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12-Membered Crown Ethers. Lipophilic Derivatives of Benzo- and Naphtho-12-crown-4 and Their Membrane Electrode Properties. Crystal Structures of Benzo-12-crown-4 NaI and KI Complexes

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Abstract. Lipophilic derivatives of benzo-12-crown-4 and naphtho-12-crown-4 have been synthesized. The behavior of the parent compounds and their derivatives in membrane ion-selective electrodes have been studied. Selectivity changes have been observed with the rise in lipophilicity. Crystal structures of the NaI and KI complexes of benzo-12-crown-4 (**1** and **2**) have been determined by X-ray analysis. The alkali metal and iodide ions are in direct contact in **2** but not in **1**. Compound **1** [Na(benzo-12-crown-4)$_2$]·I is triclinic, with $a = 13.368(8)$, $b = 10.727(7)$, $c = 10.325(4)$ Å; $\alpha = 73.56(4)$, $\beta = 77.73(4)$, $\gamma = 108.70(5)°$; $Z = 2$, space group is $P\bar{1}$. Compound **2** [K(benzo-12-crown-4)$_2$·I] is monoclinic, with $a = 15.807(8)$, $b = 12.043(4)$, $c = 15.601(6)$ Å, $\beta = 117.74(3)°$; $Z = 4$, space group $C2/c$. In both compounds the cations interact with all oxygen atoms of two crown ether molecules. Correlation of the crystal structures and behavior of the crown ethers in ion-selective membrane electrodes is discussed.

Key words: 12-Membered crown ethers, ion-selective membrane electrodes, complexes, crystal structure, X-ray analysis, conformation.

Supplementary Data related to this article have been deposited with the British Library as Supplementary Publication No. 82185 (15 pages).

1. Introduction

Small sized crown ethers, in particular 12-membered ones, have not been thoroughly studied owing to low yields in troublesome syntheses and low stability constants of the resulting complexes. However, such crown ethers are of interest because their rather high conformational rigidity facilitates preorganization of the donor atoms of the macrocycle in the formation of particular complexes. Selectivity in complex formation is related to their sizes, whereas aromatic systems condensed to the macrocycle decreases their conformational flexibility.

The cavity of 12-membered crown ethers (internal diameter 1.2–1.5 Å) topologically corresponds to the lithium cation (diameter = 1.2 Å) [1, 2] and constrains its complexation with a 1 : 1 metal : crown ether stoichiometry. The sodium cation Na^+ (D = 1.9 Å) [2] with 12-crown-4 forms sandwich-like complexes with a sodium to crown ether ratio of 1 : 2. For 12-crown-4 complexes with sodium the following structures are known: $Na(12\text{-crown-}4)_2\cdot(OH)\cdot 8H_2O$ [3], $Na(12\text{-crown-}4)_2\cdot Cl\cdot 5H_2O$ [4], $Na(12\text{-crown-}4)_3\cdot Cl\cdot(\gamma\text{-cyclodextrin})_3$ [5], $[Na(12\text{-crown-}4)_2]_2\cdot UO_2Cl_4\cdot 2MeOH$ [6] and $Na(12\text{-crown-}4)_2\cdot ClO_4$ [7]. All these crystals possess ionic structures in which there is no direct interaction of sodium with the anionic species. The sodium coordination number is 8 and the coordination polyhedron formed by the oxygen atoms of both crown ether molecules is a square antiprism.

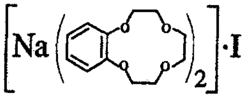
The larger potassium cation (D = 2.66 Å) [2] may induce an arrangement of the complex components in perching [8] or sandwich-type structures. Certainly, in $K(12\text{-crown-}4)_3\cdot Cl\cdot(\gamma\text{-cyclodextrin})_3$ clathrate hydrate [9] and in the cluster potassium complex $[Cu_4I_6][Cu_8I_{13}]\cdot K_7(12\text{-crown-}4)_6$ [10] there exist 1 : 2 sandwich structures with the coordination polyhedron resembling the respective sodium complexes. The smaller calcium cation forms complexes of 1 : 1 stoichiometry. The relevant example is $(\text{benzo-}12\text{-crown-}4)\cdot Ca(NCS)_2\cdot H_2O\cdot CH_3CN$ [11]. Analogously, the perching [8] type of structure has been found for some rare earth complexes like $(\text{benzo-}12\text{-crown-}4)\cdot Nd\cdot(NO_3)_3$ [11] and $(\text{benzo-}12\text{-crown-}4)\cdot La\cdot(NO_3)_3\cdot H_2O\cdot MeCN$ [12].

A search of the literature shows that the data on sodium or potassium complexes with small crown ethers (12-membered in particular) have a random character; there are no rules governing the role of the alkal metal cation as well as the counter ion. Previously we noted [13] that the behavior of benzo- and naphtho-12-crown-4 substantially differ from that of 12-crown-4.

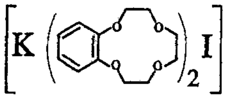
In solution benzo-12-crown-4 forms complexes with both sodium and potassium cations of 1 : 1 and 2 : 1 stoichiometry. Calorimetry revealed that in acetonitrile the stability constants are $\log K_1 = 1.88$ and $\log K_2 = 2.62$ for the 1 : 1 and 2 : 1 sodium complexes [14], respectively. According to a spectroscopic method, the respective values are 1.65 and 3.33 [15]. For potassium complexes the stability constants are 1.76 and 1.08, respectively [14, 15].

As lower $\log K_2$ values are found for potassium rather than for sodium and as the cavity size in benzo-12-crown-4 is compatible to the sodium cation, one would expect sodium selectivity in membrane ion-selective electrodes with this crown ether, in particular with its lipophilic derivatives. Some results concerning the behavior of such crown ethers in ion-selective membrane electrodes have already been presented [16, 17].

