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Structures of NaI Complexes of 16-Membered Azo- and Azoxycrown Ethers. Correlation of Crystal Structure and Carrier-Doped Membrane Electrode Selectivity

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Sodium iodide complexes of 16-membered dibenzoazocrown ether (complex I) and dibenzoazoxycrown ether (complex II) have been synthesized and their structures determined by X-ray method. Stoichiometry of both complexes is 1:1 (ligand:salt); the cation is coordinated to oxygen atoms of the oxyethylene moieties and to one nitrogen atom of azo group in the first, or to oxygen atom of the azoxy group in the last complex. Selectivities of membrane electrodes doped with ion carriers, including 16-membered azocrown and azoxycrown ethers have been compared and discussed mainly in terms of features of crystal structures of carrier complexes.

Keywords: Azocrowns, azoxycrowns, complexes, ion carriers, crystal structures, membrane electrode selectivities

INTRODUCTION

The general features and function of ion-selective membrane electrodes (ISME) have been recently described [1]. An ion carrier added to the membrane plays an important role: it influences the selectivity and sensitivity of the electrode. Despite the importance of this problem, it is very difficult to design a carrier structure that induces the required electrode properties. The selective response of a carrier-doped membrane electrode is considered to depend on certain differences: (i) the complex stabilities for the various ions, (ii) the water-membrane partition coefficients for the complexes or differences in their adsorption on the membrane surface, (iii) the diffusion coefficients for the respective complexes moving across the membrane, or (iv) differences in relay ratio of the ions from one to the another carrier molecule inside the membrane. While the complex stability constants may be measured, it is difficult to assess the other parameters noted above. Unfortunately, experimental data imply that the electrode selectivity very seldom conforms the stability constants of complexes.

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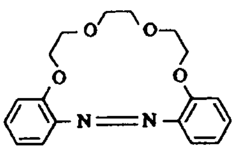
Numerous data collected in our laboratory indicate that selectivity of membrane electrodes doped with crown ethers correlate with certain structural features of carrier complexes in solid state [2]. The variables are the stoichiometry of the complex, the lipophilicity of the charged species, presence of water or solvent molecules in the crystal lattice, and the nature of the interactions between the complexed ion and the counterion. It is hoped that additional examples will either support or clarify these preliminary observations.

Previously, the structures of complexes of compounds: **3** with lithium [3], **3** and **4** with sodium [4], and **1** and **2** with potassium [5] were determined by X-ray crystallography. The parent compounds **1**–**4** and their lipophilic derivatives were applied to membranes as ion carriers. The membrane electrode was sodium selective when 13-membered compounds were present [6] and potassium selective in the case of 16-membered compounds [7].



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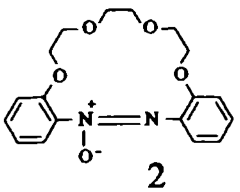

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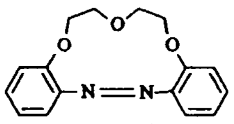

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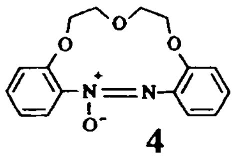

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The goal of this work was to study the sodium iodide complexes of **1** and **2** in the hope of correlating their structural features to the potassium/sodium selectivity of the membrane electrodes fabricated from them. A search for common structural features of ionophore complexes that induce high selectivity in membrane electrodes is also an important purpose of this work.

RESULTS

X-Ray Structures: Description of NaI Complex of Azocrown 1 (Complex I)

Two crystallographically independent complexes **Ia** and **Ib** of **I** present in the unit cell have essentially the same structure. The structure of complex **Ia** is shown in Figure 1. The stoichiometry of the complex is 1 : 1 (macrocycle:salt). Sodium and iodine form a "tight" ion pair with interatomic distances of 3.008Å (**Ia**) and 2.991Å(**Ib**), respectively. Sodium is additionally coordinated to four oxygens and one nitrogen atom of the macrocycle.

The —N=N— group is in the *trans* geometry with one nitrogen lone electron pair pointing inside the macrocycle. The azo group is disordered and occupies two positions with equal probability (Fig. 1). The Na—O distances are in the range 2.390–2.464Å; the Na—N distances are in the range of 2.455–2.481Å (Tab. I). The latter distances are slightly shorter than those observed for sodium sandwich complexes of **3** and **4** (2 : 1 stoichiometry) [4].

