.

Key words: Azocrown ether, azoxycrown ether, sodium complexes, crystal structure, X-ray analysis, conformation.

Supplementary Data related to this article have been deposited with the British Library as Supplementary Publication No. 82217 (19 pages).

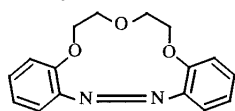
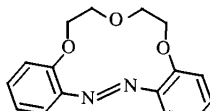
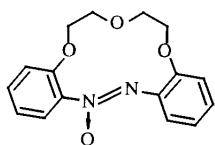
1. Introduction

The formation of cationic complexes by crown ethers and their analogues is to a great extent determined by the size of the macrocyclic unit and by the character and position of the electron donating groups in the macrocycle. There are many known examples of changes of complex character and stoichiometry (metal cation to macrocycle ratio) as a function of the mutual sizes of the metal ion and macrocycle cavity [1]. This behavior was extensively studied for Pedersen type crown ethers (12-crown-4, 15-crown-5, 18-crown-6 and their dicyclohexano- and benzo- derivatives) with oxygen electron donating atoms separated in the macrocycle by the same —CH₂—CH₂— fragment. For example, sodium ions form solid complexes

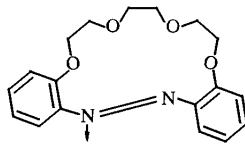
* Author for correspondence.

with 18-membered crown ethers of 1 : 1 (cavitate) [1, 2] and 1 : 2 stoichiometry with 15-membered crowns [1, 3].

In previous papers [4–6] we presented crown ethers bearing an azo or azoxy group as part of the macrocycle (**L1** and **L2**, Scheme) and their derivatives. They are of special interest as selective membrane electrode ionophores for sodium cations [4]. 13-Membered azocrown ether **L1** forms two isomers. The structure of compound **L1**(*cis*) (isomer *Z*) was established by X-ray analysis [5]. In this isomer the nitrogen lone electron pairs are directed outside the macrocycle. It is not beneficial for cation complexation inside the cavity. Pushing both of them inside the cavity seems unacceptable because of steric repulsion.

L1(*cis*)L1(*trans*)

L2



L3

Compound **I**: [Na(L1*trans*)₂].I.H₂O

Compound **II**: [Na(L2)₂].I

In compound **L2** [6] the phenyl residues are oriented *trans* to each other around the azoxy group (isomer *Z*). Here the N → O residue is directed outside, whereas the lone electron pair of the second nitrogen atom points inside the macrocycle. It could be postulated that the oxygen atom of the azoxy group will not participate in complexation of metal cations. In fact, structural studies of the potassium complex with **L3** [7] showed that the potassium coordination number is ten in the sandwich like complex cation. Four ether oxygen atoms and one nitrogen atom of both macrocyclic ligands take part in coordination without changes of the torsional angles of the azoxy fragment.

There are no literature data on the coordination behavior of crown ethers bearing an azo group in the macrocycle. The *cis* orientation of aromatic residues around the azo group and the direction of the lone electron pair prohibiting complexation of metal ions was mentioned above. To form a complex the **L1**(*cis*) ligand should change the arrangement of the substituents around the azo group. Such isomerization of a *cis* azocrown ether monolayer in the presence of sodium cations was predicted [8]. In this paper the synthesis and structure of the NaI complex with the 13-membered azo- [compound **I**; (L1*trans*)₂·NaI·H₂O] and azoxycrown ethers [compound **II**; (L2)₂·NaI] are described.

2. Experimental

2.1. SYNTHESIS

The 13-membered azocrown ether **L1** was synthesized as described [5]. Compound **L2** was obtained according to [6].

IR spectra (Nujol mull) were recorded on a Specord M80 spectrometer. ¹H-NMR spectra, all in CDCl₃, were recorded with a Varian Gemini 200 MHz instrument. Melting points are uncorrected.

2.1.1. Compounds **L1** (*cis*) and **L1** (*trans*)

The 13-membered azocrown ether **L1** [5] was dissolved in methylene chloride. After a day the solution containing a mixture of isomers **L1**(*cis*) and **L1**(*trans*) (approximately 1 : 1) was evaporated and the residue was crystallized from hexane. The crystals of both **L1**(*cis*) and **L2**(*trans*) were readily separated mechanically.

L1(*cis*) forms orange crystals, m.p. 107–108°, IR: 1584(w), 1510(w), 1288(m), 1248(m), 1136(m), 1040(w), 920(w) and 724(s) cm⁻¹. ¹H-NMR, δ [ppm]: 3.60–3.85 (2H, m); 3.85–4.15 (6H, m); 6.70–6.88 (6H, m); 7.02–7.15 (2H, m).

L1(*trans*) forms dark red, heavy crystals, m.p. 70–72° [5]. IR: 1600(m), 1570(w), 1296(s), 1265(s), 1216(s), 1152(m), 1120(w), 1040(s), 928(m), 890(w), 825(w), 760(s), 715(s) cm⁻¹. 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).

Compound **L2** IR: 1600(s), 1290(m), 1280(m), 1248(s), 1165(w), 1128(m), 1088(m), 1044(s), 920(m), 900(m), 832(w), 768(s), 725(m), 672(w) cm⁻¹. ¹H-NMR, δ [ppm]: 3.92–3.98 (4H, m); 4.23–4.29 (4H, m); 7.05–7.15 (4H, m); 7.27–7.47 (2H, m); 7.67–7.74 (2H, m).

2.1.2. Compound **I**

A mixture of ligand **L1** (114 mg; 0.4 mmol), sodium iodide (60 mg; 0.4 mmol) and methanol (5 mL) was heated at 60° until dissolution. The filtered solution was evaporated to dryness, the residue was dissolved in acetone and allowed to stand for slow evaporation of the solvent. Red monocrystals melting at 172–174° were obtained in a quantitative yield. IR of complex **I**: 3488(m), 3440(w), 1600(s), 1300(m), 1232(s), 1120(s), 1040(s), 928(m), 900(w), 764(s), 740(m) cm⁻¹. ¹H-NMR, δ [ppm] 3.8–4.1 (4H, broad m); 4.1–4.3 (4H, broad m); 6.90 (2H, dd, $J_1 = 1.1$ Hz; $J_2 = 8.1$ Hz); 7.08 (2H, dt, $J_1 = 1.3$ Hz; $J_2 = 7.6$ Hz); 7.27 (2H, dt, $J_1 = 1.8$ Hz; $J_2 = 8.1$ Hz); 7.36 (2H, dd, $J_1 = 1.7$ Hz; $J_2 = 7.8$ Hz).