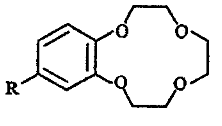
A systematic study of ion-selective membrane electrode selectivities as a function of the lipophilicity of substituted benzo-15-crown-5 and benzo-18-crown-6 ion carriers has been published [18, 19]. This work presents results on the synthesis of tertiary alkyl substituted benzo- and naphtho-12-crown-4. The *tert*-alkyl derivatives obtained were studied in ion-selective membrane electrodes. Struc-



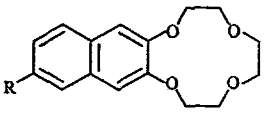
1



2



3 R = H
4 R = $C(CH_3)_3$
5 R = $C(CH_3)_2C_5H_{11}$
6 R = $C(CH_3)_2C_{12}H_{25}$



7 R = H
8 R = $C(CH_3)_3$
9 R = $C(CH_3)_2C_5H_{11}$

tural studies of complexes of sodium and potassium iodide with benzo-12-crown-4 were performed to rationalize the influence of lipophilicity of crown ethers on the selectivity of membrane ion-selective electrodes.

2. Experimental

NMR spectra were recorded on a Varian 60 MHz instrument. Mass spectra were recorded on a Varian MATT 711 instrument using the FD technique.

All materials and solvents were of analytical reagent grade. Benzo-12-crown-4 (**3**) was prepared according to Pedersen [20]. In the synthesis sodium hydroxide was replaced by lithium hydroxide; the reaction time was extended to 6 days [16]. Alternatively the synthesis was performed according to [21].

Naphtho-12-crown-4 (**7**) was prepared as described in [13].

2.1. SYNTHESIS OF COMPLEXES

2.1.1. *Sodium Iodide Complex of Benzo-12-crown-4 (**1**)*

A mixture of benzo-12-crown-4 (112 mg, 0.5 mmol) and sodium iodide (75 mg, 0.5 mmol) was dissolved in ethanol and evaporated to give a thick oil. The residue was dissolved in methanol with a small amount of acetone and left for crystallization. Single crystals with a melting point of 190° were obtained.

2.1.2. *Potassium Iodide Complex of Benzo-12-crown-4 (**2**)*

A mixture of benzo-12-crown-4 (112 mg, 0.5 mmol) and potassium iodide (84 mg, 0.5 mmol) was dissolved in ethanol and evaporated to give a thick oil. The residue was dissolved in *n*-butanol and allowed to stand for crystallization. Crystals melting at 130–132° were obtained.

2.2. SYNTHESIS OF ALKYL DERIVATIVES OF BENZO- AND NAPHTHO-12-CROWN-4

2.2.1. *tert-butyl derivatives* **4** *and* **8**

A mixture of crown ether (5 mmol), polyphosphoric acid (10 mL) and *tert*-butanol (20 mmol) was stirred and heated at 60° for 18 h. The cooled reaction mixture was diluted with ice cold water and the product was extracted with chloroform. The organic solution was washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on a silica gel column using initially heptane to remove polyisobutylene. The desired product was eluted using methylene chloride and crystallized from *n*-heptane at 0°.

The yield of 4′-*tert*-butylbenzo-12-crown-4 (**4**) melting at 48–49° [22] was 70%. NMR ($CDCl_3$; δ ppm): 1.20 (s, 9H); 3.67–4.27 (m, 12H); 6.76–6.98 (m, 3H).

6′-*tert*-Butylnaphtho-12-crown-4 (**8**) melting at 59–62° was isolated in 69% yield. NMR ($CDCl_3$; δ ppm): 1.30 (s, 9H); 3.57–4.30 (m, 12H); 7.03–7.63 (m, 5H). $m/z = 330$.

2.2.2. *tert-Alkyl Derivatives* **5**, **6** *and* **9**

These were prepared analogously, using 5 mmol of crown ether, 8–10 mmol *tert*-alcohol and 8–10 mL polyphosphoric acid. The reaction temperature was maintained (a) at 60° overnight or (b) at 70° for 4 h.

Compound **5** (method a) melting at 26–27° was obtained with 67% yield; NMR ($CDCl_3$; δ ppm): 0.5–1.83 (m, 17H); 3.77–4.30 (m, 12H); 6.80–6.97 (m, 3H). $m/z = 336$.

Compound **6** (method b) (oil) was obtained with 40% yield; NMR ($CDCl_3$, δ ppm): 0.70–1.80 (m, 31H); 3.68–4.23 (m, 12H); 6.70–7.86 (m, 3H). $m/z = 434$.

Compound **9** (method a) melting at 75–76° was obtained with 59% yield. NMR ($CDCl_3$; δ ppm): 0.53–1.80 (m, 17H); 3.70–4.37 (m, 12H); 7.10–7.70 (m, 5H). $m/z = 386$.

2.3. MEMBRANE ELECTRODES AND EMF MEASUREMENTS

High molecular weight poly(vinyl chloride) (POLANVIL S-70) and *o*-nitrophenyl octyl ether, either synthesized in our own laboratory according to [23] or obtained commercially (Fluka), were used for membrane preparation. Potassium tetrakis(4-chlorophenyl)borate (Fluka) was used as a lipophilic salt. All measurements were performed at 25 ± 1°C using a 654 pH meter (Metrohm) allowing readings with an accuracy of ±0.1 mV. Lithium acetate (1 mol dm^{-3}) was used as an external electrolyte in the double-junction reference electrode (RADELKIS OP-08020P Ag/AgCl electrode).