The ligand molecules related by two different symmetry centers $(1-x,-y,-z)$ for **Ia** and $(2-x,-y,1-z)$ for **Ib** in the crystal, partially

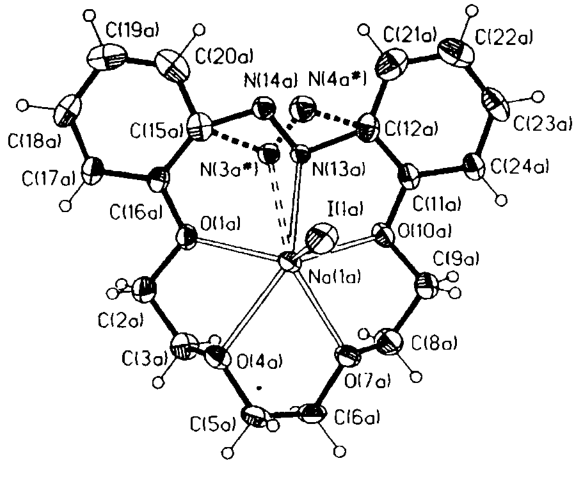

FIGURE 1 Structure of NaI complex of **1**, complex **Ia** shown. N(3a#) and N(4a#) denote nitrogen atoms of disordered azo group.

TABLE I Selected interatomic distances [Å], valence and torsion angles [°] in structures of NaI complexes with **1** and **2** (complexes I and II)