2.1.3. Compound **II**

A mixture of ligand **L2** (120 mg; 0.4 mmol) and sodium iodide (60 mg; 0.4 mmol) was treated as above. Yellowish monocrystals melting at 165–166° were obtained.

Table I. Crystal data and structure refinement for compounds **I** and **II**.

	Compound I	Compound II
Empirical formula	C ₃₂ H ₃₂ IN ₄ NaO ₆ ·H ₂ O	C ₃₂ H ₃₂ IN ₄ NaO ₈
Molecular weight	736.52	750.52
Temperature	293(2) K	293(2) K
Wavelength	0.71079 Å	0.71079 Å
Crystal system	Triclinic	Orthorhombic
Space group	$C_i = P\bar{1}$	$P2_12_12_1$
Unit cell dimensions	$a = 11.53(2)$ Å; $\sigma = 98.93(9)^\circ$ $b = 15.74(2)$ Å; $\beta = 105.51(9)^\circ$ $c = 19.17(2)$ Å; $\gamma = 89.20(9)^\circ$	$a = 12.451(2)$ Å $b = 13.796(3)$ Å $c = 18.667(4)$ Å
Volume	3310(8) Å ³	3206(1) Å ³
<i>Z</i>	4	4
Density (calc.)	1.478 Mg m ⁻³	1.555 Mg m ⁻³
Absorption coefficient	1.030 mm ⁻¹	1.069 mm ⁻¹
<i>F</i> (000)	1495	1520
Crystal size	0.25 × 0.30 × 0.60 mm	0.28 × 0.22 × 0.10 mm
Theta range for data collection	1.84–23.16 deg.	1.97–24.95 deg.
Index ranges	$-12 \leq h \leq 12$; $-16 \leq k \leq 16$; $0 \leq l \leq 20$	$0 \leq h \leq 13$; $0 \leq k \leq 15$; $0 \leq l \leq 22$
Reflections collected ($I \leq 2\sigma$)	4054	2767
Independent reflections	3786 [$R(\text{int}) = 0.0308$]	2542 [$R(\text{int}) = 0.038$]
Refinement method	Full-matrix-block least squares on F^2	Full-matrix-block least squares on F^2
Data (restraints) parameters	3786/9/811	1389/0/540
Goodness-of-fit on F^2	1.039	1.136
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0705$; $wR2 = 0.1877$	$R1 = 0.0359$; $wR2 = 0.092$
<i>R</i> indices (all data)	$R1 = 0.0724$; $wR2 = 0.2027$	$R1 = 0.0359$; $wR2 = 0.092$
Largest diff. peak and hole	0.733 and $-1.486e$ Å ⁻³	0.517 and $-0.340e$ Å ⁻³

IR of complex **II**: 1600(m), 1300(w), 1264(s), 1230(m), 1120(m), 1072(w), 1040(s), 912(s), 752(s), 720(m) cm⁻¹. ¹H-NMR, δ [ppm]: 3.90–4.06 (4H, m); 4.19–4.28 (4H, m); 6.88 (1H, dd, $J_1 = 1.1$ Hz; $J_2 = 8.3$ Hz); 6.99–7.39 (5H, m); 7.68 (1H, dd, $J_1 = 1.7$ Hz; $J_2 = 8.0$ Hz); 7.85 (1H, dd, $J_1 = 8.1$ Hz; $J_2 = 1.6$ Hz).

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

2.2.1. Compound **I**

A red colored crystal of size 0.25 × 0.30 × 0.60 mm was selected for X-ray analysis. The parameters of the elementary unit of the triclinic crystal were found based on 20 reflections in the range of $12 \leq \theta \leq 20^\circ$ collected on a RED-4 diffractometer using MoK α radiation (Table I).

The experimental data were obtained on a RED-4 diffractometer using the $\theta/2\theta$ scanning method. 9779 reflections were registered, of which 4054 fulfill the $I \geq 2\sigma(I)$ requirement. After averaging the equivalent reflections, 3786 of them were used for further calculations. The structure was solved by the heavy atom method and refined with the least squares method to obtain an R -factor = 0.0705. During elucidation of the structure it was found that one of the oxyethylene fragments in one of the four independent molecules of **L1**(*trans*) is disordered. For the C(2d) atom two positions with equivalent occupancy were found. Hydrogen atoms were found from the difference Fourier synthesis and were refined isotropically. H-atoms of water molecules were not localized. The largest difference map peaks are situated near the iodide ions.

2.2.2. Compound **II**

For the X-ray experiment a large yellowish monocrystal was taken. The experimental data were obtained on a CAD-4 (Enraf-Nonius) diffractometer using the $\theta/2\theta$ method. 2767 reflections were registered. For calculations 1389 reflections with $I \geq 2\sigma(I)$ were used (Table I). The structure was solved by the direct method and refined by the least squares method in an anisotropic variant for non-hydrogen atoms and in the isotropic variant for H-atoms. The last atoms were found from the difference Fourier synthesis. During the refinement it was found that the oxyethylene fragment O(1)—C(2)—C(3)—O(4) for macrocycle **a** is disordered. Efforts to separate two positions for this fragment failed. In molecule **b** we found a high value of U_{eq} for C(2b), C(3b) and for some of the other atoms in the aromatic ring containing C(18b)—C(21b). Separation of the two positions for this fragment was not achieved.

The data on experimental conditions and on calculations are shown in Table I. All calculations were performed using SHELX-76 and SHELXL-93 [9]. The final coordinates for the non-hydrogen atoms of both complexes **I** and **II** are shown in Tables IIa and IIb, respectively; the geometric parameters of the molecules are collected in Table III.

