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15-Hydroxybenzomonothia-15-crown-5 with the sulfur atom linked with the benzene ring and the derived sulfoxide: synthesis, structure, and complexation with the metal cations

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Novel 15-hydroxybenzomonothia-15-crown-5 containing the sulfur atom linked with the benzene ring and its *S*-oxide were synthesized. The stability constants for the complexes of the obtained benzocrown ethers and a reference 15-hydroxybenzo-15-crown-5 with Na, Ca, Ag^I, Cd, Hg^{II}, and Pb^{II} perchlorates were determined by ^1H NMR titration. In MeCN—d_3, the benzothiacrown ether demonstrates a high selectivity towards the thio- and oxothiophilic Hg^{2+} ($\log K_1 = 7.1$) and Pb^{2+} ions ($\log K_1 = 7.4$). In MeCN-d_3—D_2O mixtures, the stabilities of the most of complexes decrease sharply due to competitive hydration of the metal cations except for the "soft" Ag^+ and Hg^{2+} ions having low affinity for the "hard" oxygen atoms and, on the contrary, very high affinity for the "soft" S^{II} atoms. This results in the change in selectivity of complexation: at the water content in solution of 20%, the benzothiacrown ether binds preferably the Hg^{2+} ($\log K_1 = 5.0$) and Ag^+ ions ($\log K_1 = 2.7$). In MeCN-d_3, the benzothiacrown-derived sulfoxide is a weak and non-selective complexing agent towards all the metal cations under study; the reference 15-hydroxybenzo-15-crown-5 forms more stable complexes with the oxophilic sodium, calcium, and lead(II) cations. The conformational features of the benzocrown ethers and their metal complexes established by NMR spectroscopy and X-ray diffraction are discussed. The found characteristics of the complexing ability of benzomonothia-15-crown-5 where the sulfur atom is in conjugation with the benzene ring reveal that the macrocyclic ligands with such a structure are promising as high-selective and efficient complexing agents for the "soft" mercury(II) and silver(I) cations in acetonitrile—water mixtures.

Key words: benzothiacrown ethers, synthesis, structure, complexes, heavy metal cations, stability constants, NMR spectroscopy, X-ray diffraction study.

Thiacrown ethers possess the pronounced ability to form highly stable complexes with the "soft" thiophilic cations of the heavy, transition, and noble metals, such as Ag^+, Tl^+, Pb^{2+}, Cu^+, Cu^{2+}, Pt^{2+}, Au^{3+}, and especially Hg^{2+} ($\log K$ is up to 22.2) and Pd^{2+} ($\log K$ is up to 25.1),[1—3] thereby they may be employed as efficient and selective agents for extraction of the said ions from an aqueous medium to the organic phase, in membrane transport, as well as for removal of the toxic elements from industrial waste waters.[4—9]

Of special interest are the derivatives of thiacrown ethers that contain in the molecule the chromophoric fragment conjugated with one or two heteroatoms of the macrocycle. We proposed the use of chromogenic and photochromic benzodithiacrown ethers, *e.g.*, the styryl (**1**) and butadienyl (**2**) dyes, as efficient optical molecular sensors for the Hg^{2+}, Ag^+, and Pb^{2+} ions exhibiting the chemosensory and cation-depending photoswitchable properties in solution (including organic solvent—water mixtures), the Langmuir—Blodgett monolayers, and com-

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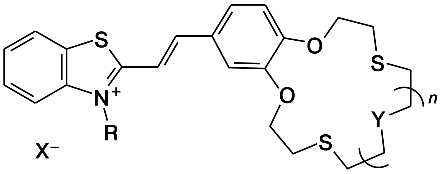
posite polymeric materials.[10—14] However, the chromoionophores of type **1** and **2** have one significant disadvantage, *i.e.*, the chromophoric fragment is in conjugation with the "hard" (in terms of the principle of hard and soft acids and bases) O atoms, which comparatively weak coordinate (especially in aqueous solutions) to the "soft" cations of the heavy and noble metals.



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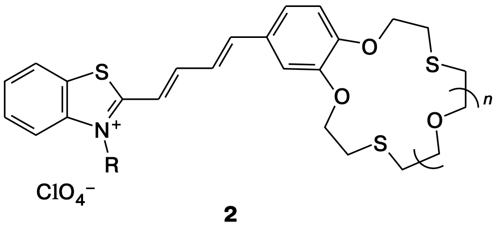


2

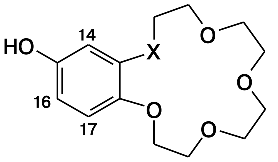
1, **2:** R = Me, Et, $C_{18}H_{37}$, $(CH_2)_kCO_2H$, $(CH_2)_kSO_3^-$ (k = 3, 4);
X = I, ClO_4; Y = O, S; n = 1, 2

In this regard, the chromogenic benzothiacrown ethers where the sulfur atom is in conjugation with the chromophoric fragment would be promising optical molecular sensors for the above-mentioned metal cations with the considerable spectral response for complexation, since it is the sulfur atoms that are mostly involved in the binding of these cations.

The monobenzothiacrown ethers and related compounds having the sulfur atom linked with the benzene ring are the poorly studied type of macroheterocyclic compounds, despite their relatively simple structure. Only separate examples of the preparation of benzodithia-15(18)-crown-5(6),[4] benzotrithia-11-crown-3,[15] benzoazatrithia-12-crown-4 compounds of the amide type,[16] and several derivatives of benzodithia[2.2.2]cryptand (see Ref. 17) are known. In all said compounds, two S atoms or the S and N atoms of the macrocycle are linked with the annulated benzene ring; note that complexing properties of the above-mentioned compounds have virtually not been studied. Benzothiacrown ethers functionalized in the benzene ring are not easily accessible. This is apparently related to the side reactions involving the sulfur atoms under the conditions of electrophilic aromatic substitution, which is the most common method for direct functionalization of the benzocrown ethers,[18] first of all, due to destruction of the sulfur-containing macrocycle under the action of strong acids.[18,19] It should be stressed that the vast majority of the known functionalized benzothiacrown ethers were prepared by coupling two acyclic precursors with one of them already functionalized, or by transformation of some functional groups to others.[20—24] However, the applicability of the coupling reaction for the preparation of functionalized benzothiacrown ethers with the sulfur atom in conjugation with the benzene ring is often limited, because the monocyclic precursors, *viz.*, the derivatives of 2-mercaptophenol and benzene-1,2-dithiol, are difficult to obtain.[25]

In this regard, we drew attention to 2-mercaptohydroquinone (**3**), which is easy to prepare by addition of sodium thiosulfate to 1,4-benzoquinone followed by reduction of *S*-aryl thiosulfonate that formed with zinc in an acidic medium.[26] Compound **3** has the *ortho*-arranged SH and OH groups, which are required for the buildup of the benzothiacrown macrocycle by coupling. The second hydroxyl group of this compound is in the *meta*- and *para*-positions with respect to the former substituents, therefore, one would expect that it will be slightly involved in the formation of the side products, *i.e.*, crown ethers isomeric to the target benzothiacrown ethers. As is known, phenols are active substrates in electrophilic aromatic substitution, thus, one can hope for further functionalization of the hydroxybenzothiacrown ethers by suitable methods, including introduction of the chromophoric groups into the *para*-position with respect to the sulfur atom of the macrocycle to obtain novel promising optical molecular sensors. At the same time, the reactive hydroxyl group in the benzene ring of the benzothiacrown ether provides yet another way for subsequent modification of such a crown ether, *viz.*, its covalent "grafting" to a polymeric carrier or an inorganic sorbent through formation of the ether or ester bond.

In the present work, we describe the synthesis of a new benzomonothia-15-crown-5 derivative with a hydroxyl substituent in the benzene ring **4** and its *S*-oxide **5**. By means of NMR spectroscopy and X-ray diffraction, the complexing ability of compounds of such type with respect to the sodium, calcium, and heavy metal cations was first studied and the conformational features of the free ligands and their metal complexes were established. As a comparison, the analogous characteristics of the structurally related compound, *viz.*, 15-hydroxybenzo-15-crown-5 (**6**)[27] having in the macrocycle only the oxygen atoms contrary to compounds **4** and **5**, were deter-



4—6

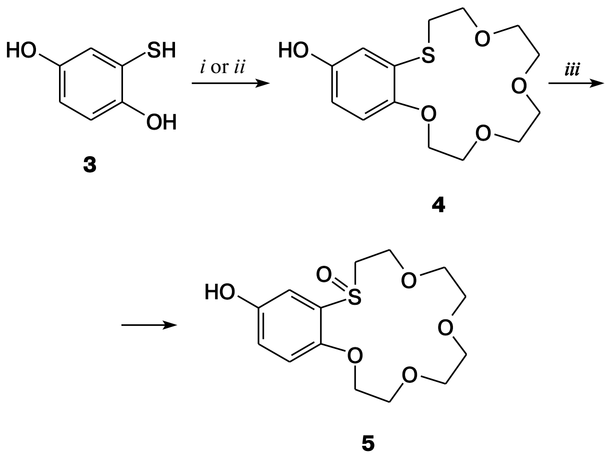
X = S (**4**), S(=O) (**5**), O (**6**)

mined. This study allows one to estimate the characteristics of the complexing ability of benzomonothia-15-crown-5 having the sulfur atoms in conjugation with the benzene ring, such as metal complex stability and selectivity of complexation, for further use of their structural fragments as constituents of efficient optical molecular sensors.