Bond or angle	Complex I		Complex II	
	molecule **a**	molecule **b**	molecule **a**	molecule **b**
	Sodium coordination polyhedron			
Na—I	3.008(3)	2.991(3)	3.015(17)	3.017(17)
Na—O(1)	2.424(5)	2.419(5)	2.62(3)	2.64(3)
Na—O(4)	2.449(5)	2.464(5)	2.40(3)	2.40(3)
Na—O(7)	2.414(6)	2.390(5)	2.37(3)	2.37(3)
Na—O(10)	2.429(5)	2.430(5)	2.67(3)	2.69(3)
Na—N(13)	2.455(7)	2.464(5)	–	–
Na—N(3#)	2.477(7)	2.481(8)	–	–
Na—O(14)	–	–	2.26(3)	2.28(3)
	Macrocyclic units			
O(1)—C(2)	1.448(9)	1.440(9)	1.43(2)	1.42(2)
C(2)—C(3)	1.475(11)	1.480(10)	1.47(2)	1.45(2)
C(3)—O(4)	1.413(9)	1.412(9)	1.42(2)	1.45(2)
O(4)—C(5)	1.424(9)	1.418(8)	1.42(2)	1.43(2)
C(5)—C(6)	1.493(12)	1.496(11)	1.46(2)	1.46(2)
C(6)—O(7)	1.435(8)	1.444(8)	1.43(2)	1.41(2)
O(7)—C(8)	1.426(10)	1.417(8)	1.44(2)	1.42(2)
C(8)—C(9)	1.490(12)	1.465(11)	1.46(2)	1.48(2)
C(9)—O(10)	1.443(9)	1.443(9)	1.43(2)	1.44(2)
O(10)—C(11)	1.364(8)	1.358(8)	1.371(18)	1.354(19)
C(11)—C(12)	1.359(10)	1.378(10)	–	–
C(12)—N(13)	1.531(8)	1.527(8)	1.44(3)	1.43(3)
N(13)—N(14)	1.237(9)	1.231(9)	1.243(19)	1.20(2)
N(14)—O(14)	–	–	1.27(2)	1.28(3)
N(14)—C(15)	1.396(9)	1.408(9)	1.47(3)	1.49(3)
C(15)—C(16)	1.402(10)	1.395(10)	–	–
C(16)—O(1)	1.355(8)	1.355(8)	1.347(17)	1.351(19)
C(12)—N(4#)	1.419(9)	1.433(9)	–	–
N(3#)—N(4#)	1.231(9)	1.233(9)	–	–
N(3#)—C(15)	1.550(9)	1.535(9)	–	–
C(16)—O(1)—C(2)	116.0(5)	115.8(6)	118(2)	116(3)
O(1)—C(2)—C(3)	107.0(6)	105.9(7)	108(3)	119(4)
C(2)—C(3)—O(4)	108.9(7)	109.5(7)	112(4)	111(4)
C(3)—O(4)—C(5)	115.4(6)	114.8(6)	121(4)	106(4)
O(4)—C(5)—C(6)	113.4(6)	112.3(6)	125(4)	113(4)
C(5)—C(6)—O(7)	106.3(6)	106.5(6)	99(4)	112(4)
C(6)—O(7)—C(8)	111.1(6)	113.7(6)	103(3)	115(4)
O(7)—C(8)—C(9)	107.9(7)	109.2(6)	111(4)	110(4)
C(8)—C(9)—O(10)	108.1(7)	107.7(6)	104(3)	106(4)
C(9)—O(10)—C(11)	117.3(6)	116.8(6)	107(3)	115(3)
O(10)—C(11)—C(12)	116.6(6)	116.5(7)	118(2)	119(3)
C(11)—C(12)—N(13)	109.3(7)	107.7(7)	128(2)	128(3)
C(12)—N(13)—N(14)	105.7(7)	105.7(7)	113(2)	111(3)
N(13)—N(14)—O(14)	–	–	132(3)	124(3)
O(14)—N(14)—C(15)	–	–	118(2)	122(3)
N(13)—N(14)—C(15)	111.0(9)	111.2(9)	110(3)	113(3)
N(14)—C(15)—C(16)	144.2(8)	144.5(8)	120(2)	115(2)
C(15)—C(16)—O(1)	116.7(6)	116.5(6)	119(2)	117(2)
C(11)—C(12)—N(4#)	146.2(9)	145.3(8)	–	–
C(12)—N(4#)—N(3#)	108.3(9)	108.9(9)	–	–
N(4#)—N(3#)—C(15)	104.1(7)	104.2(7)	–	–
N(3#)—C(15)—C(16)	106.1(7)	106.5(7)	–	–
O(1)—C(2)—C(3)—O(4)	62.8(8)	−63.6(9)	−60(5)	−38(7)
C(2)—C(3)—O(4)—C(5)	174.7(7)	−174.6(6)	177(4)	164(4)
C(3)—O(4)—C(5)—C(6)	68.3(9)	−64.0(8)	−69(6)	−158(5)
O(4)—C(5)—C(6)—O(7)	52.6(9)	−53.8(8)	−50(7)	47(7)
C(5)—C(6)—O(7)—C(8)	−166.0(7)	169.3(6)	147(4)	81(5)

TABLE I (Continued)

Bond or angle	Complex I molecule **a**	 molecule **b**	Complex II molecule **a**	 molecule **b**
C(6)—O(7)—C(8)—C(9)	– 175.9(7)	174.7(7)	171(4)	171(4)
O(7)—C(8)—C(9)—O(10)	– 58.9(10)	60.6(9)	66(5)	68(6)
C(8)—C(9)—O(10)—C(11)	– 169.2(7)	173.1(6)	173(3)	175(3)
C(9)—O(10)—C(11)—C(12)	– 179.1(7)	178.4(6)	– 159(3)	– 172(3)
O(10)—C(11)—C(12)—N(13)	4.1(9)	– 7.4(8)	– 3(3)	21(3)
C(11)—C(12)—N(13)—N(14)	– 171.6(8)	171.7(8)	– 53(3)	– 79(3)
C(11)—C(12)—N(4#)—N(3#)	29.7	– 23.9(8)	–	–
C(12)—N(13)—N(14)—C(15)	176.3(8)	– 179.0(8)	– 179(2)	– 171(2)
C(12)—N(4#)—N(3#)—C(15)	176.6(9)	– 177.5(8)	–	–
N(13)—N(14)—C(15)—C(16)	-- 9.4(20)	10.4(18)	– 131(2)	– 130(2)
N(4#)—N(3#)—C(15)—C(16)	165.5(15)	– 168.8(17)	–	–
N(14)—C(15)—C(16)—O(1)	4.7(17)	– 7.4(15)	7(3)	18(3)
C(15)—C(16)—O(1)—C(2)	– 176.6(7)	175.2(7)	168(3)	160(3)
C(16)—O(1)—C(2)—C(3)	178.2(6)	– 176.1(6)	– 166(4)	– 178(4)