3. Discussion

3.1. ORGANIZATION OF COMPLEXES **I** AND **II**

Figure 1 presents the crystal structure of complex **I**. In the elementary unit there are two crystallographically independent complexes (**I1** and **I2**) of composition $[\text{Na}(\text{L1}_{\text{trans}})_2] \cdot \text{I} \cdot \text{H}_2\text{O}$. The structure is ionic. Two crystallographically independent water molecules and two I^- anions form an associate $[\text{I}_3(\text{H}_2\text{O})_2]^{2-}$ coupled by hydrogen bonds. The water molecule determined by the O(1w) atom forms hydrogen bonds with I(1) $(-x + 1, -y, -z + 1)$ [distance = 3.68(1) Å] and with I(2) $(x, y - 1, z)$ [distance = 3.61(1) Å]. The second water molecule O(2w) forms hydrogen bonds with I(1) $(x + 1, y, z)$ [3.61(1) Å] and with I(2) $(-x + 2, -y, -z + 1)$ [3.62(1)

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

	x	y	z	$U(\text{eq})$
I(1)	1463(1)	944(1)	4225(1)	84(1)
I(2)	5902(1)	5890(1)	4212(1)	88(1)
Na(1)	5606(5)	1438(4)	2963(3)	54(2)
O(1a)	4165(9)	468(7)	3084(5)	65(3)
C(2a)	4607(16)	-12(11)	3680(8)	75(6)
C(3a)	5507(17)	532(12)	4276(8)	78(6)
O(4a)	6485(10)	801(7)	4035(5)	66(4)
C(5a)	7365(15)	183(11)	3965(8)	75(6)
C(6a)	8024(13)	382(11)	3461(7)	76(6)
O(7a)	7146(8)	393(7)	2772(5)	64(3)
C(8a)	7524(14)	409(10)	2139(7)	53(5)
C(9a)	6652(13)	235(10)	1458(7)	48(4)
N(10a)	5438(12)	-41(9)	1373(6)	66(4)
N(11a)	4972(11)	197(7)	1896(5)	47(3)
C(12a)	3780(14)	-134(10)	1817(7)	58(5)
C(13a)	3402(14)	-3(9)	2451(7)	49(4)
C(14a)	8691(15)	589(11)	2168(8)	64(5)
C(15a)	8987(14)	579(12)	1507(10)	80(6)
C(16a)	8142(17)	440(14)	829(9)	91(7)
C(17a)	6987(17)	208(12)	832(8)	77(6)
C(18a)	2270(16)	-244(12)	2423(9)	77(6)
C(19a)	1551(15)	-707(11)	1787(11)	70(5)
C(20a)	1945(16)	-847(12)	1161(9)	74(5)
C(21a)	3043(16)	-575(12)	1174(8)	80(6)
O(1b)	7204(10)	2531(8)	3352(6)	79(4)
C(2b)	6867(15)	3303(13)	3786(9)	90(7)
C(3b)	6191(16)	2974(11)	4284(8)	73(5)
O(4b)	5134(10)	2493(7)	3882(5)	73(4)
C(5b)	4106(16)	3025(13)	3648(8)	93(7)
C(6b)	3202(14)	2502(12)	3018(7)	71(5)
O(7b)	3847(8)	2299(7)	2468(4)	61(3)
C(8b)	3222(14)	2074(10)	1744(8)	62(5)
C(9b)	3861(14)	2048(10)	1221(8)	60(5)
N(10b)	5058(13)	2314(9)	1360(7)	76(5)
N(11b)	5777(11)	2269(8)	1963(6)	61(4)
C(12b)	7002(14)	2563(10)	2093(10)	64(5)
C(13b)	7676(16)	2660(10)	2804(9)	59(5)
C(14b)	2017(15)	1864(11)	1528(8)	74(6)
C(15b)	1466(16)	1681(11)	772(10)	87(7)
C(16b)	2042(18)	1655(14)	261(10)	94(7)
C(17b)	3256(16)	1867(12)	473(8)	81(6)
C(18b)	8874(20)	2929(13)	2993(11)	83(6)
C(19b)	9354(18)	3036(13)	2443(12)	92(7)
C(20b)	8708(18)	2973(15)	1697(11)	96(8)
C(21b)	7509(18)	2723(11)	1521(9)	67(5)

Table IIa. Continued.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Na(2)	10587(5)	6455(4)	2989(3)	55(2)
O(1c)	12214(9)	5454(7)	3059(5)	66(3)
C(2c)	12352(17)	4971(12)	3646(9)	89(7)
C(3c)	11966(16)	5498(12)	4244(8)	79(6)
O(4c)	10743(11)	5746(9)	4011(5)	82(4)
C(5c)	9840(20)	5167(18)	3948(10)	117(10)
C(6c)	8685(16)	5355(12)	3444(8)	76(5)
O(7c)	8948(8)	5360(8)	2754(5)	71(3)
C(8c)	8026(12)	5428(9)	2134(7)	62(5)
C(9c)	8277(14)	5245(10)	1473(7)	62(5)
N(10c)	9436(13)	4985(8)	1378(7)	68(4)
N(11c)	10325(12)	5251(9)	1866(6)	73(5)
C(12c)	11461(14)	4915(11)	1765(7)	66(5)
C(13c)	12395(15)	5015(10)	2402(8)	72(5)
C(14c)	6828(14)	5570(12)	2160(11)	88(6)
C(15c)	5968(16)	5649(13)	1549(13)	95(7)
C(16c)	6218(17)	5479(13)	896(13)	92(7)
C(17c)	7373(19)	5284(13)	847(10)	99(7)
C(18c)	13562(14)	4732(12)	2371(10)	87(6)
C(19c)	13670(18)	4281(12)	1701(12)	91(6)
C(20c)	12741(21)	4194(13)	1091(10)	99(7)
C(21c)	11627(16)	4496(11)	1121(8)	80(6)
O(1d)	9244(9)	7485(7)	3399(5)	72(3)
C(2d1)*	9771(31)	8175(19)	3933(23)	70(22)
C(2d2)*	9888(32)	8244(15)	3847(23)	72(21)
C(3d)	10952(16)	7939(13)	4390(8)	101(8)
O(4d)	11754(11)	7512(8)	3995(6)	76(4)
C(5d)	12507(19)	8065(13)	3807(10)	87(7)
C(6d)	12917(13)	7633(11)	3162(8)	69(5)
O(7d)	11823(8)	7413(7)	2595(5)	66(3)
C(8d)	11869(13)	7165(11)	1879(8)	65(5)
C(9d)	10766(14)	7147(10)	1328(7)	58(5)
N(10d)	9649(10)	7395(9)	1438(7)	78(5)
N(11d)	9506(10)	7325(9)	2043(6)	65(4)
C(12d)	8320(12)	7572(10)	2138(8)	59(5)
C(13d)	8264(12)	7668(11)	2847(8)	63(5)
C(14d)	12917(14)	6947(11)	1691(9)	76(5)
C(15d)	12892(19)	6725(14)	953(11)	100(7)
C(16d)	11843(19)	6691(12)	418(10)	86(6)
C(17d)	10783(19)	6925(12)	610(8)	91(7)
C(18d)	7158(15)	7911(12)	2994(11)	91(7)
C(19d)	6197(17)	8056(11)	2428(14)	94(7)
C(20d)	6279(17)	7960(12)	1736(14)	100(7)
C(21d)	7354(13)	7743(11)	1548(10)	73(5)
O(1w)	5754(11)	-1795(9)	4398(7)	102(5)
O(2w)	11341(14)	3259(10)	4467(10)	158(8)

* Disordered group, two positions for C(2d).