Results and Discussion

Synthesis of compounds 4 and 5. Benzothiacrown **4** was synthesized by condensation of 2-mercaptohydroquinone (**3**) with the halogen derivatives of tetraethylene glycol in the presence of a base in an inert atmosphere (Scheme 1). To avoid the formation of oligomerization products, the high dilution method was used. In order to find optimum conditions for efficient coupling, three most popular procedures for the preparation of the benzo(thia)crown ethers from the catechol derivatives were applied. Coupling in a Bu^nOH—water mixture in the presence of an alkali[4] resulted in the formation of ether **4** in a yield of only 5% due to high resinification of the reaction mixture. It appears that resinification occurs due to the high reactivity of polyphenols in the strongly basic medium inducing side reactions. However, upon coupling in aqueous ethanol in the presence of Na_2CO_3 (see Refs 19, 23, 24), product **4** was also obtained in a low yield (4%), probably, owing to the use of insufficiently strong (under these conditions) base. The use of the diiodo derivative of tetraethylene glycol and replacement of the solvent by dry acetone[28] allowed us to increase the yield of the target product **4** to 14%.

Scheme 1



Reagents and conditions: *i*. $ClCH_2(CH_2OCH_2)_3CH_2Cl$, NaOH, $Bu^nOH—H_2O$; *ii*. $ICH_2(CH_2OCH_2)_3CH_2I$, Na_2CO_3, $EtOH—H_2O$ (or Na_2CO_3, Me_2CO); *iii*. $POCl_3$, DMF.

Treatment of thiacrown ether **4** with phosphorus oxychloride in DMF led to oxidation of the sulfur atom to sulfoxide **5** in a yield of 43% (see Scheme 1). It should be noted that oxidation of thiacrown ether **4** occurs under the conditions typical of the Vilsmeier formylation of the aromatic compounds having strong electron-donating substituents. However, no formation of the derivatives of salicylaldehyde was observed in the reaction mixture, which suggests either the high rate of oxidative processes resulting in the formation of sulfoxide **5** and, partially, in destruction of the macrocycle, or deactivation of the benzene ring of compound **4** in electrophilic aromatic substitution by its adduct with the electrophile. It can be stressed that, under such conditions, compound **6** and benzo-15-crown-5 (**7**) are easily formylated in the *para*-position with respect to the alkoxyl group to form the corresponding crown-containing benzaldehydes.[29,30]

The structures of compounds **4** and **5** were confirmed by the data from ^1H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis.

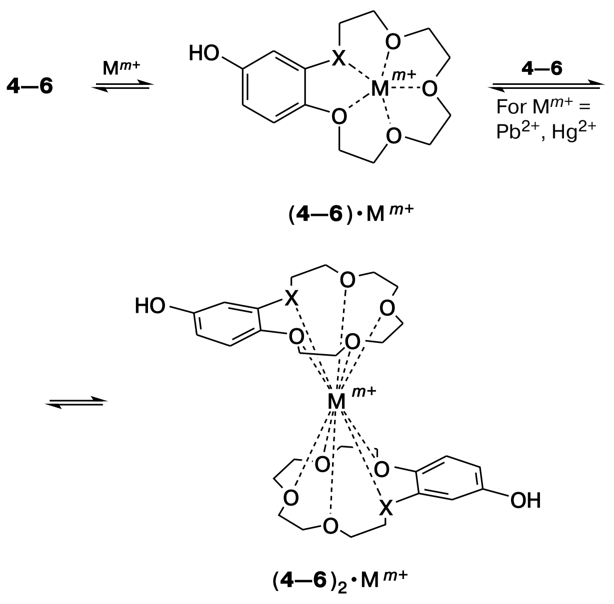
^{1}H NMR spectroscopic study. Among the features of spectral behavior of sulfoxide **5**, a complex set of signals in the aliphatic region of the ^1H NMR spectrum should be noted, which consists of the strongly overlapped multiplet signals for 16 nonequivalent hydrogen atoms of the methylene groups of the macrocycle. For example, in $CDCl_3$, the signals for two geminal hydrogen atoms of the $C\underline{H}_2S(O)Ar$ group appear at δ 2.89 and 3.70 and the signals for the $C\underline{H}_2OAr$ group appear at δ 4.06 and 4.19. This evidences the predominant existence of one conformation of compound **5** in solution, which most likely coincides with the conformation found in crystal (see below). It appears that the conversion of the sulfide group to the sulfoxide significantly restricts the conformational transitions of the 15-membered macrocycle **5** due to the structural rigidity of the fragment $CH_2S(O)Ar$ with a pronounced pyramidal bond configuration at the sulfur atom. In the region of interactions of the aromatic and aliphatic fragments of the NOESY spectrum of compound **5**, intensive cross-peaks for the through-space interacting nonequivalent hydrogen atoms of the $C\underline{H}_2OAr$ group and the *ortho* H(17) atom are observed. This is evidence of closeness of the said hydrogen atoms by <2.5 Å. Conversely, the hydrogen atoms of the methylene group of $C\underline{H}_2S(O)Ar$ and the *ortho* H(14) atom are significantly remote from each other (>3.5 Å), which follows from the absence of the cross-peaks for the interactions between them. Thus, the methylene group of the $C\underline{H}_2OAr$ fragment is nearly planar with the benzene ring, while the methylene group of the $C\underline{H}_2S(O)Ar$ fragment is significantly deviated from this plane. Such geometry of the macrocycle near the benzene fragment was confirmed upon consideration of the conformational features of the crystalline compound **5**.

The geminal hydrogen atoms of all methylene groups in benzocrown ethers **4** and **6** are equivalent, which evidences the relatively high conformational flexibility of the macroheterocycles of these compounds in the ^{1}H NMR (500 MHz) time scale. However, the pattern of the NOESY spectrum of compound **4** as regards the interactions of the aromatic and aliphatic protons is similar to that of compound **5** and suggests the closeness of the hydrogen atoms of the $C\underline{H}_2OAr$ group and the H(17) atom and, conversely, the considerable remoteness of the hydrogen atoms of the $C\underline{H}_2SAr$ group and the H(14) atom. It is obvious that the predominant conformation of macrocycle **4** in proximity to the benzene ring is close to the conformation of macrocycle **5**, *i.e.*, the methylene group of $C\underline{H}_2SAr$ is significantly deviated from the plane of the benzene ring due to the strain in the 15-membered macrocycle containing the sulfur atom. The NOESY spectrum of compound **6** evidences the equal distance between the hydrogen atoms of two $C\underline{H}_2OAr$ groups and the *ortho* hydrogen atoms of the benzene ring and, consequently, virtual coplanarity of these groups with the benzene ring, which is also confirmed by the X-ray diffraction data (see below).

The ^{1}H NMR spectroscopic study of benzocrown ethers **4**—**6** in MeCN-d$_3$ showed the significant downfield shift of the signals for the vast majority of the hydrogen atoms of these ligands ($\Delta\delta_H$) upon addition of an excess of metal perchlorates (Na, Ca, Ag^I, Cd, Hg^{II}, Pb^{II}). This behavior is typical of the crown-ether complexes and caused by the electron-withdrawing effect of the M^{m+} ion coordinated to the heteroatoms of the macrocycle, which induces the electron density shift from all ligand atoms towards the cation (Scheme 2). In the case of compound **6**, the values of $\Delta\delta_H$ are found in the narrow range for the signals for all types of the hydrogen atoms (own interval for each metal cation). The average values of $\Delta\delta_H$ increased in the order $Ag^+ << Na^+ \leq Hg^{2+} < Cd^{2+} \approx Ca^{2+} \approx Pb^{2+}$, which undoubtedly reflects the increase in the surface charge density when passing from the singly charged cations to the doubly charged ones and the increase in the oxophilicity of the cations in the above order.

For the complexes of benzothiacrown **4**, the $\Delta\delta_H$ values for different types of the hydrogen atoms are in significantly broader range as compared with the complexes of **6**. For example, the signal for the hydrogen atoms of the $C\underline{H}_2CH_2S$ group in the complexes with the sodium and silver(I) cation was upfield shifted ($\Delta\delta_H$ to −0.11) relative to the signal for the free ligand, whereas the signals for the remaining hydrogen atoms of the CH and CH$_2$ groups in these complexes were downfield shifted to 0.16 ppm (see *e.g.* Fig. 1) analogously to that observed by us earlier[31] for the complexes of benzoazacrown ethers with the Na$^+$, Ag$^+$, and EtNH$_3^+$ ions. Such spectral behavior suggests the considerable conformational reorganization of the macrocycle of the benzocrown ether as a result of complexation with the metal cation, which leads to the change in the position of the methylene groups relative to the benzene ring showing strong magnetic anisotropy. It seems that the methylene group $C\underline{H}_2CH_2S$ in compound **4** is shifted from the region of deshielding by the benzene ring to its shielding regions upon binding to the Na$^+$ and Ag$^+$ ions and this effect supersedes the electron-withdrawing influence of the singly charged cation. In the case of compound **4**, the sequence of the increase in the average values of $\Delta\delta_H$ in the series

Scheme 2*



M^{m+} is the metal ion (m = 1, 2)

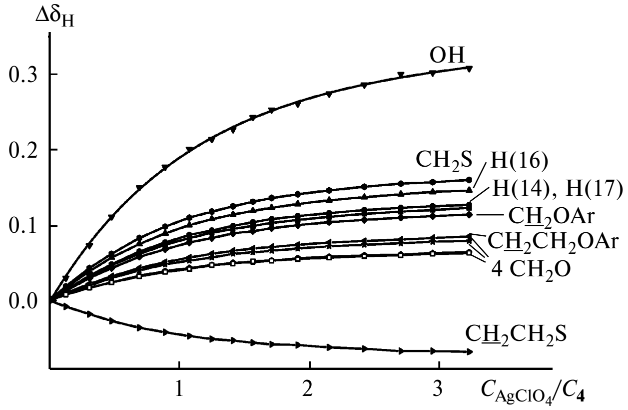


Fig. 1. Dependence of the $\Delta\delta_H$ values ($\Delta\delta_H = \delta_H(\mathbf{4}—AgClO_4) - \delta_H(\mathbf{4})$) on the ratio of concentrations of AgClO$_4$ and ligand **4** for all proton signals of the ligand (MeCN-d$_3$, 30 °C).