In this Table and on Figure 1 N(3#) and N(4#) denote the second positions of the N(13) and N(14) atoms in the disordered azo group.

overlap (aromatic rings, antiparallel mode) and form dimers due to $\pi - \pi$ stacking interactions (Fig. 2, arrangement of two **Ia** shown). The distances between the mean planes of the benzene residues of the neighboring **a**–**a** and **b**–**b** ligands are 3.516 and 3.427Å, respectively.

X-Ray Structure: Description of NaI Complex of Azoxycrown 2 (Complex II)

Again, two crystallographically independent complexes **IIa** and **IIb** are present in the asymmetric part of the unit cell. Their structures are similar; only one is shown in Figure 3. As in complex **I**, sodium and iodine form a "tight" ion pair. The interatomic Na-I distances are 3.015Å and 3.017Å in **IIa** and **IIb**, respectively. Sodium is coordinated by four of the polyoxyethylene chain oxygen atoms and, in contrast to the previously described complexes [4,5], by the oxygen atom of the azoxy group. The Na-O(14) distances are the shortest and equal 2.26Å and 2.28Å for **IIa** and **IIb**, respectively. To the best our knowledge, this is the first example of such coordination of azoxy group.

The *trans* aromatic residues are close to the mean plane of the azoxy group in both complexes. Planar aromatic moieties of crystallographically independent molecules **IIa** and **IIb** (related by noncrystallographic pseudo two-fold

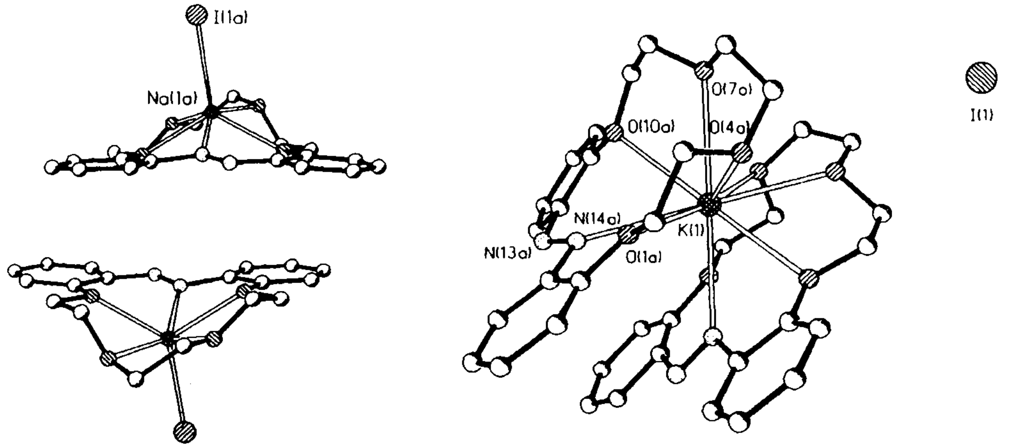

FIGURE 2 Left: NaI complex of **1**; arrangement of two **Ia** complexes. Right: structure of KI complex with azocrown **1** [5].

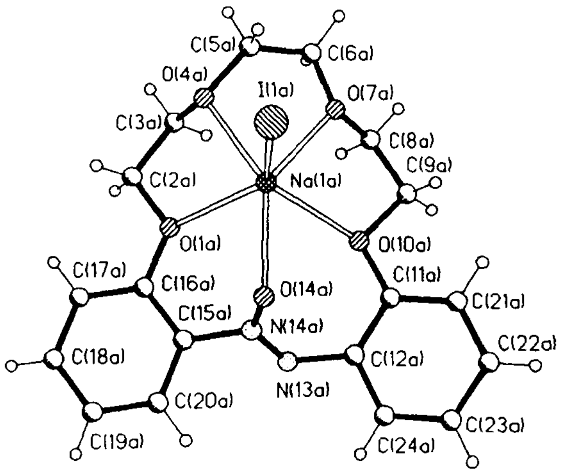

FIGURE 3 Structure of NaI complex with azoxycrown 2; complex IIa shown.

axes) lie in almost parallel planes and overlap partially. The distances between atoms of the respective part of molecule **IIa** and the mean plane of aromatic fragment of **IIb** are in the range 3.45–4.22Å suggesting $\pi-\pi$ stacking interaction similarly to that found for complex I (Fig. 4).