Poly(vinyl chloride) membranes for ion-selective electrodes were prepared in a conventional way [18, 19]. A typical composition (w/w) of a membrane was as follows: 9% of the respective ionophore, 30.2% of poly(vinyl chloride), 60.5% of 2-nitrophenyl octyl ether and 0.3% potassium tetrakis (4-chlorophenyl) borate. All the components were dissolved in freshly distilled tetrahydrofuran, the solution was poured into a glass ring located on a glass plate and left to evaporate. The discs were incorporated into Ag/AgCl electrode bodies, with 10^{-2} mol dm^{-3} NaCl as the internal electrolyte. The average thickness of the membranes thus obtained was 0.28 mm. The electrode was conditioned for 1 day in 10^{-2} mol dm^{-3} NaCl solution before measurements. The slope and the detection limit of the electrodes were determined according to IUPAC [24] recommendations. The selectivity coefficients log $K^{\mathrm{pot}}_{\mathrm{Na,K}}$ were determined by the separate solution method (SSM) at a 10^{-2} mol dm^{-3} concentration of the corresponding metal chlorides. The fixed (10^{-2} mol dm^{-3} KCl) interference method (FIM) [25] was used to determine the log $K^{\mathrm{pot}}_{\mathrm{Na,K}}$.

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

The unit cell parameters and intensities of reflections were measured on an RED-4 automated four-circle diffractometer (produced by the Institute of Crystallography, Moscow, Russia) at 293 K by the ω-$\theta/2\theta$ scanning method at a constant rate of 8 ° min^{-1} using Mo$_{K_\alpha}$ radiation. Parameters of the unit cells were refined based on 12 reflections of the $h00$, $0k0$ and $00l$ type in the range of θ angles within 7–10°. The reflections were collected up to $\theta = 23°$ for **1** and 25° for **2**. The variation of standard intensities was monitored every hour. The intensity differences did not exceed 3%.

Crystallographic and experimental data for **1** and **2** are presented in Table I.

The structures were solved by the heavy atom method based on 1188 reflections for **1** and 1183 reflections for **2** with $I(hkl) \geq 3\sigma(I)$. All calculations were performed with the SHELX76-system in the SHELX-SM [26] package on an SM-4 computer. Refinement of the nonhydrogen atoms was performed with anisotropic temperature factors. Hydrogen atoms were located partly from a difference Fourier map and refined with an overall isotropic temperature factor. Both benzene groups were refined assuming ideal geometry (C—C distance = 1.40 Å; C—C—C angle = 120°). See Tables II and III.

3. Discussion

3.1. SYNTHESIS

The *tert*-alkyl derivatives were obtained by alkylation of the parent crown ethers. The reactivity of the benzene ring in benzo-12-crown-4 towards alkylation is reduced compared to larger sized benzocrown ethers [27]. The composition of

TABLE I. Summary of crystal data, experimental details and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{48}O_8INa$	$C_{24}H_{48}O_8IK$
Temperature	293 (2) K	293 (2) K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions	$a = 13.368(8)$ Å	$a = 15.807\ (8)$ Å
	$b = 10.724(7)$ Å	$b = 12.043(4)$ Å
	$c = 10.325(4)$ Å	$c = 15.601(6)$ Å
	$\alpha = 73.56(4)^\circ$	$\alpha = 90^\circ$
	$\beta = 77.73(4)^\circ$	$\beta = 117.74(3)^\circ$
	$\gamma = 108.70(5)^\circ$	$\gamma = 90^\circ$
Volume	1267.6 $Å^3$	2629 $Å^3$
Z	2	4
Density (calculated)	1.568 g cm^{-3}	1.553 g cm^{-3}
Absorption coefficient	1.347 mm^{-1}	1.437 mm^{-1}
$F(000)$	608	1248
Crystal size	0.15 × 0.15 × 0.40 mm	0.20 × 0.15 × 0.35 mm
Theta range for data collection	2–22.9°	2–25.2°
Index ranges	$-13 \le h \le 13$	$-17 \le h \le 0$
	$-10 \le k \le 11$	$0 \le k \le 13$
	$0 \le l \le 11$	$-18 \le l \le 18$
Reflections collected	1250	1086
Independent reflections	1188	1029
Refinement method	Full matrix LSM	Full matrix LSM
Goodness-of-fit on F	0.780	1.029
Final R indices $[I > 3\sigma(I)]$	$R1 = 0.052$	$R1 = 0.067$
	$wR = 0.058$	$wR = 0.058$
w	$1/[\sigma(F)^2 + 0.005F^2]$	$1/[\sigma(F)^2 + 0.005F^2]$
Largest diff. peak (e $Å^{-3}$)	0.735	0.973

the alkylation products was confirmed by field desorption mass spectrometry. Location of the substituents in naphtho-12-crown-4 was established by NMR spectroscopy.

3.2. EMF MEASUREMENTS

The EMF experiments revealed that potassium selectivities of the conditioned membrane electrodes containing unsubstituted benzo-12-crown-4 and 2-nitrophenyl octyl ether as plasticizer exceeds that for sodium (Figure 1). The introduction of lipophilic *tert*-butyl, dimethylhexyl or dimethyltridecyl substituents onto the benzene ring significantly changes the order of selectivities. The elec-

TABLE IIa. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2$) for **1**.