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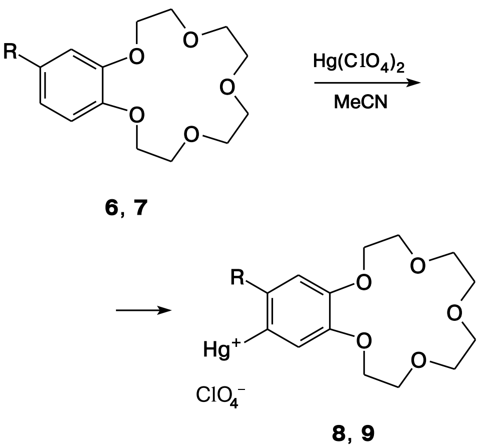
* Complex $(\mathbf{4})_2 \cdot Hg^{2+}$ may have a linear structure where only the sulfur atoms of the macrocycle are involved in coordination to the metal cation.

of metal cations is as follows: $Na^+ < Ag^+ < Ca^{2+} \approx Cd^{2+} \approx Pb^{2+} < Hg^{2+}$. It appears that the sulfur-containing macrocycle shows increased affinity to the "soft" thiophilic metal cations, which is confirmed by the maximum downfield shifts of the signals for the hydrogen atoms of the CH_2S group ($\Delta\delta_H$ to 0.75) in the complexes with the Ag^+ and Hg^{2+} ions as compared with the $\Delta\delta_H$ values for the CH_2O groups in all the studied complexes of compound **4** ($\Delta\delta_H$ to 0.43).

A complicated spectral pattern in the case of *S*-oxide **5** and its complexes due to the nonequivalence of the geminal hydrogen atoms of all methylene groups strongly hinders the precise determination of the $\Delta\delta_H$ values. Note that the positions of the signals for all types of the hydrogen atoms for compound **5** in the presence of the singly charged metal cations (Na^+, Ag^+) is changed slightly ($\Delta\delta_H$ to 0.09), while all the studied doubly charged metal cations induce significantly larger shifts ($\Delta\delta_H$ to 1.2). The sequence of the increase in the average values of $\Delta\delta_H$ in the series of cations ($Ag^+ < Na^+ < Cd^{2+} < Hg^{2+} < Ca^{2+} < Pb^{2+}$) undoubtedly indicates higher affinity of the oxophilic metal cations for the combination of the heteroatoms in the macrocycle **5**. Thus, the conversion of the "soft" sulfide-type sulfur atom (compound **4**) to the "hard" sulfoxide group (compound **5**) results in the loss of affinity for the "soft" Ag^+ and Hg^{2+} ions. It is of note that complexation of compound **5** with the doubly charged cations has almost no influence on the position of the signal for the H(14) atom, which is *ortho* with respect to the sulfoxide group, while the signals for the hydrogen atoms of the $C\underline{H}_2S(O)Ar$ group undergo the maximum downfield shifts among found ones. This suggests the significant change in the conformation of the macrocycle near the sulfur atom upon binding to M^{2+}. It appears that the methylene group of $C\underline{H}_2S(O)Ar$ is shifted to the region of deshielding by the benzene ring and the H(14) atom, conversely, comes out of the region of deshielding of the sulfoxide group. This means a twisting of the $CH_2S(O)Ar$ fragment along the S—Ar bond that facilitates the expansion of the cavity of the macrocycle for better binding to the metal cation.

It should be noted that, when the excess of mercury(II) perchlorate was added to a solution of benzocrown ether **6**, the signals for this ligand in the ^1H NMR spectrum disappeared relatively fast (within ~1 h), and a new set of signals appeared, which evidences the formation of a substitution product at the benzene ring. The shape of the signals for the aromatic hydrogen atoms of this product, *viz*., two singlets at δ 6.64 and 6.91 (according to the integrated intensity, each corresponds to one hydrogen) suggests that the substitution occurred in the position 16 of the benzene ring. The compound formed appears to be the mercuration product **8** (Scheme 3). It can be stressed that the electrophilic mercuration reaction under the action of the mercury(II) salt is typical of the electron-rich aromatic compounds (see *e.g.* Refs 32, 33). Isolation of product **8** failed due to its fast resinification in air.

Scheme 3



R = OH (**6**, **8**), H (**7**, **9**)

We also observed relatively slow mercuration (conversion <50% within 20 h) of benzocrown ether **7** under the action of $Hg(ClO_4)_2$ to form product **9** due to the high electron-donating ability of the benzene ring in this compound. Compound **9** was isolated and characterized by the physicochemical methods. No mercuration of benzocrown ethers **4** and **5**, as well as of 15-nitrobenzo-15-crown-5 (**10**), 18-nitrobenzo-18-crown-6 (**11**), and benzo-18-crown-6 (**12**), which were used as competitive ligands in measuring the stability constants for complexes, proceed at all. Obviously, in the case of *S*-oxide **5** and nitro derivatives **10**, **11**, the benzene ring is deactivated for the electrophilic substitution reaction by the strong electron-withdrawing substituent. This is evidenced by the literature data[34] on the absence of mercuration of benzo-15-crown-5 ethers having the electron-withdrawing substituents in the benzene ring under the action of mercury(II) acetate. The formation of the strong complex of the Hg^{2+} ion with the crown-ether fragment apparently makes the benzo(thia)crown nonreactive due to the electron-withdrawing effect of the metal cation in the cavity of the macrocycle. This may explain the absence of the mercuration products in the mixtures of compounds **4** and **12** with an excess of $Hg(ClO_4)_2$; the high stability of the complexes of these compounds with Hg^{2+} (in $MeCN-d_3$, $\log K_1 = 7.1$ and >5, respectively) was also confirmed by the results from NMR titration. The evidence for mercuration of compounds **6** and **7** indirectly indicates the relatively low stability of the complexes of the all-oxygen benzo-15-crown-5 with the mercury(II) cations. This fact was also confirmed (see below).

The quantitative measurement of the stability of the complexes of benzo(thia)crown ethers **4**—**6** with the above-mentioned metal perchlorates in MeCN-d_3 and in its mixtures with D_2O was performed using ^1H NMR titration. The dependence of the change in the position of the signals for the hydrogen atoms of the ligand (L) on the change in the ratio of concentrations of M^{m+} and L was well described in most instances by the model taking into account the equilibrium

$$L + M^{m+} \xrightleftharpoons{K_1} L \cdot M^{m+}, \qquad (1)$$

where K_1/L mol^{-1} is the stability constant for the complex $L \cdot M^{m+}$. In the case of the Pb^{2+} and Hg^{2+} ions, good results were obtained taking into account both the equilibrium (1) and (2)

$$L \cdot M^{m+} + L \xrightleftharpoons{K_2} L_2 \cdot M^{m+}, \qquad (2)$$

where K_2/L mol^{-1} is the stability constant for the complex $L_2 \cdot M^{m+}$ (see Scheme 2). If the upper validity limit of direct titration was exceeded ($K_1 > 10^5$ L mol^{-1}), then the procedure of competitive ^1H NMR titration was used (see Experimental). The determined values of the stability constants ($\log K_1$ and $\log K_2$) are given in Table 1.

A comparison of the values of the stability constants for the complexes of compounds **4**—**6** showed that there is no strict correlation between the average values of $\Delta\delta_H$ and the magnitudes of $\log K_1$, although these parameters are somewhat in parallel. This may mean that the ion-dipole interaction of the metal with the heteroatoms of the ligand (depending on the nature of the metal cation and its charge) and the change in the conformation of the macrocycle due to complexation make different total contribution to $\Delta\delta_H$.

Compound **6** formed the most stable complexes with the Na^+, Ca^{2+}, and Pb^{2+} ($\log K_1 \geq 4.7$) ions, in the latter instance, the slow (in the ^1H NMR time scale) ligand exchange between the free state and, probably, the complexes with the composition $\mathbf{6} \cdot Pb^{2+}$ and $(\mathbf{6})_2 \cdot Pb^{2+}$ was observed. This led to the emergence of several overlapping sets of signals and to the strong broadening of the spectra of **6**—Pb^{2+} mixtures, which prevented determination of K_1 and K_2. The same spectral behavior has been found earlier[31] in the reaction of benzocrown ether **7** and its formyl derivative with $Pb(ClO_4)_2$, for complexes of which the values of stability constants were larger than the upper validity limit of direct ^1H NMR titration ($\log K_1 > 5$). Conversely, the stability of the complex of ether **6** with the Ag^+ ion was less than the lower validity limit of NMR titration ($\log K_1 < 0.5$) and the experimental values of $\Delta\delta_H$ in the system **6**—Ag^+ were no more than 0.01. Despite the low stability of the complex $\mathbf{6} \cdot AgClO_4$, it was isolated in the crystalline form (see below). Undoubtedly, the high values of stability constants for the complexes of the all-oxygen benzocrown ether **6** with the "hard" Group I and II metal cations and the Pb^{2+} ions are explained by their high affinity for this type of the macrocyclic ligands,[2] as well as by the better correspondence of the cavity size of the 15-membered macrocycle and the diameter of the Na^+ and Ca^{2+} ions.