In all complexes involving the above azo or azoxy ligands the geometry of $-N=N-$ or $-N(O)=N-$fragment is *trans* with respect to phenyl residues. It is known, that the electron density of the azo group in *cis* azobenzene is larger than that in isomer *trans* [8]. However, the cooperative interaction of $-N=N-$ group and the oxyethylene fragment of the macrocycle favors coordination of metal cation by *E*-ligand.

DISCUSSION

We previously found that 16-membered dibenzoazocrown **1** and its more lipophilic derivatives are good ion carriers for membrane electrodes. The electrodes show high potassium over sodium selectivity [7]. These electrodes show up to 4000 times higher sensitivity for potassium than for sodium (according [9] the potentiometric selectivity coefficient $\log K^{pot}_{K,Na}$ equals up to -3.6). However, the stability constants for potassium and sodium iodide complexes of **1** (1 : 1 stoichiometry) are nearly the same [10] ($\log K = 3.15$ and 3.69, respectively). Considering

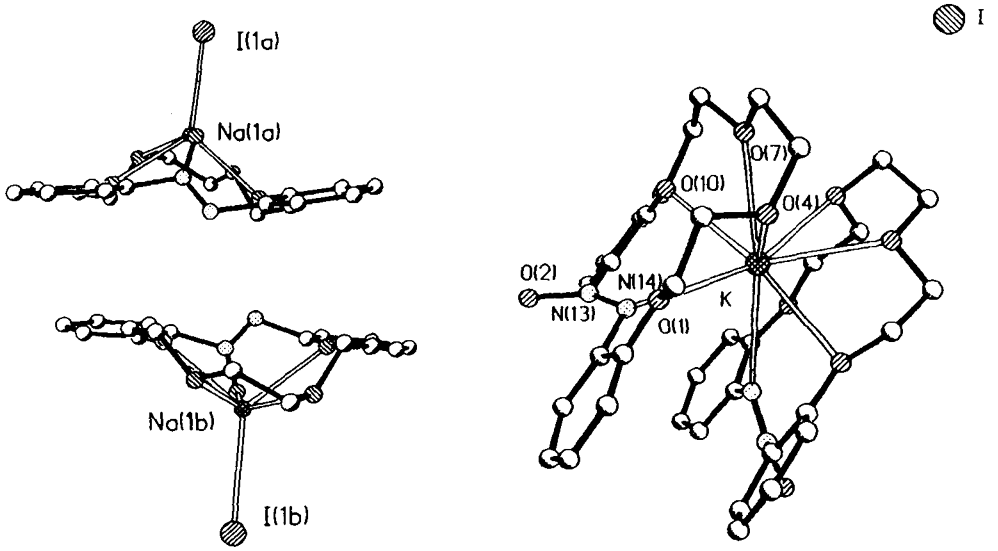

FIGURE 4 Left: arrangement of complex **IIa** and **IIb**. Right: structure of potassium iodide complex of 16-membered azoxycrown ether **2** [5].

only the stability constants, the high selectivity of the doped membrane electrode seems to be unreasonable. Like **1**, azoxy compound **2** induces rather high potassium over sodium selectivity.

The crystal structures of the KI and NaI complexes of **1** and **2** were expected to reveal factors controlling selectivity in the membrane electrode. The 2 : 1 (ligand : cation) KI complexes of **1** and **2** have been reported by us [5]. In the previously reported complexes, the charged species were well separated. In contrast to the KI complexes of **1** and **2**, the NaI complex of **1** has 1 : 1 stoichiometry. Since sandwich complex $(\mathbf{1})_2 \cdot K^+$ (Fig. 2) has a higher ratio of ligand to cation, it is expected to be more lipophilic than $\mathbf{1} \cdot K^+$. The more lipophilic complex is expected to partition into the membrane from water. Alternatively, membrane adsorption [1b] should be higher. The complexes that show NaI as "tight" ion pairs may transfer into the low polarity membrane in an effectively uncharged form, thus not affecting the electrode response [11]. These principles also apply to Na^+ and K^+ complexes of 16-membered azoxycrown ether (Fig. 4).