	x/a	y/b	z/c	B (eq)	x/a	y/b	z/c	B (eq)
	Molecule **1a**				Molecule **1b**			
I	2610(2)	133(3)	−101(3)	4.19(7)				
Na	7587(8)	3642(11)	3653(11)	3.2(3)				
O(1)	6262(14)	4852(16)	3375(18)	3.3(5)	9063(13)	3160(18)	4579(17)	3.1(5)
C(2)	6639(19)	6273(21)	3221(29)	3.4(9)	8842(22)	2826(33)	6042(23)	5.0(10)
C(3)	7619(17)	6593(27)	3727(28)	3.9(9)	8220(19)	3633(31)	6524(31)	4.8(10)
O(4)	8469(13)	6266(18)	3100(18)	3.3(5)	7247(14)	3454(18)	6216(18)	3.9(6)
C(5)	9105(23)	7148(26)	1619(29)	3.9(8)	6326(24)	2173(36)	7270(34)	5.6(12)
C(6)	9635(24)	6334(33)	1006(30)	5.5(10)	5655(31)	1290(56)	6662(41)	10.5(21)
O(7)	8846(14)	5012(18)	1145(17)	4.0(5)	6083(16)	1288(23)	5354(23)	5.7(7)
C(8)	8267(21)	5068(24)	159(25)	4.0(8)	6366(20)	154(27)	5393(28)	5.0(8)
C(9)	7380(18)	3615(26)	567(23)	4.0(9)	6974(19)	457(26)	3879(30)	4.5(8)
O(10)	6590(13)	3177(19)	1940(16)	3.6(5)	7940(13)	1699(18)	3217(20)	4.2(6)
C(11)	5666(11)	3509(17)	1984(17)	2.7(7)	8922(10)	1628(17)	3276(17)	3.2(7)
C(12)	5522(11)	4396(17)	2701(17)	3.2(8)	9498(10)	2341(17)	4009(17)	2.2(6)
C(13)	4602(11)	4756(17)	2783(17)	3.6(8)	10511(10)	2280(17)	4087(17)	3.8(8)
C(14)	3827(11)	4229(17)	2150(17)	4.3(8)	10949(10)	1507(17)	3432(17)	4.3(8)
C(15)	3970(11)	3341(17)	1433(17)	4.8(9)	10373(10)	795(17)	2699(17)	5.2(9)
C(16)	4890(11)	2981(17)	1350(17)	3.9(7)	9360(10)	856(17)	2621(17)	4.1(8)

trodes with benzo-12-crown-4 derivatives in the membrane are sodium selective showing, log $K^{\mathrm{pot}}_{\mathrm{Na,K}}$ values equal to −0.95, −1.0 or −0.92 for compounds **4**, **5** and **6**, respectively.

The more lipophilic naphtho-12-crown-4 (**7**), in contrast to benzo-12-crown-4 (**3**), is sodium selective and the lipophilic substituents do not significantly improve the selectivity. The respective selectivity values log $K^{\mathrm{pot}}_{\mathrm{Na,K}}$ are −0.73, −0.90 and −0.95 for compounds **7**, **8** and **9**.

Compounds **4**–**9** show good selectivities towards other biologically important cations present in physiological fluids. The slopes for sodium ions are within the range of 58–60 mV/decade and the detection limits (10 g $\mathrm{LD}_{\mathrm{Na}}$ varied from −4.40 for **3** up to −4.90 to −5.65 for the remaining ionophores. It is worth noting that the introduction of the *tert*-butyl substituent significantly improves these parameters as compared with the parent benzo-12-crown-4 (Figure 1).

Comparison of the data on selectivity of benzo-15-crown-5 and naphtho-15-crown-5 as well as the respective alkyl derivatives led to the conclusion that the differences in stoichiometry of the respective sodium (1 : 1) and potassium (2 : 1) complexes enhance the potassium selectivity due to the significant differences in lipophilicity [28, 18, 19]. It was also shown, that both ligands: benzo-15-crown-5 and naphtho-15-crown-5 are comparatively well preorganized to form complexes

TABLE IIb. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2) for **2**.

	x/a	y/b	z/c	B (eq)
I	0	-1204(2)	2500	6.77(6)
K	0	1945(4)	2500	4.5(1)
O(1)	1131(8)	2722(8)	480(8)	6.2(4)
C(2)	914(14)	2296(15)	−226(11)	8.1(6)
C(3)	206(20)	1392(25)	106(13)	14.9(14)
O(4)	−446(8)	1305(10)	1005(7)	6.8(4)
C(5)	−1360(14)	1395(22)	1174(18)	12.4(13)
C(6)	−2078(13)	2020(22)	2009(15)	11.0(9)
O(7)	−1818(6)	2623(8)	2557(7)	5.0(3)
C(8)	−1978(10)	3736(16)	2534(14)	8.4(7)
C(9)	−1184(9)	4451(12)	1868(12)	5.9(5)
O(10)	−308(7)	4034(10)	1707(9)	7.7(4)
C(11)	526(5)	4532(8)	1066(6)	4.3(4)
C(12)	1262(5)	3853(8)	421(6)	4.3(4)
C(13)	2151(5)	4311(8)	−196(6)	5.4(4)
C(14)	2303(5)	5449(8)	−168(6)	6.3(5)
C(15)	1567(5)	6127(8)	477(6)	6.4(6)
C(16)	678(5)	5669(8)	1094(6)	5.2(5)