Despite the above-mentioned fast mercuration reaction of benzocrown ether **6**, we succeeded in determining the stability constants for its complex with $Hg(ClO_4)_2$ and for the complex $\mathbf{8} \cdot Hg^{2+}$. Since, during ^1H NMR titration, the signals for compound **6** steadily disappeared and the intensities of the signals for the mercurated benzocrown ether **8**, conversely, increased, the calculation of the running concentrations of ligands **6** and **8** in each titration point was performed in view of the ratio of integrated intensities of their signals. Simultaneously, we made correction for the concentration of the Hg^{2+} ions taking into account their consumption in the mercuration reaction. The thus determined changes in the δ_H values depending on the concentration of $Hg(ClO_4)_2$ fitted in the scheme of the formation of 1 : 1 complexes for both compounds (two equilibria of type (1) were used simulta-

Table 1. The stability constants (K) for the complexes of benzocrown ethers **4**—**6** with different metal perchlorates[a]

Ligand	$\log K_1$ ($\log K_2$)[b]					
	Na^+	Ca^{2+}	Ag^+	Cd^{2+}	Hg^{2+}	Pb^{2+}
4	2.4	3.7	2.7	3.2	>5 7.1 (2.9)[c]	> 5 7.4 (4.1)[d]
4[e]	1.0	<0.5	2.8	<0.5	>5 5.8 (3.4)[f]	2.8 (2.2)
4[g]	<0.5	—	2.7	—	5.0 (4.0)	1.9
5	1.2	3.3	<0.5	2.2	2.4	3.7 (3.0)
6	4.7	6.1[d]	<0.5	2.6	2.8[h]	>5[i]

[a] ^1H NMR titration in MeCN-d_3, 30 °C.

[b] K_1/L mol^{-1} = $[L \cdot M^{m+}]/([L] \cdot [M^{m+}])$, K_2/L mol^{-1} = $[(L)_2 \cdot M^{m+}]/([L] \cdot [L \cdot M^{m+}])$; the errors of measurument of constants are ±20 and ±30% for direct and competitive titration, respectively.

[c] Competitive ligand is 18-nitrobenzo-18-crown-6 (**11**); the stability constant for complex $\mathbf{11} \cdot Hg^{2+}$ ($\log K_1 = 5.7$) was determined from the data of competitive titration with benzo-15-crown-5 (**7**); the direct titration in the system **7**—$Hg(ClO_4)_2$ affords $\log K_1 = 2.0$.

[d] Competitive ligand is 15-nitrobenzo-15-crown-5 (**10**), for its complex with Ca^{2+}, $\log K_1$ is 4.2, and for its complexes with Pb^{2+}, $\log K_1$ is 4.5 and $\log K_2$ is 5.0 (see Ref. 31).

[e] ^1H NMR titration in MeCN-d_3—D_2O (9 : 1), 30 °C.

[f] Competitive ligand is **11**; $\log K_1$ for complex $\mathbf{11} \cdot Hg^{2+}$ under these conditions is 2.8.

[g] ^1H NMR titration in MeCN-d_3—D_2O (4 : 1), 30 °C.

[h] Fast mercuration of compound **6** occurs during titration; $\log K_1$ for complex **8** formed with the Hg^{2+} ions is 2.2.

[i] A slow exchange in the ^1H NMR time scale, which prevents the precise measurement of the $\Delta\delta_H$ values.

neously); the values of stability constants for complexes **6** • Hg^{2+} and **8** • Hg^{2+} ($\log K_1$) were 2.8 and 2.2, respectively. Likewise, the stability constants for complexes **7** • Hg^{2+} and **9** • Hg^{2+} were measured; the $\log K_1$ are 2.0 and 1.4, respectively. Thus, the conclusion on the relatively low stability of the complexes of the all-oxygen benzo-15-crown-5 with the Hg^{2+} ions was confirmed. As anticipated, introduction of a positively charged substituent in the benzene ring reduces the stability of the metal complexes of the mercurated benzo-15-crown-5 ethers compared to the starting ligands.

Sulfoxide **5** was found to be ineffective complexing agent for the singly charged metal cations. The stability of its complexes with the studied doubly charged metal cations increased in the order $Cd^{2+} \approx Hg^{2+} < Ca^{2+} < Pb^{2+}$, however, the selectivity of complexation in this case was low (see Table 1). Thus, the conclusion on the "hardness" of all heteroatoms of the macrocycle of **5** and, consequently, its higher affinity to the oxophilic calcium and lead(II) cations was confirmed. The lesser stability of the complexes of compound **5** compared to that of the analogous complexes of compound **6** can be explained by the low electron-donating ability of the sulfoxide group, as well as by the necessity for considerable conformation reogranization of the macroheterocycle upon binding to the metal cation as noted above.

In MeCN-d_3, benzothiacrown ether **4** showed a high selectivity to the thio- and oxothiophilic Hg^{2+} and Pb^{2+} ions ($\log K_1$ = 7.1 and 7.4, respectively), while, as for remaining metal cations under study, the values of the logarithm of stability constants for the complexes with the composition 1 : 1 were no more than 3.7. In contrast to ligands **5** and **6**, compound **4** can very effectively coordinate to the Ag^+ ions, which is, undoubtedly, due to the high affinity of the "soft" sulfide S atom to this metal cation.

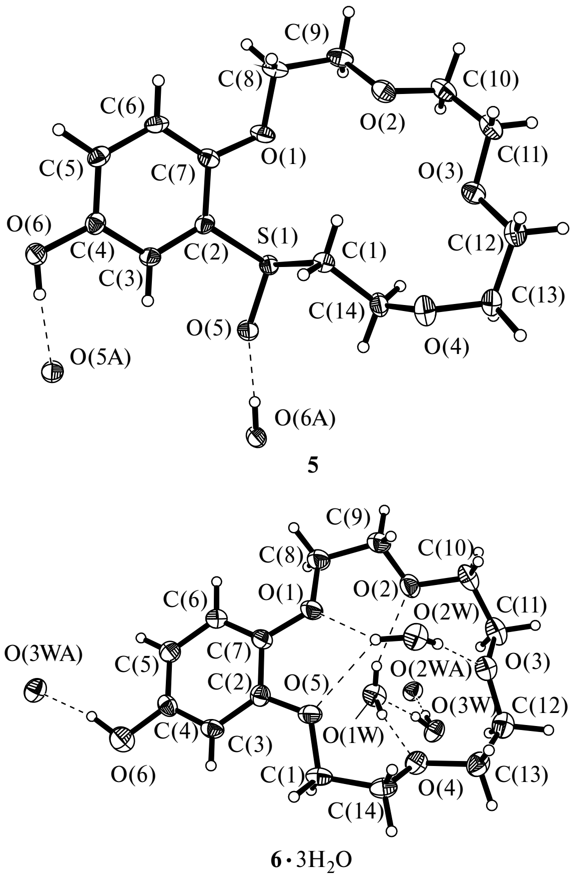
When MeCN-d_3 was replaced by MeCN-d_3—D_2O mixtures, the selectivity of complexation of compound **4** significantly changed (see Table 1), its ability to bind the Na^+, Ca^{2+}, Cd^{2+}, and Pb^{2+} sharply reduced with the increase in the water content in solution; the first three cations do not virtually form complexes at the D_2O content of 20%. Such behavior is certainly caused by competitive hydration of the oxophilic metal cations, for which the oxygen atoms of the water molecules are sufficiently efficient complexing agents and therefore displace the macrocyclic ligand from the coordination sphere of the cation. Our investigations[12,35] into the complexation features of the chromogenic dithiacrown ethers **1**, **2** and the model benzodithiacrown ethers with the heavy metal cations have shown that the O and S atoms of the macrocycles take approximately equal part in coordination to the Pb^{2+} ions, whereas the contribution of the sulfur atoms to the bonding strength of the silver(I) and mercury(II) cations is significantly larger than that of the oxygen atoms. Thus, the strong decrease in the stability of the complexes of compound **4** with the Pb^{2+} ions in the presence of water in solution correlates well with the previously established features of coordination of these cations to the O and S atoms. The stability of the complex **4** • Hg^{2+} is also successively decreased upon increase in the content of D_2O in a water-acetonitrile mixture, however, even in a 20% solution, $\log K_1$ for this complex is equal to 5.0. It is of note that the stability of the complex $(\mathbf{4})_2$ • Hg^{2+} is, conversely, increased upon increase in the water content in solution. It is important to note that the stability of the complex of **4** with the Ag^+ ions does not virtually depend on the water content ($\log K_1$ = 2.7—2.8). All the mentioned data also confirm the previously[12,35] established features of coordination of the "soft" Hg^{2+} and Ag^+ ions to the sulfur and oxygen atoms.

Thus, the results for the NMR study of the complexing ability of benzomonothia-15-crown-5 **4** containing the sulfur atom linked with the benzene ring showed its high efficacy with respect to the mercury(II) and silver(I) cations. It must be emphasized the increase in the selectivity with respect to these ions in the presence of water, which is the most common solvent for the inorganic substrates. This makes the macrocyclic ligands of type **4** promising complexing agents and allows one to expect that efficacious and selective optical sensors containing the sulfur atom in conjugation with the chromogen will be prepared on the basis of these ligands, which can provide the considerable spectral response to complexation.

X-ray diffraction studies. The free benzocrown ethers **5**, **6** and the complexes **5** • $NaClO_4$ and **6** • $AgClO_4$ were prepared as single crystals that were studied by X-ray diffraction. The structures of these compounds are shown in Figs 2 and 3 (for ease of the comparison of geometric parameters, the same numbering of the same-type atoms was used, which differs from the IUPAC rules).