As a rule, membrane electrodes doped with 16-membered azocrown ethers display better potassium over sodium selectivity than the corresponding azoxycrown ethers. The potentials shown by membrane electrodes doped with azo- and azoxycrown ethers are comparable for potassium salt solutions; for sodium salt solutions they are higher for azoxy compounds. This indicates preferential sodium coordination by the oxygen atom of the azoxy group than by the nitrogen atom in the azocrown ether. Sodium may fit better in the azoxycrown ether cavity. This is reflected in ^1H NMR spectra of sodium complexed ligand **2**. The *ortho* hydrogen to $-N(O)=$ residue is deshielded by 0.5 ppm compared to the free ligand.

Previously we have also shown that 13-membered azo- and azoxycrown ethers based membrane electrodes display good sodium selectivity [6]. Sodium iodide forms complexes with 13-membered dibenzoazocrown **3** and dibenzoazoxycrown **4** in which sodium cation is coordinated by two ligands to form sandwich structures [4]. Lithium bromide forms a complex with **3** of 1 : 1 : 1 (crown : LiBr : H_2O) stoichiometry in which the complex cation is hydrated [3]. This suggests a high water affinity. The stability constant of the lithium complex exceeds considerably that for sodium and potassium [10]. Also in this case the stability constants do not correlate with selectivities of the respective membrane electrodes. Inspection of the crystal structures of lithium [3, 12] and sodium [4] complexes with **3** and **4** permitted explanation of high sodium over lithium selectivity in ISME. The same carrier causes high sodium over potassium selectivity of an electrode [6].

Other examples of ion carriers are known for which the structural features of their complexes correlate well with the selectivities of doped ISME's, in accordance with the above statements. Thus, benzo- and naphtho-15-crown-5 and their lipophilic derivatives form 1 : 1 complexes (methanol) with sodium and potassium ions of comparable stabilities, and slightly more stable complexes with potassium of 2 : 1 stoichiometry [13]. These crowns added to membrane made the ISME highly potassium selective, with $\log K^{pot}_{K,Na}$ up to -3.5 for lipophilic derivatives of benzo-15-crown-5 [14, 15]. In this respect, they behave like **1**. Moreover, benzo-15-crown-5 [16] and naphtho-15-crown-5 [17] form with potassium ion a sandwich like complex (2 : 1 stoichiometry) in a solid state. In these complexes the charged species are well separated. Benzo-15-crown-5 forms complex with sodium ion of 1 : 1 stoichiometry. In the sodium iodide complex the sodium ion is coordinated by crown ether and, in addition, by water molecule, which in turn binds iodide anion [18].

Both types of crown ethers *i.e.*, 16-membered azo- as well as azoxycrown ethers, and benzo- or naphtho-15-crown-5 ethers behave analogously by many respects. Structures of their

TABLE II Comparison of structures of ion carrier complexes and selectivities of the respective ion-selective membrane electrodes (ISME)

Ligand	Stoichiometry of complex in solid state (ligand/cation). Cation/anion interactions		Selectivity predicted for ISME	Potentiometric selectivity coefficient [9] $\log K^{pot}$ found
1	$K^+(2:1)$ separated ions [5]	Na^+ (1:1) "tight" ionic pair [*]	potassium over sodium	(K/Na) − 3.4 [7]
2	$K^+(2:1)$ separated ions [5]	Na^+ (1:1) "tight" ionic pair [*]	potassium over sodium	(K/Na) − 2.6 [7]
3	$Na^+(2:1)$ separated ions [4]	Li^+ (1:1) hydrated complex cation [3]	sodium over lithium and potassium	(Na/Li) − 2.1 [6] (Na/K) − 1.9 [6]
4	$Na^+(2:1)$ separated ions [4]	Li^+ (1:1) hydrated complex cation [12]	sodium over lithium and potassium	(Na/Li) − 2.2 [6] (Na/K)− 0.9 [6]
Benzo-15-Crown-5	K^+ (2:1) separated ions [16]	Na^+ (1:1) hydrated complex cation [18]	potassium over sodium	(K/Na) − 2.0 [14] (K/Na) − 3.5 [14]**
Benzo-12-Crown-4	Na^+ (2:1) separated ions [20]; K^+ (2:1) "tight" ionic pair [20]	Li^+ (1:1) "tight" ionic pair [19]	sodium over lithium and potassium	(Na/Li) − 2.3 [21]** (Na/K) − 1.0 [21]**