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

	x	y	z	$U(\text{eq})$
I	-2206(1)	4885(1)	5377(1)	86(1)
Na	2199(4)	5037(3)	3727(2)	43(1)
O(1a)	548(9)	5827(8)	3942(5)	53(3)
O(2a)	1488(9)	6777(9)	1613(5)	68(3)
O(4a)	2352(9)	6151(6)	4748(6)	54(3)
O(7a)	3086(8)	6659(8)	3436(6)	67(3)
N(10a)	1883(11)	6364(9)	2163(8)	46(4)
N(11a)	1381(12)	6010(9)	2677(6)	45(3)
C(2a)	424(15)	6405(15)	4575(9)	60(4)
C(3a)	1305(14)	6127(14)	5069(8)	58(4)
C(5a)	2759(21)	7073(14)	4604(12)	68(6)
C(6a)	3597(19)	6965(19)	4067(11)	79(6)
C(8a)	3664(14)	6499(11)	2794(8)	48(4)
C(9a)	3073(15)	6336(11)	2158(10)	49(4)
C(12a)	259(13)	6068(11)	2695(7)	37(4)
C(13a)	-174(14)	5998(11)	3391(8)	46(4)
C(14a)	3592(15)	6183(14)	1532(9)	59(5)
C(15a)	4697(16)	6204(14)	1513(11)	63(5)
C(16a)	5261(15)	6423(15)	2107(13)	67(6)
C(17a)	4745(15)	6542(13)	2742(9)	56(5)
C(18a)	-456(15)	6129(11)	2110(9)	45(4)
C(19a)	-1549(14)	6147(13)	2243(9)	51(5)
C(20a)	-1926(14)	6103(11)	2935(8)	57(4)
C(21a)	-1266(13)	6015(13)	3514(8)	53(4)
O(1b)	3834(10)	4362(11)	4042(7)	87(4)
O(2b)	3254(10)	3160(8)	1723(6)	69(3)
O(4b)	1957(10)	3713(8)	4693(7)	66(3)
O(7b)	1213(9)	3528(9)	3336(5)	64(3)
N(10b)	2750(14)	3662(10)	2204(7)	53(4)
N(11b)	3133(10)	4090(10)	2720(8)	55(4)
C(2b)	3743(36)	3721(65)	4628(35)	369(52)
C(3b)	3047(28)	3252(22)	4834(16)	106(10)
C(5b)	1190(23)	3000(15)	4502(9)	74(7)
C(6b)	507(16)	3303(16)	3935(9)	59(5)
C(8b)	834(18)	3668(13)	2651(10)	62(5)
C(9b)	1572(15)	3757(12)	2120(9)	43(4)
C(12b)	4268(17)	4045(12)	2830(10)	62(5)
C(13b)	4608(14)	4171(13)	3542(9)	62(5)
C(14b)	-266(17)	3662(14)	2487(13)	67(6)
C(15b)	-586(18)	3801(13)	1790(14)	69(6)
C(16b)	121(19)	3952(16)	1259(12)	75(6)
C(17b)	1209(18)	3893(13)	1403(8)	57(5)
C(18b)	5058(18)	3973(20)	2326(14)	82(7)
C(19b)	6093(20)	3978(19)	2457(20)	98(9)
C(20b)	6449(19)	4047(18)	3153(22)	114(10)
C(21b)	5700(20)	4171(15)	3693(14)	87(7)

Table III. Selected interatomic distances (Å) and selected valence and torsion angles (grad.) for compounds **I** and **II**.

Bond	Compound I				Compound II	
	Ligand a	Ligand b	Ligand c	Ligand d	Ligand a	Ligand b
Na—O(1)	2.35(2)	2.42(2)	2.422(11)	2.414(11)	2.361(11)	2.314(13)
Na—O(4)	2.400(11)	2.395(11)	2.37(2)	2.444(14)	2.456(10)	2.583(13)
Na—O(7)	2.464(11)	2.479(11)	2.477(14)	2.423(14)	2.554(12)	2.525(13)
Na—N(11)	2.555(11)	2.53(2)	2.593(14)	2.50(2)	2.586(13)	2.57(2)
O(1)—C(2)	1.44(2)	1.47(2)	1.43(2)	1.39(2); 1.44(2)*	1.43(2)**	1.41(3)
C(2)—C(3)	1.48(2)	1.53(3)	1.47(2)	1.49(2); 1.51(2)*	1.48(2)**	1.15(6)
C(3)—O(4)	1.42(2)	1.41(2)	1.43(2)	1.44(2)	1.44(2)**	1.52(3)
O(4)—C(5)	1.41(2)	1.45(2)	1.36(3)	1.39(2)	1.39(2)**	1.42(4)
C(5)—C(6)	1.45(2)	1.50(2)	1.48(2)	1.50(2)	1.46(3)	1.42(3)
C(6)—O(7)	1.44(1)	1.44(2)	1.44(2)	1.43(2)	1.40(2)	1.46(2)
O(7)—C(8)	1.40(2)	1.38(2)	1.38(1)	1.38(2)	1.42(2)	1.38(2)
C(8)—C(9)	1.41(2)	1.39(2)	1.36(2)	1.42(2)	1.41(2)	1.36(2)
C(9)—N(10)	1.43(2)	1.39(2)	1.44(2)	1.40(2)	1.48(3)	1.48(2)
N(10)—N(11)	1.27(2)	1.24(2)	1.22(2)	1.23(2)	1.24(2)	1.23(2)
N(11)—C(12)	1.44(2)	1.44(2)	1.46(2)	1.47(2)	1.40(2)	1.43(2)
C(12)—C(13)	1.38(2)	1.36(2)	1.38(2)	1.36(2)	1.41(2)	1.41(2)
C(13)—O(1)	1.40(2)	1.35(2)	1.40(2)	1.39(2)	1.39(2)	1.37(3)
O(2)—N(10)					1.27(2)	1.30(2)
C(13)—O(1)—C(2)	115(1)	117(2)	117(1)	116(2); 113(1)*	117(1)**	118(3)
O(1)—C(2)—C(3)	109(2)	106(2)	109(1)	111(2); 107(2)*	107(1)**	132(4)
C(2)—C(3)—O(4)	112(1)	112(1)	112(1)	116(2); 109(2)*	114(1)**	112(3)
C(3)—O(4)—C(5)	116(1)	113(1)	119(2)	114(2)	116(1)**	111(2)
O(4)—C(5)—C(6)	111(1)	108(1)	114(2)	110(2)	108(2)**	113(2)
C(5)—C(6)—O(7)	106(1)	104(1)	105(2)	104(1)	107(2)	106(2)
C(6)—O(7)—C(8)	120(1)	120(1)	120(1)	120(1)	122(1)	122(1)
O(7)—C(8)—C(9)	118(2)	118(2)	118(1)	117(1)	118(2)	117(2)
C(8)—C(9)—N(10)	124(1)	126(1)	124(1)	126(1)	121(2)	126(2)
C(9)—N(10)—N(11)	118(1)	120(2)	118(1)	116(1)	120(2)	115(2)
N(10)—N(11)—C(12)	117(1)	119(2)	115(1)	115(1)	120(1)	119(2)
N(11)—C(12)—C(13)	115(1)	116(2)	114(1)	114(1)	114(1)	115(2)
C(12)—C(13)—O(1)	118(2)	122(2)	120(1)	121(1)	117(1)	117(2)
O(2)—N(10)—N(11)					127(1)	128(2)
O(2)—N(10)—C(9)					113(2)	117(2)

