X-ray diffraction study of benzothiacrown compounds and their complexes with heavy metal cations

L. G. Kuz´mina,[a]★ A. I. Vedernikov,[b] S. N. Dmitrieva,[b] J. A. K. Howard,[c] and S. P. Gromov[b]★

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 954 1279. E-mail: kuzmina@igic.ras.ru*
[b]*Photochemistry Center, Russian Academy of Sciences, 7A ul. Novatorov, 119421 Moscow, Russian Federation. Fax: +7 (495) 936 1255. E-mail: gromov@photonics.ru*
[c]*Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK*

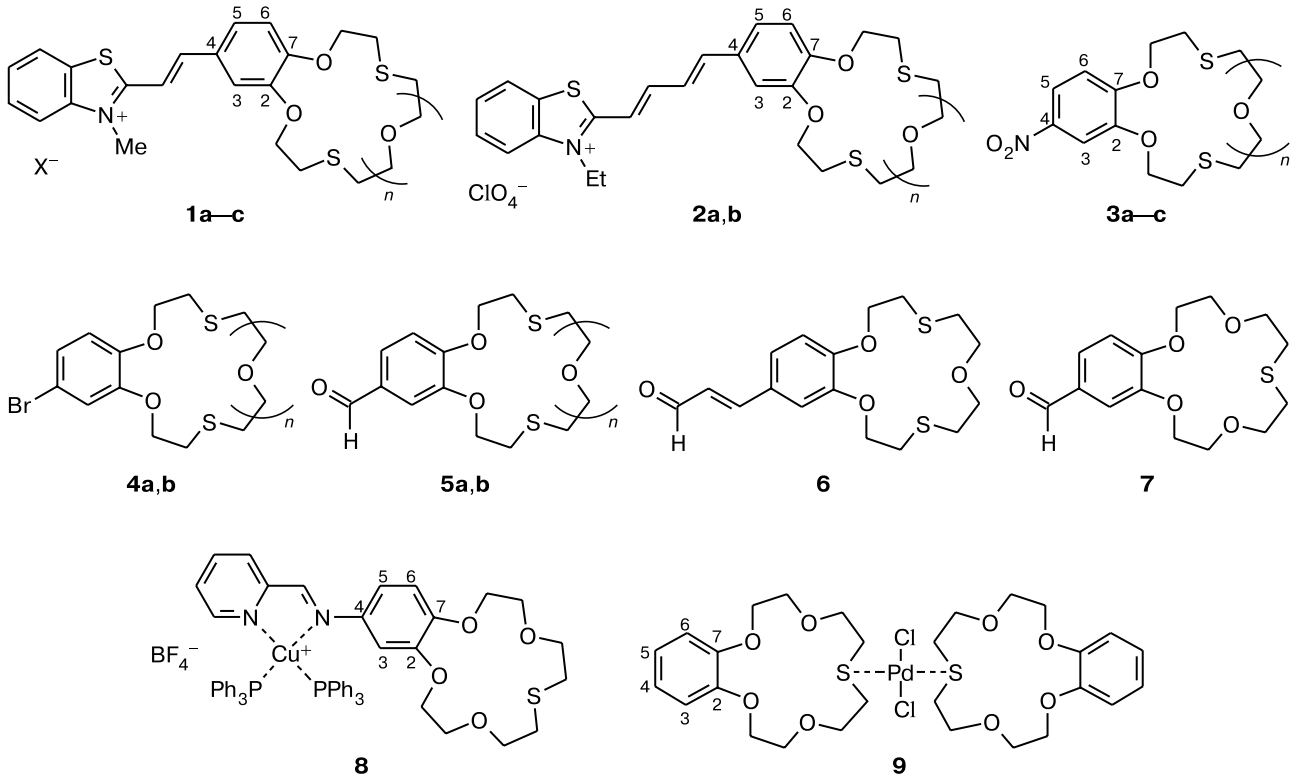
The structures of a series of substituted benzothiacrown compounds containing the dithia-15-crown-5, dithia-18-crown-6, or monothia-15-crown-5 fragment and their complexes with Ag^+ and Pb^{2+} ions were studied by X-ray diffraction. In free benzothiacrown compounds, the sulfur atoms are preferably located outside the macrocyclic cavity, and their lone electron pairs (LEPs) point away from the center of the macrocycle, which is unfavorable for the formation of inclusion complexes. Flexible macrocyclic fragments can change their conformations in accord with the coordination requirements of heavy metal cations. As a result, benzothiacrown compounds involved in complexes adopt a crown conformation, in which LEPs of all heteroatoms point toward the cation. The sulfur atoms are involved in coordination of Ag^+ to a greater degree than the oxygen atoms due to high affinity of soft sulfur atoms for silver cations. On the contrary, the sulfur and oxygen atoms are involved to approximately the same degree in coordination of Pb^{2+} ions.