*This paper.
**The best selectivity found for lipophilic derivatives of ligand. For explanation see [14] and [21].

corresponding sodium and potassium complexes possess identical stoichiometry, similar mode of anion-cation interaction and behave similarly in ion-selective membrane electrodes.

Another example is benzo-12-crown-4 forming with lithium ion a 1:1 complex [19]. The same crown ether forms sandwich like complexes with potassium and sodium iodides [20]. In the potassium complex, there is close contact between the complexed cation and the iodide anion, whereas there is no contact in the last. Consequently, lipophilic derivatives of benzo-12-crown-4 make membrane electrodes selective for sodium in the presence of lithium and potassium [20, 21].

Correlations exemplifying structures of complexes of azo-, azoxycrown and benzocrown ethers and properties of the respective ISME are collected in Table II.

CONCLUSIONS

The X-ray structures provide information on the stoichiometries of complexes with target and interfering ions, on the lipophilicities of the charged species and, on the ability to form molecular or ionic lattices. These factors are apparent in complex structures and, to a great extent, determine membrane electrode properties. Inspection of complex structures could help to determine the applicability of various ligands as ion carriers in membrane electrodes and allow for selectivity predictions.

EXPERIMENTAL

^1H NMR spectra, in $CDCl_3$, were recorded with a Varian Gemini 200 MHz instrument.

Compounds **1** and **2** were obtained as described previously [5]. Melting points are uncorrected. Data on membrane electrodes and their selectivities were taken from papers published earlier by us [6,7,14,21]. These data were measured using membrane electrodes prepared in a standard way; selectivity were determined using procedure recommended by IUPAC [9].

Synthesis of Sodium Iodide Complex of 1 (Complex I)

Compound **1** (69 mg; 0.2 mmol) [5] and sodium iodide (30 mg; 0.2 mmol) were dissolved in methanol. The solution was evaporated in vacuum and the glassy residue was dissolved in an acetone-2-propanol mixture (1 : 1 v/v). The solution was left to evaporate slowly. The orange crystals (m.p. 214–216°C) were separated from a small amount of mother liquor. ^{1}H NMR, δ [ppm]: 3.88 (4H, s); 4.01–4.06 (4H, m); 4.35–4.40 (4H, m); 7.10–7.19 (4H, m); 7.45 (2H, dt, $J_1 = 1.5$ Hz, $J_2 = 8.8$ Hz); 7.80 (2H, *d*, $J \approx 8$ Hz). The respective chemical shifts for the free ligand are: 3.73; 3.92–3.99; 4.21–4.31; 7.00–7.10; 7.31–7.40; 7.66 [5].

Synthesis of Sodium Iodide Complex of 2 (Complex II)

The synthesis was performed in a similar way from azoxycrown ether **2** [5]. The crystals were washed with 2-propanol. M.p. 228–230°. ^{1}H NMR, δ [ppm]: 3.81 (4H, s); 3.90–4.00 (4H, m); 4.34–4.42 (4H, m); 7.00–7.18 (4H, m); 7.37 (1H, dt, $J_1 = 1.6$ Hz, $J_2 = 8.0$ Hz); 7.49 (1H, dt, $J_1 = 1.7$ Hz, $J_2 = 7.9$ Hz); 7.71 (1H, dd, $J_1 = 1.7$ Hz, $J_2 = 8.0$ Hz); 8.27 (1H, d, $J \approx 8$ Hz). The respective chemical shifts for free ligand are: 3.69; 3.88–3.98; 4.22–4.31; 6.99–7.12; 7.30; 7.42; 7.65; 7.75 [5].