Å]. Distances of the associates from $[\text{Na}(\text{L1}trans)_2]^+$ are in the limits of the sum of van der Waals radii of the respective atoms.

A sandwich-like complex cation is present in compound **I** with the ratio of $\text{Na}/\text{L1}(trans) = 1 : 2$ (Figure 2). Two macrocycles **L1}(trans) coordinate the sodium cation with the donor atoms forming the corners of an antiprism (Figures 2 and 3).**

Table III. Continued.

Bond	Compound I				Compound II	
	Ligand a	Ligand b	Ligand c	Ligand d	Ligand a	Ligand b
C(13)—O(1)—C(2)—C(3)	174(1)	172(1)	-172(2)	-167(3); -177(3)*	-178(1)**	-121(1)
O(1)—C(2)—C(3)—O(4)	-58(2)	-61(2)	59(2)	47(5); 65(4)*	51(1)**	-32(1)
C(2)—C(3)—O(4)—C(5)	-78(2)	-83(2)	79(2)	89(3); 81(3)*	72(1)**	142(1)
C(3)—O(4)—C(5)—C(6)	157(1)	160(1)	-157(2)	-156(1)	-160(1)**	-139(1)
O(4)—C(5)—C(6)—O(7)	-59(2)	-61(2)	58(2)	59(2)	67(1)**	58(1)
C(5)—C(6)—O(7)—C(8)	-168(1)	-159(1)	173(3)	167(2)	179(1)	167(1)
C(6)—O(7)—C(8)—C(9)	167(1)	168(2)	-166(2)	-166(2)	-171(1)	-172(1)
O(7)—C(8)—C(9)—N(10)	-7(2)	-7(3)	0(3)	3(3)	2(1)	4(1)
C(8)—C(9)—N(10)—N(11)	29(2)	29(2)	-30(3)	-28(3)	-39(1)	-45(1)
C(9)—N(10)—N(11)—C(12)	-176(1)	-179(1)	176(2)	-179(1)	178(1)	-179(1)
N(10)—N(11)—C(12)—C(13)	168(1)	167(1)	-162(2)	-167(1)	-157(1)	-154(1)
N(11)—C(12)—C(13)—O(1)	3(2)	-3(2)	-3(3)	-4(3)	-4(1)**	-3(1)
C(12)—C(13)—O(1)—C(2)	-116(2)	-99(2)	118(2)	-68(4); -79(3)*	135(1)**	121(1)

* Disordered group at C(2d) of compound I.

** Calculated for the average atom positions for disordered fragment of compound II.

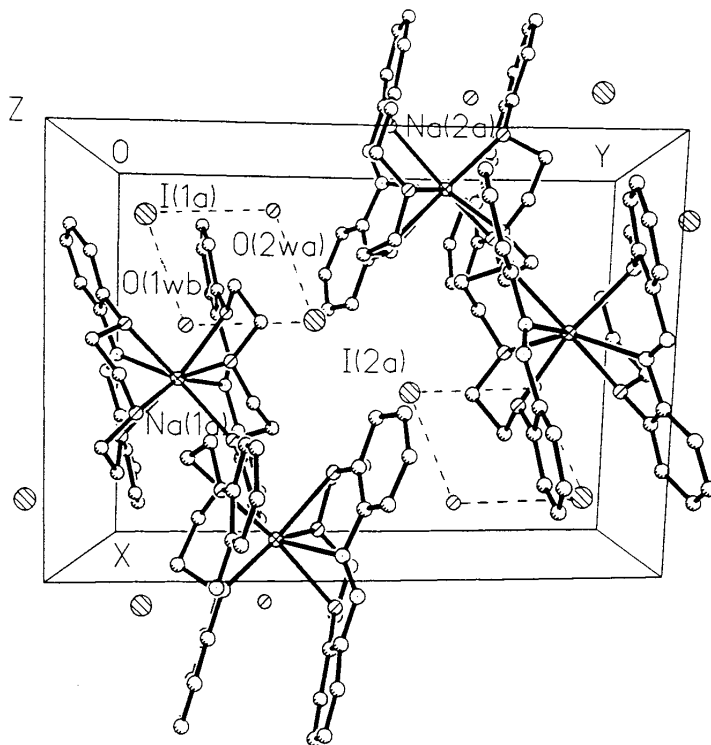


Figure 1. Crystal structure of compound I: $[\text{Na}(\text{L1trans})_2] \cdot \text{I} \cdot \text{H}_2\text{O}$.