In the crystal, the molecules of **5** form centrosymmetric dimers through H-bonding between the OH group of one molecule and the oxygen atom of the sulfoxide group of another molecule. The distance O(6)—H...O(5A) is equal to 1.84(4) Å and the angle at the H atom is 170°.

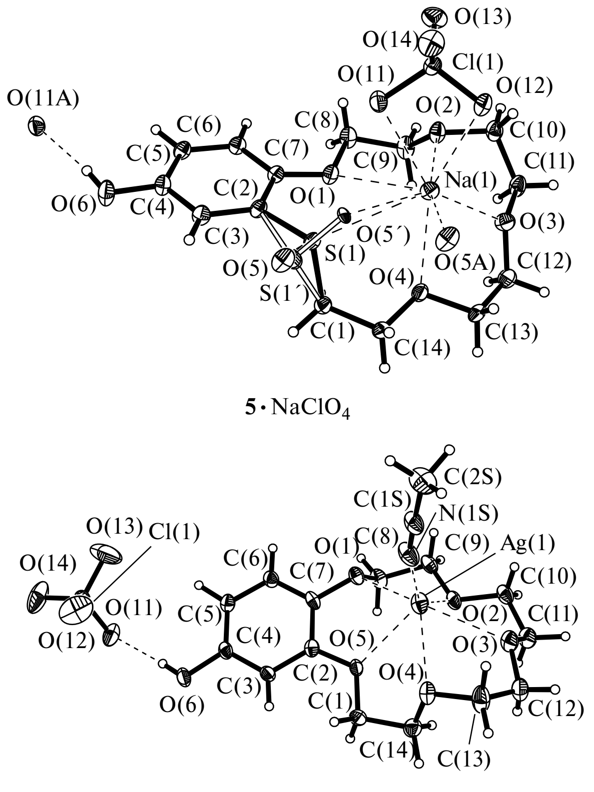
In the unit cell of **6**, three independent molecules of water of solvation were found. The H_2O(1W) and H_2O(2W) molecules are arranged on the different sides of the macrocycle plane and form the directed or bifurcate hydrogen bonds with its oxygen atoms. The parameters of the hydrogen bonds are as follows: the distances O(1W)—H...O(2), O(1W)—H...O(4), O(2W)—H...O(1), O(2W)—H...O(5), and O(2W)—H...O(3) are equal to 2.18(4), 2.10(4), 2.20(4), 2.33(4), and 1.95(4) Å and the angles at the H atoms are 162, 171, 145, 137, and 173°, respectively. The water molecule H_2O(3W) connects the H_2O(1W) and H_2O(2WA) molecules from the neighboring aquacomplexes in the unit cell through H-bonds, which are associated by symmetry operations. Here, the



5

$6 \cdot 3H_2O$

Fig. 2. The stuctures of compounds **5** and $\mathbf{6} \cdot 3H_2O$. The oxygen atoms obtained by symmetry operations are labeled by an additional letter A. The hydrogen bonds are shown by dashed lines. The thermal ellipsoids are shown with 50% probability.



$\mathbf{5} \cdot NaClO_4$

$\mathbf{6} \cdot AgClO_4 \cdot MeCN$

Fig. 3. The structures of complexes $\mathbf{5} \cdot NaClO_4$ and $\mathbf{6} \cdot AgClO_4 \cdot MeCN$. The oxygen atoms obtained by symmetry operations are labeled by an additional letter A. The bonds in the minor conformer of the complex $\mathbf{5} \cdot NaClO_4$ are shown by nonfilled lines. The coordination and hydrogen bonds are shown by dashed lines. The thermal ellipsoids are shown with 50% probability.

characteristics of the hydrogen bonds are as follows: the distances O(3W)—H...O(1W) and O(3W)—H...O(2WA) are equal to 1.98(3) and 1.80(4) Å and the angles at the H atoms are 166 and 173°, respectively. The hydroxyl group of crown ether **6** forms, in turn, the hydrogen bond with the H_2O(3WA) molecule being at a distance of translation from the H_2O(3W) molecule. The distance O(6)—H...O(3WA) is 1.64(2) Å and the angle at the H atom is 168°. All the above-mentioned characteristics conform to the rather strong and medium hydrogen bonding. Thus, the molecules of **6** form two-dimensional layers in the lattice owing to the said hydrogen bonds with the solvate water molecules.

For crown ethers **5** and **6**, weakely expressed alternation of the bond lengths in the benzene rings is observed, *i.e.*, the C(2)—C(7), C(3)—C(4), and C(5)—C(6) bonds are slightly elongated (the average value is 1.401(3) Å) and the C(2)—C(3), C(4)—C(5), and C(6)—C(7) bonds are, conversely, slightly shortened (the average value is 1.381(3) Å) compared to the standard value 1.39 Å. The C(2)—C(7) bond common to the bicyclic system of the benzocrown ether is elongated, which, obviously, reflects the steric repulsion of the atoms in the *ortho*-position with respect to the C(2) and C(7) atoms. In this case, the values of the bond angles at the C(2) and C(7) atoms, which are exocyclic with respect to the benzene ring have a pronounced tendency to increase in the case of C(3)—C(2)—O and C(6)—C(7)—O (on average, 125.3(2)°) and to decrease in the case of C(2)—C(7)—O and C(7)—C(2)—O (on average, 115.2(2)°) (Table 2). Such a deformation of the bond angles relative to the ideal value 120° is typical of the most of benzocrown ethers and results in close proximity of the *ortho* heteroatoms. Earlier,[31,35,36] we have explained this phenomenon by the existence of the effective conjugation of the lone electron pairs (LEP) on the p-orbitals of the said heteroatoms with the benzene ring. Such a conjugation is promoted by the conformation of the fragments C(3)—C(2)—O—C and C(6)—C(7)—O—C, whereby the torsion angles discussed are sufficiently small (–13.7—19.9°), *i.e.*, fairly close to the value 0°, which is ideal for conjugation. The occurrence of conjugation follows also from the state of these

Table 2. Selected bond lengths (*d*), deviation of the metal cation from the middle plane passing through all heteroatoms of the macrocycle (ΔM^{m+}), bond (ω) and torsion (φ) angles and the sum of the bond angles at the S atom (Σ_{ω}) in crown ethers **5**, **6** • $3H_2O$ and in the complexes **5** • $NaClO_4$, **6** • $AgClO_4$ • MeCN

Parameter	**5**	**6** • $3H_2O$	**5** • $NaClO_4$	**6** • $AgClO_4$ • MeCN
Bond			d/Å	
M^{m+}...$O_{\text{macrocycle}}$	—	—	2.392(1)—2.999(1)	2.453(3)—2.582(3)
M^{m+}...S	—	—	3.0060(8), 3.596(17)[a]	—
M^{m+}...O=S or M^{m+}...NCMe	—	—	2.23(2), 2.323(1)[b]	2.198(4)
C(2)—O/S	1.787(2)	1.377(3)	1.780(1), 1.749(10)[a]	1.372(5)
C(7)—O(1)	1.354(3)	1.381(3)	1.372(1)	1.394(5)
C(4)—O(6)	1.368(3)	1.386(3)	1.366(2)	1.371(5)
S(1)—O(5)	1.502(2)	—	1.495(1), 1.57(3)[a]	—
Deviation			ΔM^{m+}/Å	
	—	—	1.26, 1.30[a]	1.14
Angle			ω/deg	
M^{m+}...O—C_{Ar}	—	—	127.4(1)	112.6(2), 114.4(2)
M^{m+}...O—C_{Alk}	—	—	103.0(1)—118.7(1)	106.7(3)—117.6(3)
M^{m+}...S(1)—C(1)	—	—	97.1(1)[c]	—
M^{m+}...S(1)—C(2)	—	—	114.0(1)[c]	—
M^{m+}...S(1)—O(5)	—	—	128.3(1)[c]	—
C(3)—C(2)—O/S	119.1(2)	124.4(2)	119.6(1), 102.5(5)[a]	123.8(4)
C(7)—C(2)—O/S	118.9(2)	114.9(2)	118.3(1), 135.5(5)[a]	115.9(4)
C(2)—C(7)—O(1)	115.5(2)	115.3(2)	115.6(1)	118.9(4)
C(6)—C(7)—O(1)	125.9(2)	125.5(2)	125.9(1)	121.2(4)
C(2)—O/S—C(1)	98.1(1)	117.1(2)	99.6(1), 107.5(6)[a]	118.6(3)
C(7)—O(1)—C(8)	117.7(2)	116.6(2)	117.5(1)	113.8(3)
Sum of angles			Σ_{ω}/deg	
	308.6(1)	—	312.7(1), 301.8(9)[a]	—
Angle			φ/deg	
C(3)—C(2)—O/S—C(1)	−107.4	19.9	96.1, 117.4[a]	3.6
C(3)—C(2)—S—O	1.3	—	−14.4, −139.2[a]	—
C(6)—C(7)—O(1)—C(8)	14.0	−13.7	8.0	84.7

[a] For two conformations.

[b] The Na^+...O=S intra- and intermolecular bonds.

[c] For predominant conformation.

O atoms close to the sp^2-hybrid one, which is characterized by the increased values of the bond angles C_{Ar}—O—C_{Alk} (on average, 117.2(2)°) compared to the angles C_{Alk}—O—C_{Alk} (on average, 113.0(2)°).