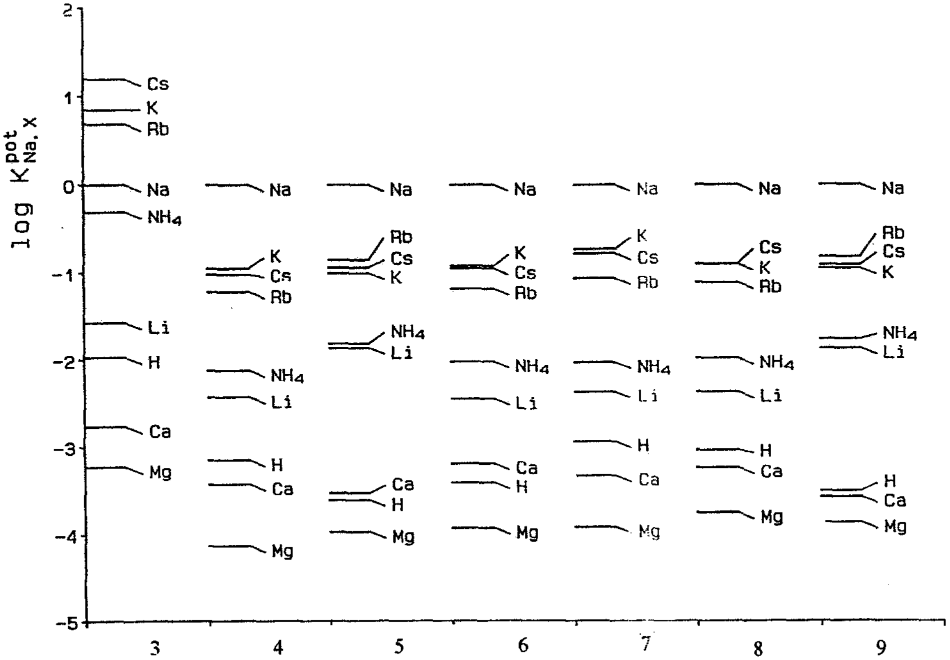


Fig. 1. Selectivities of membrane electrodes based on compounds **3–9**.

TABLE III. Interatomic distances (Å), bond and torsion angles (deg) for **1** and **2**.

	Molecule **1a**	Molecule **1b**	Molecule **2**
Na(K)—O(1)	2.52(2)	2.50(2)	2.95(1)
Na(K)—O(4)	2.51(2)	2.52(2)	2.83(1)
Na(K)—O(7)	2.47(2)	2.49(2)	2.948(9)
Na(K)—O(10)	2.49(2)	2.41(2)	2.94(1)
O(1)—C(2)	1.39(3)	1.39(3)	1.40(3)
C(2)—C(3)	1.49(4)	1.49(5)	1.47(4)
C(3)—O(4)	1.38(3)	1.37(4)	1.30(2)
O(4)—C(5)	1.44(3)	1.44(3)	1.35(3)
C(5)—C(6)	1.48(5)	1.46(6)	1.48(3)
C(6)—O(7)	1.42(4)	1.36(5)	1.33(3)
O(7)—C(8)	1.40(4)	1.38(4)	1.37(2)
C(8)—C(9)	1.50(3)	1.49(4)	1.48(2)
C(9)—O(10)	1.42(3)	1.38(2)	1.38(2)
O(10)—C(11)	1.39(3)	1.35(2)	1.37(1)
C(11)—C(12)	1.40(3)	1.40(3)	1.40(1)
C(12)—O(1)	1.37(3)	1.39(3)	1.37(1)
C(11)—C(16)	1.40(2)	1.40(3)	1.40(1)
C(12)—C(13)	1.40(2)	1.40(3)	1.40(1)
C(13)—C(14)	1.40(2)	1.40(3)	1.40(1)
C(14)—C(15)	1.40(2)	1.40(3)	1.40(1)
C(15)—C(16)	1.40(2)	1.40(3)	1.40(1)
O(1)—C(2)—C(3)	108.0(2)	110.0(3)	115.0(2)
C(2)—C(3)—O(4)	116.0(3)	116.0(3)	122.0(2)
C(3)—O(4)—C(5)	116.0(2)	111.0(2)	116.0(2)
O(4)—C(5)—C(6)	107.0(2)	114.0(3)	122.0(2)
C(5)—C(6)—O(7)	113.0(2)	122.0(3)	120.0(2)
C(6)—O(7)—C(8)	116.0(2)	113.0(3)	114.0(2)
O(7)—C(8)—C(9)	109.0(2)	105.0(2)	119.0(1)
C(8)—C(9)—O(10)	110.0(2)	115.0(2)	112.0(1)
C(9)—O(10)—C(11)	117.0(2)	118.0(2)	121.0(1)
O(10)—C(11)—C(12)	118.0(2)	119.0(2)	118.0(1)
C(11)—C(12)—O(1)	119.0(2)	118.0(2)	119.0(1)
C(12)—O(1)—C(2)	118.0(2)	116.0(2)	113.0(1)
O(1)—C(2)—C(3)—O(4)	54	56	28
C(2)—C(3)—O(4)—C(5)	70	83	117
C(3)—O(4)—C(5)—C(6)	−158	−133	−139
O(4)—C(5)—C(6)—O(7)	57	27	8
C(5)—C(6)—O(7)—C(8)	78	100	117
C(6)—O(7)—C(8)—C(9)	−173	−171	−96
O(7)—C(8)—C(9)—O(10)	62	60	−29
C(8)—C(9)—O(10)—C(11)	91	92	176
C(9)—O(10)—C(11)—C(12)	−118	−115	−135
O(10)—C(11)—C(12)—O(1)	−3	−4	−2
C(11)—C(12)—O(1)—C(2)	137	124	102
C(12)—O(1)—C(2)—C(3)	−155	−171	−142

with sodium and potassium cations [29]. In the case of 12-membered crown ethers **3** and **7** [30] the X-ray structures yielded clues as to why the derivatives bearing lipophilic substituents have increased selectivity towards sodium ions. Both complexes possess sandwich like structures with a 2 : 1 ratio of ligand to metal cation. The sodium cation is bonded to all oxygen atoms of the macrocyclic units and is separated from the counter ion. The potassium cation is also bonded to eight oxygen atoms and, in addition, to the iodide ion forming a tight ionic pair. The partition of both complexes between water and the ion-sensing membrane creates an electrical response preferentially to sodium because the potassium complex tight ionic pair is uncharged. Otherwise it could be assumed that in the presence of water the anion in the potassium complex may be replaced by less lipophlic particles. This would decrease the overall lipophilicity of the potassium complex as compared to the sodium complex and consequently lead to a higher selectivity of the membrane towards sodium.