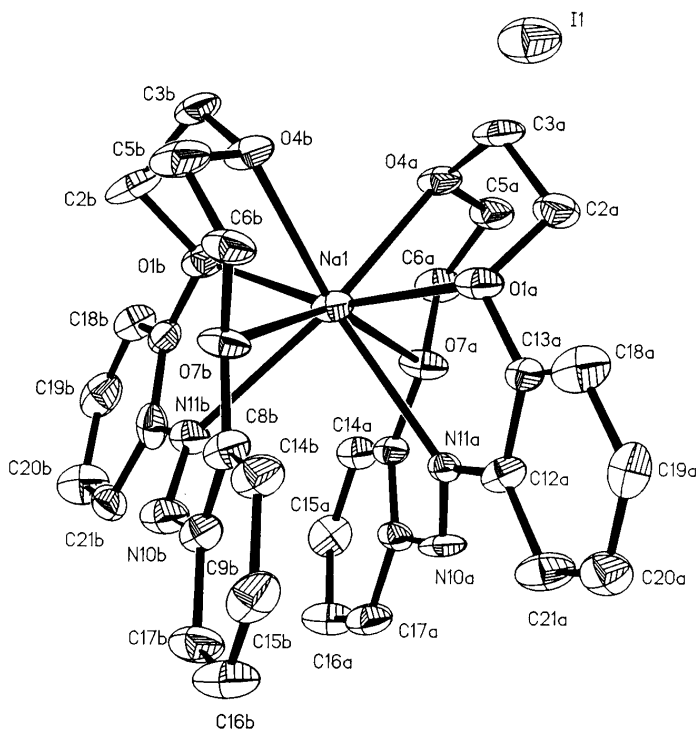


Figure 2. Compound **I** in a view parallel to the macrocycle mean planes and the atom numbering scheme.

Two base planes of the antiprism determined by the O(1), O(4), O(7) and N(11) atoms (Figure 3) form a dihedral angle of 7.3° for complex **II** and 6.9° for complex **I2**. The lone electron pairs of the donor atoms are pointing inside the macrocycle. The coordinating atoms O_3N of each macrocycle are practically coplanar. The highest deviation from the mean plane is equal to ± 0.07 Å. The distance of the sodium cation from the coordinating mean plane is within the limits of 1.52–1.55 Å. Such coordination is possible only when the $-N=N-$ fragment possesses *trans* (isomer *E*) attached substituents.

For the four independent ligands **L1**(*trans*) in compound **I** the Na—O distances are in the range of 2.35–2.48 Å, Na—N 2.50–2.59 Å. These distances are typical for Na—O and Na—N bonds and are similar to those found for sodium complexes with classical crown ethers [10].

The structure of the complex cation in compound **II** $[Na(L2)_2] \cdot I$ is in principle similar to that in compound **I**. The geometry of the azoxy group in free ligand **L2** is preserved in compound **II**. The coordination sphere of the sodium atom is formed by two O_3N fragments of both ligands (Figure 3). The distances Na—O and Na—N are within the limits 2.31–2.55 and 2.57–2.59 Å, respectively. Essentially, they do not differ from those found for compound **I**.

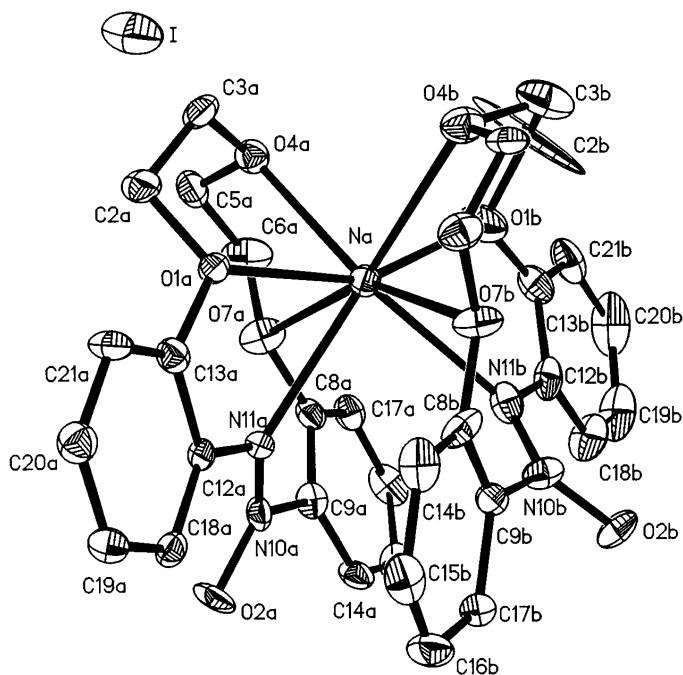


Figure 3. Compound **II** in a view parallel to the macrocycle mean planes and the atom numbering scheme.

The interatomic distances for compound **I** and for compound **II** are similar to those found in topologically analogous sandwich complexes of sodium with 12-membered crown ethers [11] where the Na—O distances are in the range of 2.43–2.54 Å. As a consequence of the similarity of 12-membered crown ethers and 13-membered azo and azoxy crown ethers, sodium forms sandwich-like complexes.

3.2. GEOMETRY AND CONFORMATION OF MACROCYCLE **L1**(*trans*) AND **L2** IN THE COMPLEXES

In compound **I** there exist two independent **I1** and **I2** complexes with four independent ligand molecules: **a–b** and **c–d**, respectively. Assuming the position of the aromatic residues in relation to the macrocycle all these ligands have a boat-like shape. The dihedral angles between the respective coordinating planes and the aromatic moieties in ligands **a–d** are:

Molecule		
a	20.1°	13.6°
b	14.6°	8.2°
c	22.4°	14.3°
d	16.4°	13.9°

The dihedral angles between the aromatic moieties of different macrocycles forming one sandwich cation are close to 20° . Considering this and the shielding magnitude of aromatic residues (Figure 2) intramolecular π - π interaction in the sandwich could not be excluded (compare compound **II**, Figure 3).

The interatomic distances and valence angles for **L1**(*trans*) in compound **I** are shown in Table III. Generally, they do not differ from those found for free **L1**(*cis*) or free **L2** [5-7] analogues. The average values for interatomic distances for ligands **a-d** are: C(*sp*³)—O 1.42, C(*sp*²)—O 1.39, C(*sp*³)—C(*sp*³) 1.49, N=N 1.24, N—C 1.43 Å. The geometry of the azo group is similar to that found by other authors [12].

The conformations of each of the **L1**(*trans*) molecules (**a-d**) are similar; small fluctuations in values of torsional angles are observed. These conformations could be described by the following set of torsional angles: $a \pm g \pm ga \pm gaacc (\pm 30^\circ) aac \pm g$ ($a = anti$, $g = gauche$, $c = cis$) (Table III). The torsion angles of C(9)—N(10) bonds for all four molecules equal 28 – 30° . Three of the C—O bonds exist in *anti* conformation, whereas the remaining three have convenient $\pm gauche$ conformation (Table III). Both C—C bonds in oxyethylene residues of all ligands (**a-d**) exist in *gauche* conformation. The polyoxyethylene fragments of **L1**(*trans*) at C(3) atoms have two *gauche-gauche* conformations (biangular fragment according to Dale [1, 13]).