In compound **5**, the angles C(3)—C(2)—S(1) and C(7)—C(2)—S(1) are almost not distorted relative to the ideal value (119.1(2) and 118.9(2)°), which may imply weak conjugation of the LEP of the sulfoxide sulfur atom with the π-system of the benzene ring. The S—O bond is virtually coplanar with the benzene ring: the torsion angle C(3)—C(2)—S(1)—O(5) is only 1.3°, whereas the value of the angle C(3)—C(2)—S(1)—C(1) (−107.4°) characterizes the considerable deviation of the alkyl substituent at the sulfur atom from the plane. Thus, the S atom in compound **5** is predominantly in the sp^3-hybrid state and has a distinct pyramidal bond configuration, which is also follows from the sum of bond angles at the sulfur atom being equal to 308.6(1)° (see Table 2). It seems that the 15-membered macroheterocycle containing the sulfur atom linked with the benzene ring is fairly strained and rotation around the S—C_{Ar} bond is hindered. Note that the conformation of the macrocycle of **5** found in crystal most likely remains in solution as it follows from ^{1}H NMR spectral data (*vide supra*). In the NOESY spectrum of compound **5**, the absence of the cross-peaks between the hydrogen atoms of the methylene group $C\underline{H}_2S(O)Ar$ and the *ortho* hydrogen atom and, conversely, the presence of an intense cross-peak for the through-space interacting hydrogen atoms of the $C\underline{H}_2OAr$ group and the *ortho* hydrogen atom correlate with the X-ray diffraction data. Indeed, the shortest distances C(6)H...H_2C(8) and C(3)H...H_2C(1) in the crystal are 2.34 and 3.52 Å, respectively.

In the complex **5** • $NaClO_4$, the tendency to the C(2)...C(7) bond length equalization of the benzene ring

(1.386(2)—1.398(2) Å) as compared with the free ligand **5** is observed, which is typical of complexation of benzocrown ethers.[31] The values of the bond angles C_{Ar}—C_{Ar}—O(1) and C_{Ar}—C_{Ar}—S(1) in the complex do not virtually differ from the analogous parameters of the free ligand **5** (see Table 2) suggesting small changes in hydridization of the O and S atoms linked with the benzene ring.

The sodium cation is coordinated to two oxygen atoms of the perchlorate anion and three oxygen atoms of macrocycle of **5** that are remote from the benzene ring (see Fig. 3). The distances between the said O atoms and the Na^+ ion are in the range of 2.392(1)—2.551(1) Å, which characterizes the coordination bond of medium strength. The distance O(1)...Na(1) (2.999(1) Å) is considerably increased compared to the remaining O...Na bonds and significantly exceeds the sum of the van der Waals radius of the oxygen atom and the ionic radius of the sodium cation (~2.4 Å). This indicates insignificant participation of the sp^2-hybrid O(1) atom linked with the benzene ring in complexation with the Na^+ ion. The distance S(1)...Na(1) is equal to 3.0060(8) Å and, apparently, also very large for realization of sufficiently strong coordination bond (the sum of the van der Waals radius of the S atom and the ionic radius of Na^+ is ~2.8 Å).

It is worth noting that the disorder of the sulfoxide group over two positions with the population of conformers 0.96 : 0.04 was found in the structure of the complex **5** • $NaClO_4$. The structure of the minor conformer corresponds to the configurational inversion of the tetrahedral sulfur atom in compound **5**, which results in bringing the O(5´) oxygen atom of the sulfoxide group closer to the cation at a distance of 2.23(2) Å. Small content of this conformer seems to be caused by the strong angular strains in the fragment C_{Ar}—C_{Ar}—S(1´) (see Table 2). The coordination sphere of the Na^+ ion also includes the O(5A) atom of the sulfoxide group of the predominant conformer of the complex neighboring in the unit cell, which is connected with the basic complex by the symmetry center. The O(5A)...Na(1) bond length equal to 2.323(1) Å suggests its relatively high strength.

The hydroxyl group of the base complex **5** • $NaClO_4$ forms the hydrogen bond with the O(11A) atom of the perchlorate anion from the neighboring complex connected with the base one by another symmetry center. The parameters of the hydrogen bond are as follows: the distance O(6)—H...O(11A) is equal to 1.94(2) Å and the angle at the H atom is 174°. Thus, in the crystal lattice, the linear polymers built of the binuclear complexes $(\mathbf{5} \cdot NaClO_4)_2$ interlinked through the hydrogen bonds are formed.

The Cambridge Crystallographic Data Center (Version 5.27, August 2006)[37] contains about 20 structures of the complexes of benzo-15-crown-5 (**7**) and its derivatives with sodium salts. With exception of the structures of the sandwich complexes with the composition $L_2 \cdot Na^+$ where the cation is equidistant from two macrocycles, the most typical deviation of the Na^+ ion from the middle plane of all heteroatoms of the macrocycle in the complexes $L \cdot Na^+$ lies in the range of 0.60—1.09 Å. A comparison of these values with the analogous deviation of the Na^+ ion in the complex **5** • $NaClO_4$ (1.26 Å) clearly evidences the narrowing of the cavity of the 15-membered macrocycle in crown ether **5** compared to compound **7**. Obviously, such narrowing is associated with the above-noted strain in the sulfur-containing macrocycle of **5** where complexation with the singly charged cation has a weak influence on its conformation in proximity to the benzene ring. This is visualized in Fig. 4, which shows overlap of the structures of the free ligand **5** and the complex **5** • $NaClO_4$ through the benzene rings. It is well seen that the conformation of the ligand in the chain between the C(1) and C(9) atoms comprising the benzene ring is almost not changed upon complex formation. At the same time, the other half of the macrocycle of **5** undergoes significant conformational perturbation, which provides the maximum involvement of the oxygen atoms remote from the benzene ring in formation of the coordination bonds with the cation. Taking into account the above-drawn conclusion that the macrocycle of **5** exists predominantly in one conformation, one can explain the low stability of its complexes with the singly charged cations by the necessity of conformational perturbation leading to the considerable increase in the steric strains, which appear to be poorly compensated by the ion-dipole interaction of the cation with the heteroatoms of the macrocycle.

In contrast to the complex **5** • $NaClO_4$, the anion in the complex of compound **6** with silver(I) perchlorate is not involved in coordination to Ag^+, which results in the isolated metal complexes in the crystal lattice. The hydroxyl group of ligand **6** forms the medium-strength H-bond with the oxygen atom of the anion: the distance

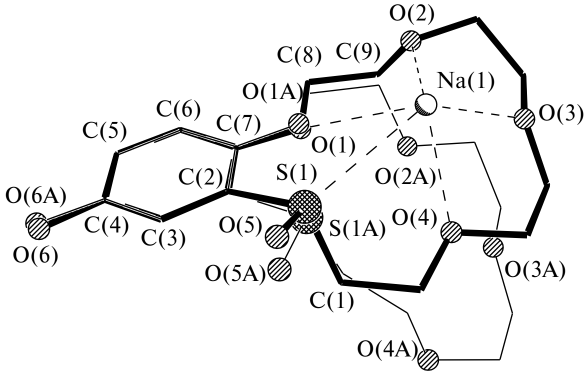


Fig. 4. Superposition of the structures of **5** (thin lines) and **5** • $NaClO_4$ (bold lines; for the major component) through the benzene rings. The coordination bonds are shown by dashed lines. The perchlorate anion and the hydrogen atoms are not shown.

O(6)—H...O(11) is equal to 1.97(5) Å and the angle at the H atom is 175° (see Fig. 3).

The cation in the complex **6** • $AgClO_4$ is situated approximately above the center of the macrocycle. The lone electron pairs of all the oxygen atoms of the macrocycle are directed to the silver(I) cation with the angles Ag(1)...O—C varying in the range of 106.7(3)—117.6(3)°, which is, in general, favorable for the interaction of the sp^2- or sp^3-hybrid O atoms with the metal cation. A comparison of the distance Ag(1)...O (2.453(3)—2.582(3) Å) and the sum of the van der Waals radius of the oxygen atom and the ionic radius of the silver cation (~2.5 Å) evidences the presence of the coordination bond of medium strength. Earlier,[38] we have found the similar parameters of the coordination bond for the complex of a chromogenic benzo-15-crown-5 with $AgNO_3$. The sandwich complex of compound **7** with $AgSbF_6$ was also described,[39] wherein the Ag^+...O coordination bond lengths are increased to 2.55—2.75 Å. A strikingly smaller value of the stability constant for the solution of the complex **6** • Ag^+ (see Table 1) in acetonitrile can be explained by the preferential solvation of the "soft" silver(I) cations with the solvent molecules, which are strong competitors for complexation as compared with the oxygen-containing ligand.[12] The solvate molecule of MeCN found in the unit cell of the complex **6** • $AgClO_4$ entering the coordination sphere of the Ag^+ ion directly confirms this conclusion. The Ag(1)...N(1S) coordination bond length is only 2.198(4) Å, whereas the sum of the van der Waals radius of the nitrogen atom and the ionic radius of the silver(I) cation is ~2.6 Å.