3.3. CRYSTAL STRUCTURES OF **1** AND **2**

The crystal structures of **1** and **2** are presented in Figures 2 and 3. Complex **1** is of the ionic type, analogous to a distorted structure of NaCl, where the large complex cations $[Na(benzo\text{-}12\text{-}crown\text{-}4)_2]^+$ dominates the packing in the crystal, and the anions occupy the vacancies. The minimum Na· · ·I separation in the crystal is equal to 6.17 Å.

In **2**, as a consequence of the additional bonding of crown complexed potassium with I^-, an uncharged complex of composition $[K(benzo\text{-}12\text{-}crown\text{-}4)_2I]$ is formed.

3.4. COORDINATION OF THE ALKALINE CATION

3.4.1. *Coordination of Sodium in* **1**

In compound **1** eight oxygen atoms belonging to two crystallographically independent crown ether molecules coordinate the sodium cation. The Na—O distances are in the range of 2.43–2.53 Å with an average value of 2.49 Å. These distances are close to that found in sandwich structures of 12-membered crown ether complexes:

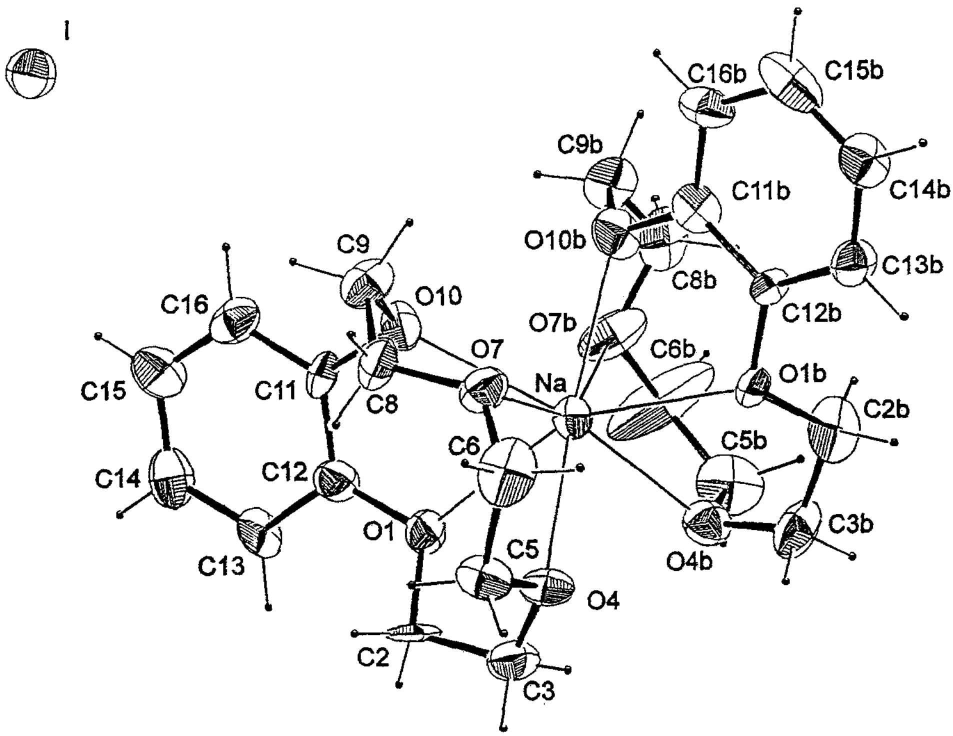


Fig. 2. Coordination geometry about the Na$^+$ ion and atom labelling scheme in complex 1.

[Na(12-crown-4)$_2$]·(OH)·8H$_2$O [3]	2.47 Å
[Na(12-crown-4)$_2$]Cl·5H$_2$O [4]	2.50 Å
[Na(12-crown-4)$_3$]·Cl·(γ-cyclodextrin)$_3$ [5]	2.50 Å
[Na(12-crown-4)$_2$]$_2$·UO$_2$Cl$_4$·2MeOH [6]	2.43–2.52 Å
[Na(12-crown-4)$_2$]·ClO$_4$ [7]	2.50 Å

The sodium coordination number is **8**; its coordination polyhedron is a distorted square antiprism. The mean oxygen atom planes of both crown ether molecules form a dihedral angle of about 7°. In these planes the distances between neighbouring oxygen atoms O···O are equal to 2.71–2.84 Å. The distances between oxygen atoms belonging to different crown ether molecules in the complex cation are 3.03–3.69 Å. The sodium cation is located outside the mean plane of the oxygen atoms of both crown ether molecules **1a** and **1b** at a distance of 1.57 and 1.53 Å, respectively. It is close to that found for sandwich like structures in sodium complexes [3–6]. The oxygen atoms in the crown ether molecule are coplanar within the range of ±0.14 for **1a** and ±0.19 Å for **1b**.