The azoxy fragment in both independent ligands **a** and **b** in compound **II** do not differ from that in the free ligand **L2** [6]. It is characterized by a *trans-trans-gauche* conformation in both cases (Table III). As a consequence, the polyoxyethylene residue has a corner fragment at C(3). From these two molecules the ligand **b** is more strained. The fragment C(13)—O(1)—...—C(5) could be described by the following set of torsional angles: $122, 121, -121, -32, 142, -139^\circ$ which differ significantly from the standard values of 60 and 180° (Table III). Apparently self-organization of the ligand takes place for the formation of the sandwich structure.

The dihedral angle between the two mean planes of donor atoms O(1), O(4), O(7) and N(11) of the two ligands forming the complex is 3.2° . Deviation of the donor atoms from the mean plane does not exceed 0.117 for molecule **a** and 0.033 Å for molecule **b**. The benzo groups are located similarly to that found for **L1**(*cis*) and form with the mean plane of the donor atoms the following angles: 20.8 and 21.6 for **a** and 21.7 and 20.7 for **b**, respectively. As in the case of compound **I** there is shielding of the aromatic moieties of the crown ethers. The distances between the planes are 3.22 – 3.43 Å, the dihedral angle does not exceed 10° . The interatomic distances and valence angles [except the disordered fragment O(1)—C(2)—C(3)—O(4) of ligand **b**] are similar to that found for the free ligand **L2**.

The interaction of the azo- and azoxycrown ethers with sodium ions in chloroform solution was examined by comparing the ¹H-NMR spectra of free ligands and their complexes. In complex **I** the signals of the aliphatic CH₂ protons broaden because of strong interaction with sodium cations. The aromatic protons are more

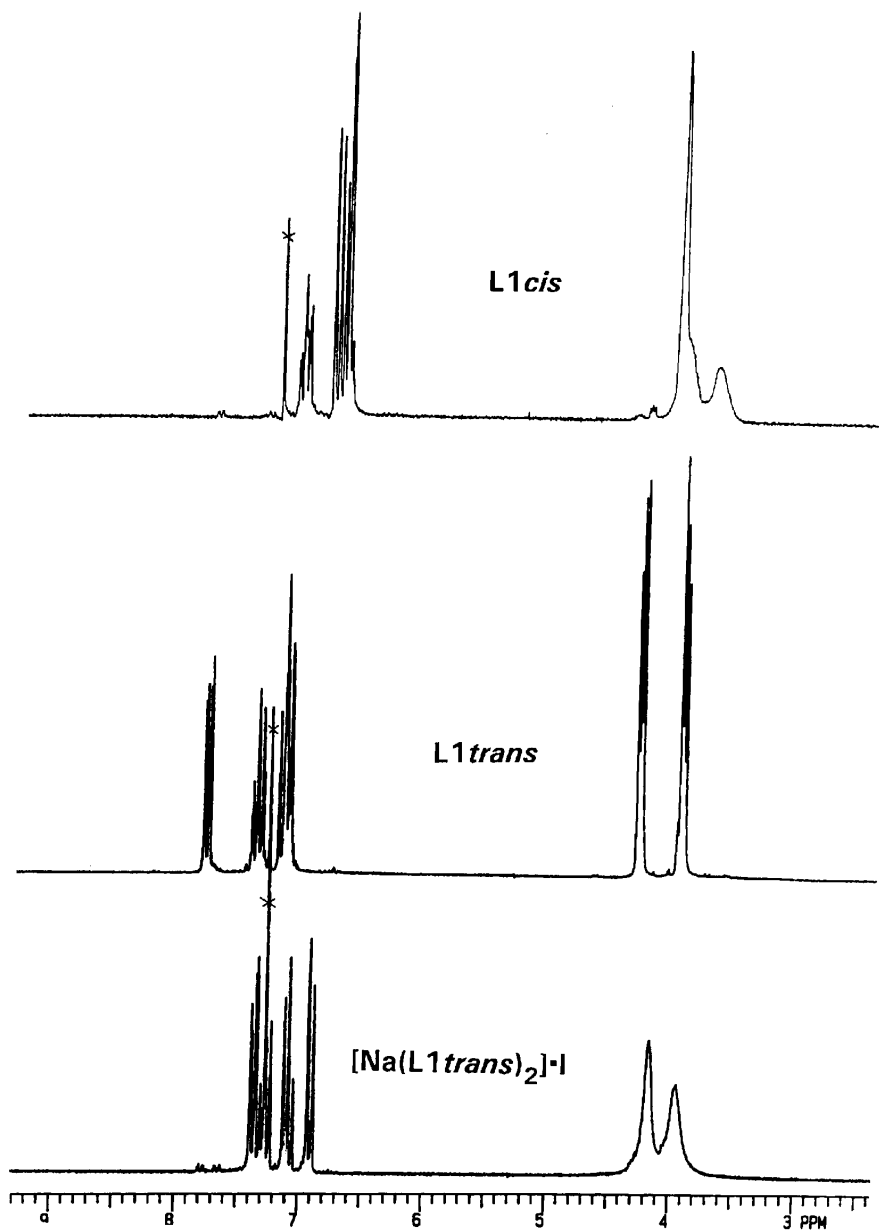


Figure 4. $^1\text{H-NMR}$ spectra of ligand **L1(cis)**, **L1(trans)** and complex **I**.

shielded as compared with the respective protons in free ligand **L1(trans)**. The last statement applies in particular to protons in a position *ortho* to the azo group.

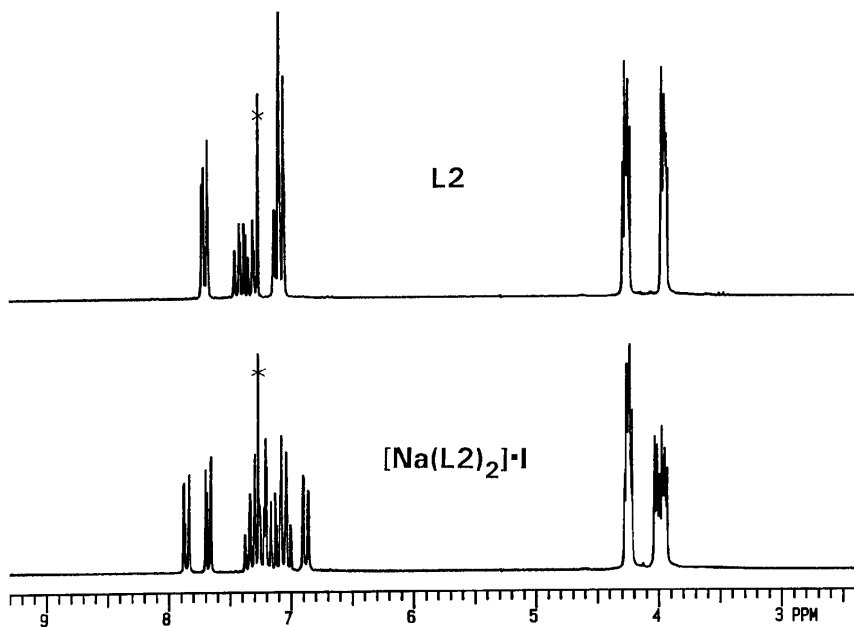


Figure 5. $^1\text{H-NMR}$ spectra of ligand **L2** and complex **II**.