The distribution of the bond lengths in the benzene fragment of the complex **6** • $AgClO_4$ as in the complex **5** • $NaClO_4$ has a tendency to their equalization. The above-noted feature of the benzocrown ethers, *viz.*, the systematic deviation of the values of the bond angles that are exocyclic with respect to the benzene ring and are at the carbon atoms common to the bicyclic system from the ideal value 120°, is observed in complex **6** only for the C(2) atom: the angle C(3)—C(2)—O(5) is increased to 123.8(4)° and the angle C(7)—C(2)—O(5) is decreased to 115.9(4)°. Conversely, the analogous bond angles at the C(7) atoms are almost equalized: 118.9(4) and 121.2(4)°. This can be caused by different degrees of conjugation of the LEP of the O(1) and O(5) atoms with the benzene ring. Indeed, the torsion angle C(3)—C(2)—O(5)—C(1) is only 3.6°, which corresponds to the effective conjugation and the value of the angle C(2)—C(7)—O(1)—C(8) (84.7°) implies almost full loss of conjugation for the O(1) atom. As a result of such conformation of the macrocycle, the O(1) atom becomes predominantly sp^3-hybridized as compared with that in the free ligand **6**: the bond angle C(7)—O(1)—C(8) is decreased to 113.8(3)°. At the same time, the O(5) atoms remains in the sp^2-hybrid state: the bond angle at this atom is equal to 118.6(3)°. Thus, as exemplified by the complex **6** • $AgClO_4$, we confirmed once again our assumption of the interrelation between the angular strains at the carbon atoms of the benzene ring in the benzocrown ethers and the degree of conjugation of the LEP of the heteroatoms linked with the said carbon atoms, with the π-system of the benzene ring.

Thus, novel hydroxybenzomonothia-15-crown-5 and its sulfoxide were synthesized that contain the sulfur atom linked with the benzene ring. By means of NMR spectroscopy and X-ray diffraction analysis, the geometric characteristics of the ligands obtained and their metal complexes were established. The quantitative investigation of the complexing ability of the benzothiacrown ethers with respect to the Group I and II metal cations and the heavy metal cations showed that the crown ether containing the sulfur(II) atom is the most promising as the complexing agent. In MeCN, this thiacrown ether is highly effective and selective with respect to the thio- and oxothiophilic Hg^{2+} and Pb^{2+} ions. Its selectivity in water—acetonitrile mixtures is changed in favor of the Hg^{2+} and Ag^+ ions, the stability of the complexes with the silver(I) cation being independent of the water content in the solution. This allows us to consider the ligands of such a structure as ionophoric blocks for the design of the promising selective optical molecular sensors for the heavy metal cations.

Experimental

Melting points (uncorrected) were measured in capillaries on a Mel-Temp II instrument. Mass spectra were obtained on a Varian MAT 311A instrument at the ionization energy 70 eV with the direct inlet of the sample into the ionization chamber. Elemental analysis was performed at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS (Moscow). TLC monitoring was carried out on DC-Alufolien Kieselgel 60 F_{254} (Merck) plates. Column chromatography was performed on SiO_2 (Kieselgel 60, 0.063—0.100 mm, Merck). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 (500.13 and 125.76 MHz, respectively) spectrometer in $CDCl_3$ and DMSO-d_6 at 25—30 °C using the solvent as the internal standard (δ_H 7.27 and 2.50, δ_C 77.00 and 39.43, respectively). Chemical shifts were measured with the accuracy of 0.01 ppm and spin-spin coupling constants were measured with the accuracy of 0.1 Hz. Two-dimensional homonuclear (^1H—^1H COSY and NOESY) and heteronuclear (^1H—^{13}C COSY (HSQC and HMBC)) spectra were used for the assignment of the signals for the hydrogen and carbon nuclei.

1,11-Dichloro-3,6,9-trioxaundecane, 1,11-diiodo-3,6,9-trioxaundecane, 15-hydroxybenzo-15-crown-5 (**6**), benzo-15-crown-5 (**7**), 15-nitrobenzo-15-crown-5 (**10**), 18-nitrobenzo-18-crown-6 (**11**), and benzo-18-crown-6 (**12**) were purchased from the A. V. Bogatsky Physicochemical Institute of the National Academy of Sciences of Ukraine (Odessa). 2-Mercaptohydroquinone (**3**) was prepared according to a known procedure.[26] $NaClO_4$ and $Ca(ClO_4)_2$ (Aldrich) were dried *in vacuo* at 200 °C. $AgClO_4 \cdot H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $Hg(ClO_4)_2 \cdot 4H_2O$, and $Pb(ClO_4)_2 \cdot 3H_2O$ (Aldrich) were used without additional purification.

2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzotetraoxathiacyclopentadecyn-15-ol (4). *A*. To a boiling solution of 2-mercaptohydroquinone (**3**) (500 mg, 3.52 mmol) in Bu^nOH (20 mL), a solution of NaOH (310 mg, 7.74 mmol) in water (1 mL) was added with stirring under argon. Then a solution of 1,11-dichloro-3,6,9-trioxaundecane (813 mg, 3.52 mmol) in Bu^nOH (10 mL) was added in 10 min. The reaction mixture was refluxed with stirring for 5 h under argon, cooled, acidified with 2% HCl (30 mL), and extracted with $CHCl_3$ (3×20 mL). The combined extracts were concentrated *in vacuo*, the residue was chromatographed on SiO_2 using benzene—AcOEt mixture as the eluent (gradient elution up to 60% of AcOEt). Compound **4** (55 mg, 5%) was obtained as a pale yellow oil that slowly crystallized on storage, m.p. 59—62 °C. Found (%): C, 55.87; H, 6.71. $C_{14}H_{20}O_5S$. Calculated (%): C, 55.98; H, 6.71. ^{1}H NMR ($CDCl_3$), δ: 3.14 (t, 2 H, CH_2S, *J* = 7.3 Hz); 3.65, 3.72 (both m, 4 H each, 4 CH_2O); 3.73 (t, 2 H, $C\underline{H}_2CH_2S$, *J* = 7.3 Hz); 3.89 (m, 2 H, $C\underline{H}_2CH_2OAr$); 4.12 (m, 2 H, $C\underline{H}_2OAr$); 6.03 (br.s, 1 H, OH); 6.67 (d, 1 H, H(17), *J* = 8.7 Hz); 6.69 (dd, 1 H, H(16), *J* = 8.7 Hz, *J* = 2.6 Hz); 6.95 (d, 1 H, H(14), *J* = 2.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 33.93 (CH_2S); 68.51 ($\underline{C}H_2OAr$); 69.59 ($\underline{C}H_2CH_2OAr$); 70.42 (CH_2O); 70.47 ($\underline{C}H_2CH_2S$, CH_2O); 70.71 (CH_2O); 70.99 (CH_2O); 113.07 (C(17)); 115.32 (C(16)); 121.24 (C(14)); 124.18 (C(13a)); 149.56 (C(15)); 152.72 (C(17a)). MS, *m/z* (I_{rel} (%)): 300 $[M]^+$ (95), 168 (95), 167 (36), 153 (36), 152 (97), 142 (18), 141 (49), 140 (63), 113 (21), 112 (100).

B. To a boiling solution of $Na_2CO_3 \cdot 10H_2O$ (6.61 g, 23.1 mmol) in a water—EtOH mixture (1 : 1) (80 mL), a solution of compound **3** (328 mg, 2.31 mmol) and 1,11-diiodo-3,6,9-trioxaundecane (958 mg, 2.31 mmol) in EtOH (25 mL) was added with stirring under argon for 40 min. The reaction mixture was refluxed for 46 h and concentrated *in vacuo* to ~40 mL. Sulfuric acid (1%, 60 mL) was added and the mixture was extracted with $CHCl_3$ (3×30 mL). The combined extracts were concentrated *in vacuo* and the residue was chromatographed on SiO_2 (gradient elution with benzene—AcOEt, up to 70% of AcOEt). Compound **4** (27 mg, 4%) was obtained as a yellowish oil.

C. To a boiling mixture of Na_2CO_3 (1.22 g, 11.6 mmol) and dry acetone (50 mL), a solution of compound **3** (328 mg, 2.31 mmol) and 1,11-diiodo-3,6,9-trioxaundecane (958 mg, 2.31 mmol) in dry acetone (20 mL) was added for 1.5 h with stirring under argon. The reaction mixture was refluxed for 30 h, solids were filtered off, and the filtrate was concentrated *in vacuo*. Sulfuric acid (1%, 30 mL) was added to the residue and the mixture was extracted with $CHCl_3$ (3×15 mL). The combined extracts were concentrated *in vacuo* and the residue was chromatographed on SiO_2 (gradient elution with benzene—AcOEt, up to 100% of the latter). Compound **4** (98 mg, 14%) was obtained as yellowish oil.

15-Hydroxy-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzotetraoxathiacyclopentadecyne 13-oxide (5). To a solution of $POCl_3$ (43 μL, 0.46 mmol) in dry DMF (0.5 mL), a solution of compound **4** (92 mg, 0.31 mmol) in dry DMF (0.5 mL) was added and the mixture was stirred for 1 h at room temperature. The reaction mixture was stirred for 2 h at 70 °C, water (90 mL) was added, and the mixture was extracted with Et_2O (3×30 mL). The combined extracts were concentrated *in vacuo* and the residue was chromatographed on SiO_2 (eluent AcOEt—EtOH, 9 : 1) to obtain compound **5** (42 mg, 43%) as a white powder, m.p. 151—152 °C. Found (%): C, 52.38; H, 6.29. $C_{14}H_{20}O_6S \cdot 0.25H_2O$. Calculated (%): C, 52.40; H, 6.44. ^{1}H NMR ($CDCl_3$), δ: 2.89 (dt, 1 H, $C\underline{H}H'S$, *J* = 13.2 Hz, *J* = 3.4 Hz); 3.63—3.80 (m, 9 H, $CH\underline{H}'S$, 4 CH_2O); 3.82—3.92 (m, 3 H, $C\underline{H}H'CH_2S(O)$, $C\underline{H}_2CH_2OAr$); 4.05 (m, 1 H, $C\underline{H}H'OAr$); 4.16—4.23 (m, 2 H, $CH\underline{H}'CH_2S(O)$, $CH\underline{H}'OAr$); 6.77 (d, 1 H, H(17), *J* = 8.7 Hz); 6.90 (dd, 1 H, H(16), *J* = 8.7 Hz, *J* = 2.8 Hz); 7.66 (d, 1 H, H(14), *J* = 2.8 Hz); 8.35 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 56.45 ($CH_2S(O)$); 64.67 ($\underline{C}H_2CH_2S(O)$); 68.66 ($\underline{C}H_2OAr$); 69.32 ($\underline{C}H_2CH_2OAr$); 70.15 (CH_2O); 70.55 (CH_2O); 70.74 (CH_2O); 70.89 (CH_2O); 111.78 (C(14)); 113.21 (C(17)); 118.69 (C(16)); 131.14 (C(13a)); 147.16 (C(17a)); 152.62 (C(15)). MS, *m/z* (I_{rel} (%)): 316 $[M]^+$ (9), 300 (38), 184 (28), 168 (48), 167 (16), 156 (16), 153 (43), 141 (20), 140 (38), 112 (100).