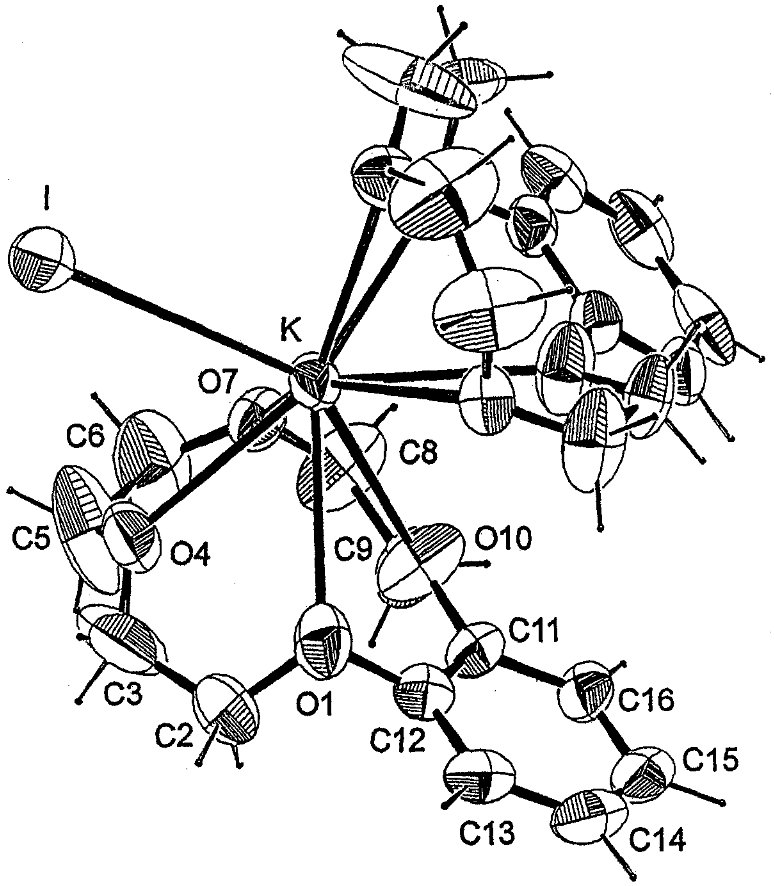


Fig. 3. Coordination geometry about the K^+ ion and atom labelling scheme in complex **2**.

Two crown ether molecules are located in such a manner that the bases of the antiprism are rotated to each other by an angle equal to about 45° in the plane of the crown ether. It decreases the steric O···O interactions inside the complex.

3.4.2. *Coordination of Potassium in* 2

In compound **2** the potassium cation and the iodide anion form a tight ionic pair with a K—I distance of 3.792 Å. This distance is slightly longer than that found for $[KI(OH_2)\cdot(NO_2$ benzo-15-crown-5$)]_2$ [31], which is 3.448 Å, and is close to those found in the literature [32–35]. As a consequence of K···I bond formation the coordination number of potassium in the sandwich structure (Figure 3) increases to 9. The potassium cation coordinates 8 oxygen atoms of two benzo-12-crown-4 molecules (related by twofold symmetry axis) with the K—O distances equal to 2.83–2.95 Å and to the iodide anion. The K—O distances are close to those found in sandwich like structures of 12-crown-4 complexes with potassium, e.g., they are within the range 2.80–2.99 Å in [K(12-crown-4)$_3$Cl]·(γ-cyclodextrin)$_3$ [9]. It is worth emphasizing that the coordination polyhedron for the last structure [9] is similar to that found for the respective compounds of sodium. In the cyclodextrin complex the coordination number of potassium is 8 (8 oxygen atoms of two crown ether molecules) and the coordination polyhedron is a square antiprism. The symmetry of the complex is close to C_4 or S_8. As in complex **1**, the mean planes of the coordinated crown ether molecules are practically parallel.

In complex **2** the situation is quite different. The dihedral angle between the mean planes of both macrocycles equal 41° (for **1** it equals about 7°). Whereas in **1** the two macrocycles are rotated with respect to each other by 45°, the corresponding angle in **2** equals nearly 90° and the respective oxygen atoms are facing each other; the steric O· · ·O hindrances decrease due to the increase of the M· · ·O distances in the sandwich.

A slight disorder was observed for C(3), C(5) and C(6) in complex **2** which leads to increased thermal parameters for these atoms.

3.5. GEOMETRY OF BENZO-12-CROWN-4 IN 1 AND 2

The geometric parameters of benzo-12-crown-4 are similar to other structures which are listed in Table IV.

The bond distances in the 12-membered macrocycle have the following average values:

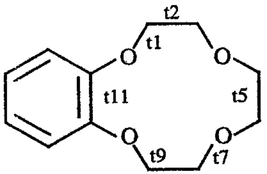
	$C_{(sp^2)}$—O	$C_{(sp^3)}$—O	$C_{(sp^3)}$—$C_{(sp^3)}$
for 1	1.38/1.37	1.41/1.39	1.49/1.48Å;
for **2**	1.37	1.35	1.48Å;

and the endocyclic angles are:

	$C_{(sp^2)}$—O—$C_{(sp^3)}$	$C_{(sp^3)}$—O—$C_{(sp^3)}$	O—$C_{(sp^3)}$—$C_{(sp^3)}$
for 1	118/117	116/112	110/114°
for **2**	117	115	118°

The overall conformation of the macrocycles is such that the dihedral angles between the mean planes formed by four oxygen atoms and the benzo group for two independent molecules equals 33 and 30° in **1**, whereas it equals 12° in **2**, indicating that the ligand in complex **2** is more planar.

TABLE IV. Comparison of the conformations of the benzo-12-crown-4 (and derivatives) macrocyclic framework in the complexes and free crown ethers (torsion angles are shown starting from C(12)—O(1)—C(2)—C(3) along the macrocycle).



Compound	*t*1	*t*2	*t*3	*t*4	*t*5	*t*6	*t*7	*t*8	*t*9	*t*10	*t*11	*t*12	Reference
1a	149	−74	133	−86	−78	173	−100	63	152	140	−1	−141	13
1b	176	61	−129	77	68	−172	76	65	−158	76	−6	155	13
2a	154	66	−80	175	−72	−73	134	62	179	−164	9	−71	36
2b	151	−82	88	−179	66	90	−119	66	−170	168	−11	−83	36
3a	154	−66	−80	173	−72	−72	134	−62	180	−164	8	−73	37
3b	149	−83	88	−179	67	91	−119	65	−171	166	−12	−84	37
4	126	−82	160	−84	**−10**	154	−122	69	−154	159	1	−123	37
5	170	45	79	−168	54	85	−173	56	98	−129	2	138	38
6	−166	36	95	−158	39	95	−160	34	114	−118	−3	138	11
7	−173	43	71	−165	56	87	−176	59	88	−120	2	151	12
8	−177	56	84	−147	44	95	178	54	92	−123	5	118	12
9a	−161	63	79	−168	69	79	−136	58	−179	159	−8	78	12
9b	−161	60	82	−169	68	77	−134	59	−176	157	−7	76	12
10a	−166	54	70	−158	57	78	−173	62	91	−118	−3	137	Compd. **1a***
10b	−171	56	83	−133	27	100	−171	60	92	−115	−4	124	Compd. **1b***
11	−142	**28**	117	−139	**8**	116	−96	**−29**	176	−135	−2	102	Compd. **2***

*This paper.