For compound **II** the bands of the CH_2OCH_2 protons are more affected by sodium ions as compared with the ArOCH_2 bands. One of the protons *ortho* to the oxyethylene chain is significantly more shielded in the complex. Simultaneously, one proton *ortho* to the azoxy group is more deshielded in the complex as compared with free ligand **L2** (Figures 4, 5).

4. Conclusions

Azocrown ether **L1**(*cis*) is not well preorganized to form a complex with sodium cation; it therefore undergoes complexation by **L1**(*trans*). The quantitative yield of compound **I** from a mixture of both isomers and sodium iodide indicate *cis*–*trans* conversion accompanying complex crystallization. The azoxycrown ether **L2** forms a complex by using the nitrogen free electron pair originally directed inside the macrocycle. The ionic form of the sodium complex with 13-membered azocrown ether and its 2 : 1 stoichiometry favor high sodium selectivity of the membrane electrodes [4, cf. also 11a, 14].

Acknowledgements

The authors express their thanks to Dr V. Ch. Kravtsov for help in preparing the material for printing and to Professor V. K. Bel'skij for helpful discussion.

Financial support of this study from the KBN Grant No. 3T09A15508 is kindly acknowledged.

References

1. M. Hiraoka: *Crown Compounds. Their Characteristics and Applications*, Kodansha Ltd.: Amsterdam-Oxford-New York (1982).
2. D. E. Fenton, M. Merger, and M. R. Truter: *Biochem. Biophys. Res. Commun.* **48**, 10 (1972); W. Dreissig, Z. Dauter, A. Cygan, and J. F. Biernat: *Inorg. Chim. Acta* **96**, 21 (1985); N. R. Streltsova, A. A. Varnek, A. S. Glebov, and V. K. Bel'skii: *Problemy Kristalloghimii*, Nauka, Moscow, p. 47 (1989).
3. M. A. Bush and M. R. Truter: *J. Chem. Soc. Perkin Trans. 2*, 341 (1972); M. A. Bush and M. R. Truter: *J. Chem. Soc. B*, 1440 (1971).
4. E. Luboch, J. F. Biernat, E. Muszalska, and R. Bilewicz: *Supramol. Chem.* **5**, 201 (1995).
5. J. F. Biernat, E. Luboch, A. Cygan, Yu. A. Simonov, A. A. Dvorkin, E. Muszalska, and R. Bilewicz: *Tetrahedron* **48**, 4399 (1992).
6. J. F. Biernat, A. Cygan, E. Luboch, Yu. A. Simonov, and A. A. Dvorkin: *J. Incl. Phenom.* **16**, 209 (1993).
7. E. Luboch, L. F. Biernat, Yu. A. Simonov, and V. E. Zavodnik: *VIth International Seminar on Inclusion Compounds*, Tarabya-Istanbul, Turkey, Programme and Abstract Book, p. 88 (1995).
8. H. Huesmann, J. Maack, D. Möbius and J. F. Biernat: *Sensors and Actuators* **B29**, 148 (1995).
9. G. M. Sheldrick: in *SHELX-76 Program for Crystal Structure Determination*, University of Cambridge, England (1976); *SHELXL-93 Program for Crystal Structure Refinement*, Universität Göttingen, Germany (1993).
10. Yu. A. Simonov, A. A. Dvorkin, M. S. Fonari, T. I. Malinowski, E. Luboch, A. Cygan, J. F. Biernat, E. V. Ganin, and Yu. A. Popkov: *J. Incl. Phenom.* **15**, 79 (1993); J. F. Biernat, A. Cygan, E. Luboch, Yu. A. Simonov, T. I. Malinowski, V. K. Bel'skii and N. V. Bolotina: *J. Incl. Phenom.* **16**, 369 (1993); Yu. A. Simonov, A. A. Dvorkin, T. J. Malinowski, A. Cygan, E. Luboch, and J. F. Biernat: *Polish J. Chem.* **68**, 1783 (1994); K. A. Arnold, J. Mallen, J. E. Trafton, B. D. White, F. R. Fronczek, L. M. Oehrin, R. D. Gandour, and G. W. Gokel: *J. Org. Chem.* **53**, 5652 (1988); F. R. Fronczek, V. J. Gatto, C. Minganti, R. A. Schultz, R. D. Gandour, and G. W. Gokel: *J. Am. Chem. Soc.* **106**, 7244 (1984); B. D. White, F. R. Fronczek, R. D. Gandour, and G. W. Gokel: *Tetrahedron Lett.* **28**, 1753 (1987).
11. (a) E. Luboch, Yu. A. Simonov, and A. A. Dvorkin: *J. Incl. Phenom.* **20**, 335 (1995); (b) F. P. Boer, M. A. Neuman, F. P. van Remoortere, and E. C. Steiner: *Inorg. Chem.* **13**, 2826 (1974); (c) F. P. van Remoortere and F. P. Boer: *Inorg. Chem.* **13**, 2071 (1974); (d) S. Kamitori, K. Hirotsu, and T. Higuchi: *Bull. Chem. Soc. Jpn.* **61**, 3825 (1988); (e) R. D. Rogers: *Acta Crystallogr.* **C44**, 638 (1988).
12. S. N. Whittleton and J. F. Dunitz: *Acta Crystallogr. B* **38**, 2053 (1982).
13. J. Dale: *Acta Chem. Scand.* **27**, 1115 (1974).
14. E. Luboch, A. Cygan, and J. F. Biernat: *Tetrahedron* **46**, 2461 (1990); J. Wasilewski and J. F. Biernat: *J. Incl. Phenom.* **10**, 109 (1991).