Crystal Structure Determination of Complex I

For X-ray studies an orange crystal of prismatic habitus was selected. Data were collected on a CAD-4 (Enraf-Nonius) diffractometer, using graphite-monochromated MoK_α radiation. Lattice parameters were determined by least-squares from 25 centered reflections. Intensities were measured in the $\omega/2\theta$ scan mode. Three standard reflections, controlled every hour show no decay during the experiment. Structure was solved by the heavy atom method. Two crystallographically independent iodine atoms, corresponding to two similar complexes **Ia** and **Ib** in the asymmetric part of the unit cell, were located by Patterson method and the remaining non-hydrogen atoms by the successive Fourier synthesis, with except of azo group for both complexes in the asymmetric part of the unit cell. On this stage the partial model of structure was refined anisotropically. Analysis of differential Fourier synthesis showed that the —N=N— group in complexes is disordered and occupies two positions with equal probability. Disordered nitrogen atoms and hydrogens were refined isotropically. Details of the computer programs used are given in reference [22]. Crystallographic, experimental and model refinement data are summarized in Table III.

Crystal Structure Determination of Complex II

For X-ray studies an orange block monocrystal was cut off from a conglomerate. Data were collected on DAR-UMB diffractometer using graphite monochromated MoK_α radiation and corrected for Lorentz and polarization effects. Lattice parameters were determined by least squares from 25 centered reflections in θ-range 11.3–16.7°. Standard reflections controlled every hour showed no decay during the experiment. Structure was solved by the heavy atom method and refined using full-matrix least squares (SHELXS86, SHELXL93) [22, 23]. Two essentially similar complexes **IIa** and **IIb** were found in the asymmetric part of the unit cell. The crystal diffracted very weakly (only 1210 reflections could be labelled as "observed" [$I > 2\sigma(I)$] in the 2.29 to 25.2° θ-range, and were included in crystal structure solution and refining process.

TABLE III Crystal data and structure refinement for complex I and complex II

	Complex I	Complex II
Empirical formula	$C_{18}H_{20}IN_2NaO_4$	$C_{18}H_{20}IN_2NaO_5$
Formula weight	478.25	494.25
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pca2_1$
Unit cell dimensions	$a = 15.976(3)$ Å; $b = 14.817(3)$ Å; $\beta = 94.02(3)°$ $c = 16.850(3)$ Å;	$a = 14.957(3)$ Å; $b = 13.032(3)$ Å $c = 21.100(4)$ Å
Volume	3978.9(13) $Å^3$	4112.8(15) $Å^3$
Z	8	8
Density (calculated)	1.597 $g \cdot cm^{-3}$	1.596 $g \cdot cm^{-3}$
Absorption coefficient	1.656 mm^{-1}	1.608 mm^{-1}
$F(000)$	1904	1968
Crystal size	0.2 × 0.2 × 0.7 mm	0.4 × 0.3 × 0.2 mm
Theta range for data collection	1.83 to 24.97°	2.29 to 25.20°
Index ranges	$-18 \leq h \leq 0$, $-17 \leq k \leq 0$, $-18 \leq l \leq 18$	$-16 \leq h \leq 15$, $-15 \leq k \leq 0$, $0 \leq l \leq 20$
Reflections collected	3216	1210
Independent reflections	3090 [$R(\text{int}) = 0.0617$]	1210/1210 [$R(\text{int}) = 0.0000$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3090/16/468	1210/360/445
Goodness-of-fit on F^2	1.066	1.142
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0490$, $wR^2 = 0.1111$	$R_1 = 0.0672$, $wR2 = 0.1525$
R indices (all data)	$R_1 = 0.0490$, $wR^2 = 0.1111$	$R_1 = 0.0672$, $wR2 = 0.1525$
Extinction coefficient	0.0025(3)	0.07(11)
Largest diff. peak and hole	1.137 and $-1.410 e \cdot Å^{-3}$	0.664 and $-0.448 e \cdot Å^{-3}$

To decrease the number of parameters and to improve data/parameters ratio the aromatic residues were refined as rigid moieties of ideal hexagon (C—C = 1.39Å). Positions of the hydrogen atoms were calculated from geometrical considerations and were refined as constrained to bonding atoms in the 'ride' mode. Crystal and data collection and solution details for complexes II are shown in Table III.

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