3.5.1. *Conformation of the Macrocyclic Ligand*

Table IV summarizes data from the conformation study of free benzo-12-crown-4 ligand and its complexes. The structural material can be conditionally divided into three groups:

1. the free molecule of benzo-12-crown-4 and its derivatives with the substituents in the aromatic moiety:
   (a) benzo-12-crown-4 and naphtho-12-crown-4 [13]
   (b) acetylbenzo-12-crown-4 [36]
   (c) diphenylacetylbenzo-12-crown-4 [37]
2. Monomeric complexes with direct metal ion – crown ether oxygen atomic interaction
   (a) LiNCS·benzo-12-crown-4 [38]
   (b) Ca·(benzo-12-crown-4)·$CH_3CN \cdot H_2O$ [11]
   (c) $Nd(NO_3)_3$·(benzo-12-crown-4) [12]
   (d) $La(NO_3)_3$·(benzo-12-crown-4)·H_2O [12]
3. Sandwich-type complexes presented in this paper
4. Complexes of the host–guest type represented by the structure of $[Er(NO_3)_3 \cdot 3H_2O]$·(benzo-12-crown-4)$_2$·MeCN [12].

In all metal complexes [11, 12, 38] including the present ones the same type of macrocyclic entity conformation is realized. It is characterized by three corner fragments [39] at the atoms C(3), C(6) and C(9). It means that three of the eight C—O bonds are in a *gauche* conformation. Some difference is observed for the dioxyphenylene fragment. In most cases it is described by the following sequence of torsion angles: *anti-cis-anti*. However, for the Ca [11], La [12], Na and Li [38] complexes, one of the C—O bonds in this fragment has the proper torsion angle in the range of 118–138°. Obviously it is connected with the macrocycle organization for metal coordination. All C—C bonds (with the exception of the dioxyphenylene residue) are in a *gauche* conformation. Such a conformation ensures the most favourable arrangement of oxygen atom electron pairs for their coordination by the metal cation.

In the host-guest complex presented in [12] the migration of the *gauche* bond takes places from the periphery of the macrocycle to the dioxyphenylene moiety. The appropriate fragment has a *gauche-cis-anti* conformation. In the two independent molecules of benzo-12-crown-4 in **1** two corner conformations are found with the corner fragments at the C(3) and C(6) atoms. The conformation of free benzo-12-crown-4 was discussed in [13]. The peculiarity of the last structure is the appearance of an intramolecular C—H· · ·O interaction which defines the macrocycle conformation.

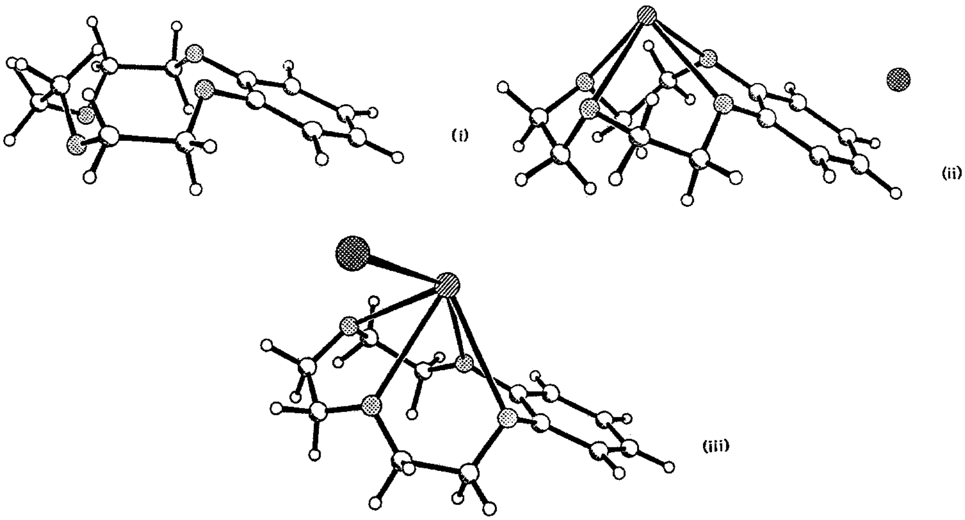


Fig. 4. Comparison of conformations of (i) free benzo-12-crown-4 (molecule **a**) [13], (ii) in the sodium (molecule **a**), and (iii) potassium complexes.

For **1** the oxygen atoms are coplanar within the limits of ±0.14 and ±0.19 Å for molecules **a** and **b**, respectively, whereas the dihedral angle between the aromatic moiety and the average plane of the heteroatoms is 32.7° for **a** and 29.7° for **b**.

In the case of complex **2** the ligand possess an unusual conformation in which all C—C bonds in the 12-membered crown ether residue acquire *cis* or close to *cis* conformations. Probably the energetic losses of the crown ether ligand are compensated by interaction of the potassium cation with all four oxygen atoms of the crown ether and by coordination with the iodine. Such a conformation assures the maximal deviation of oxygen atoms from the mean plane of the macrocycle. The conformations of benzo-12-crown-4 (molecule **a**) in the free state and in the sodium (molecule **a**) and potassium complexes are compared in Figure 4.

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