15-Mercurio-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyne perchlorate (9) (complex with $Hg(ClO_4)_2$). A solution of benzocrown ether **7** (32 mg, 0.12 mmol) and $Hg(ClO_4)_2 \cdot 4H_2O$ (51 mg, 0.11 mmol) in dry MeCN (15 mL) was heated for 60 h at 80 °C. The solvent was evaporated *in vacuo* and the residue was triturated with warm MeOH (2 mL) and cooled to 5 °C. Solids were separated by decantation, washed with cold MeOH (2 mL), and dried *in vacuo* at 80 °C to yield the complex **9** $\cdot$ $0.25Hg(ClO_4)_2$ (25 mg, 43%) as a white powder, m.p. >185 °C (with decomp.). Found (%): C, 24.84; H, 2.91. $C_{14}H_{19}ClHgO_9 \cdot 0.25Hg(ClO_4)_2 \cdot 0.5H_2O$. Calculated (%): C, 24.87; H, 2.98. ^{1}H NMR (DMSO-d_6), δ: 3.61 (s, 8 H, 4 CH_2O); 3.77 (m, 4 H, 2 $C\underline{H}_2CH_2OAr$); 4.02 (m, 4 H, 2 $C\underline{H}_2OAr$); 6.93 (br.d, 1 H, H(16), *J* = 8.0 Hz); 6.98 (d, 1 H, H(17), *J* = 8.0 Hz); 7.00 (br.s, 1 H, H(14)). ^{13}C NMR (DMSO-d_6), δ: 68.09 ($\underline{C}H_2OAr$); 68.53 ($\underline{C}H_2OAr$); 68.74 ($\underline{C}H_2CH_2OAr$); 68.84 ($\underline{C}H_2CH_2OAr$); 69.64 (CH_2O); 69.71 (CH_2O); 70.34 (CH_2O); 70.37 (CH_2O); 113.51 (C(17)); 121.46 (C(14)); 129.35 (C(16)); 148.18 (C(13a)); 148.72 (C(17a)) (the signal for C(15) is not detected due to a great number of the mercury isotopes with different magnetic properties).

X-ray diffraction study. The crystals of free benzocrown ethers were obtained by slow evaporation of their solutions in a CH_2Cl_2—hexane mixture at room temperature and crystalline complexes of benzocrown ethers with the metal perchlorates were obtained by slow saturation of solutions of equimolar mixtures of the ligands and the salts in MeCN with benzene vapor at room temperature.

The single crystals of benzocrown ethers and their metal complexes were mounted on a Bruker SMART-CCD diffractometer under a cooled nitrogen stream (*T* = 120.0(2) K) where the intensities of the experimental reflections at a Mo-Kα radiation were measured (λ = 0.71073 Å, graphite monochromator, ω-scan mode). The data interpretation was performed according to the SAINT program.**[40]** For the crystals of metal complexes, the correction for crystal absorption of the X-ray radiation was taken into account by the SADABS method. All structures were solved by the direct methods and refined by the least squares method in the full-matrix anisotropic approximation over F^2 for the non-hydrogen atoms. The positions of the hydrogen atoms at the carbon atoms were calculated geometrically and refined in the isotropic approximation for **5** $\cdot$ $NaClO_4$ and **6** $\cdot$ $AgClO_4 \cdot MeCN$ or according to the mixed scheme (the isotropic approximation and the riding model) for **5** and **6** $\cdot$ $3H_2O$. The hydrogen atoms of the water molecules in **6** $\cdot$ $3H_2O$ and of the OH groups in all structures were localized

Table 3. Crystal parameters and X-ray diffraction data for **5**, **6** • $3H_2O$, **5** • $NaClO_4$, and **6** • $AgClO_4$ • MeCN

Parameter	**5**	**6** • $3H_2O$	**5** • $NaClO_4$	**6** • $AgClO_4$ • MeCN
Molecular formula	$C_{14}H_{20}O_6S$	$C_{14}H_{26}NO_9$	$C_{14}H_{20}ClNaO_{10}S$	$C_{16}H_{23}AgClNO_{10}$
M/g mol^{-1}	316.36	338.35	438.80	532.67
Crystal symmetry	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$
a/Å	11.7912(19)	10.4734(8)	9.3808(3)	28.9888(12)
b/Å	8.0915(13)	14.0197(10)	9.9652(3)	7.3262(3)
c/Å	15.899(3)	12.8619(9)	11.0984(3)	20.5380(9)
α/deg	90	90	103.9470(10)	90
β/deg	93.454(5)	113.561(3)	93.5940(10)	112.076(2)
γ/deg	90	90	112.3890(10)	90
V/Å^3	1514.2(4)	1731.1(2)	917.11(5)	4042.0(3)
Z	4	4	2	8
d_{calc}/g cm^{-3}	1.388	1.298	1.589	1.751
F(000)	672	728	456	2160
μ(Mo-Kα)/mm^{-1}	0.238	0.109	0.398	1.184
Crystal size/mm	0.34×0.14×0.12	0.32×0.24×0.08	0.34×0.24×0.22	0.24×0.12×0.08
Scan type/region in θ/deg	ω/2.83—29.00	ω/2.13—29.00	ω/1.92—29.00	ω/2.11—29.00
Intervals of reflection indexes	$-15 \le h \le 16$, $-10 \le k \le 10$, $-18 \le l \le 21$	$-11 \le h \le 14$, $-16 \le k \le 19$, $-15 \le l \le 17$	$-12 \le h \le 12$, $-10 \le k \le 13$, $-15 \le l \le 11$	$-39 \le h \le 39$, $-9 \le k \le 9$, $-27 \le l \le 25$
Number of reflections measured	9537	12628	6371	12770
Number of independent reflections	3955 (R_{int} = 0.0396)	4516 (R_{int} = 0.0632)	4774 (R_{int} = 0.0120)	5175 (R_{int} = 0.0509)
Number of reflections with $I > 2\sigma(I)$	3033	2483	4109	3743
Number of refinement parameters	263	308	343	355
R Factors over $I > 2\sigma(I)$	R_1 = 0.0632, wR_2 = 0.1524	R_1 = 0.0671, wR_2 = 0.1492	R_1 = 0.0306, wR_2 = 0.0826	R_1 = 0.0544, wR_2 = 0.1131
over all reflections	R_1 = 0.0853, wR_2 = 0.1613	R_1 = 0.1317, wR_2 = 0.1669	R_1 = 0.0371, wR_2 = 0.0853	R_1 = 0.0850, wR_2 = 0.1214
GOOF	1.065	1.036	1.067	1.066
Residual electron density (min/max)/e Å^{-3}	−0.384/1.272	−0.403/1.339	−0.390/0.622	−2.051/1.103

objectively from the difference Fourier syntheses followed by the refinement in the isotropic appoximation.

All calculations were performed using the SHELXTL-Plus program package.[41] The crystal parameter and X-ray diffraction data are given in Table 3. The atomic coordinates and other experimental data have been deposited at the Cambridge Crystallographic Data Center* (Nos. 712252 (**5**), 712254 (**6** • $3H_2O$), 712251 (**5** • $NaClO_4$), and 712253 (**6** • $AgClO_4$ • MeCN)).

^{1}H NMR titration was performed on a Bruker DRX 500 spectrometer. MeCN-d_3 (water content <0.05%, FSUE RRC "Applied chemistry", St. Petersburg) and its mixtures with D_2O (Aldrich) at 30 °C were used as solvents. The residual signal of MeCN-d_2 (δ_H 1.96) served as the internal signal. The composition and stability constants for the complexes of benzocrown ethers with the salts $M^{m+}(ClO_4^-)_m$ were determined by analyzing the changes in the signals for the protons of a ligand (L) depending on the concentration of the added salt upon direct titration and on the concentration of the competitive ligand (L^c) upon competitive titration. In the case of direct titration, the salt concentration varied in the range from 0 to 0.007—0.06 mol L^{-1}, the total concentration of the ligand remained unchanged and was ~$2.5 \cdot 10^{-3}$ or $5 \cdot 10^{-3}$ mol L^{-1}. In the case of competitive titration, the concentraion of L and the salt were constant and were ~$2.5 \cdot 10^{-3}$ (or $5 \cdot 10^{-3}$) and $3 \cdot 10^{-3}$ (or $6 \cdot 10^{-3}$) mol L^{-1}, respectively, and the concentration of L^c varied in the range from 0 to 0.05—0.1 mol L^{-1}. The crown ether whose signals in the spectrum slightly overlapped with the signals of L was chosen as L^c with preliminary determination of the stability constant for the corresponding complex. The L^c used are listed in Table 1. The $\Delta\delta_H$ values were measured with the accuracy of 0.001. The stability constants for complexes were calculated using the HYPNMR program.[42]

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