Key words: benzothiacrown compounds, structure, X-ray diffraction study, complexes, silver, lead.

Crown ethers have found wide use in different fields of chemistry due to their ability to selectively bind alkali and alkaline-earth metal cations.[1,2] The replacement of one or several oxygen atoms in the macrocycle by sulfur atoms leads to a substantial change in the complexation properties. It is known that thiacrown compounds virtually do not bind alkali and alkaline-earth metal cations but selectively coordinate soft heavy metal cations (particularly, Hg^{2+}) and noble metal cations not only in organic solvents but also in water.[3—7] The introduction into thiacrown compounds of the annulated benzene fragment conjugated with two heteroatoms of the macrocycle provides the basis for the synthesis of chromoionophoric compounds by chemical modifications of these benzothiacrown compounds.[8—11] In chromoionophoric compounds, coordination of metal cations by the macrocycle can lead to a substantial electron density redistribution in the chromophoric fragment and, as a consequence, to a hypsochromic or bathochromic effect. Dithiacrown-containing styryl (**1a—c**) and butadienyl (**2a**,**b**) dyes[12—14] are examples of chromoionophores with cation-induced hypsochromic changes. This allows the use of such macrocyclic ligands as selective optical molecular sensors for heavy metal cations.[15] In this connection, it is of importance to study the conformational features of benzothiacrown compounds and their complexes with metal cations with the aim of estimating the degree of preorganization of the macroheterocyclic fragment for guest—host binding and the involvement of S and O atoms in coordination of a metal ion. We solved this problem for a series of compounds (**1—9**) of this class.

The structures of derivatives of benzothiacrown compounds in the crystalline state have received little study. Only three structures of sulfur-containing derivatives of benzoannulated 15-crown-5 compounds and their metal complexes[4,6,17] were retrieved from the Cambridge Structural Database (Version 5.27, August 2006 update).[16] Three structures of benzodithia-18-crown-6 compounds and their metal complexes were determined,[18—20] two of them being studied by our research group. The structure of the only complex of the benzodithia-12-crown-4 compound with the mercury(II) ion is known,[21] whereas data on the structures of benzodithia-21-crown-7 compounds are lacking.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 967—976, May, 2007.
1066-5285/07/5605-1003



1, **2**, **4**, **5:** *n* = 1 (**a**), 2 (**b**, **c**); X = ClO_4 (**a**, **b**), I (**c**)
3: *n* = 0 (**a**), 2 (**b**), 3 (**c**)

Recent X-ray diffraction studies[14,18,19,22] of dyes **1b**,**c** and **2a**,**b** and nitrobenzodithiacrown compounds **3a**—**c** have shown that the dithiacrown fragments predominantly adopt an extended conformation with the sulfur atoms located outside the macrocyclic cavity, their lone electron pairs (LEPs) pointing away from the center of the macrocyclic cavity. Nevertheless, dyes **1** and **2** efficiently and selectively bind Hg^{2+} and Ag^{+} ions in acetonitrile and its mixtures with water, which indicates that the polyether fragment is sufficiently flexible for conformational rearrangements necessary for location of the metal cation in the center of the macrocyclic cavity.

In the present study, we report the X-ray diffraction data for a series of derivatives of benzothia-15(18)-crown-5(6) compounds **4**—**7** and compare their structures with those of compounds **1**—**3** and **8** (see Ref. 17) and **9** (see Ref. 4) with the aim of revealing the common conformational features of the macrocyclic fragments. The conformational changes, which occur upon complex formation with Ag^{+} and Pb^{2+} ions, and the characteristic features of coordination of these cations are discussed.

The syntheses of bromo- and formylbenzodithiacrown compounds **4a**,**b** and **5a**,**b**, dithia-15-crown-5-containing cinnamaldehyde **6**, and formylbenzomonothia-15-crown-5 compound **7** have been described earlier.[8,9,23,24] The structures of compounds **4a**,**b**, **5a**,**b**, **6**, and **7** are shown in Fig. 1. For convenience of the comparison of the geometric parameters, we used the same numbering of the analogous atoms, which is different from the IUPAC nomenclature. The crystal unit cell of **4a** contains two independent molecules with different conformations of the polyether chain. In the structures of **4b** and **5b**, the bromine atom and the formyl substituent are disordered over two positions in the benzene ring (substitution at the C(4) or C(5) atom) with occupancies of 0.80 : 0.20 for **4b** and 0.83 : 0.17 for **5b**.

Table 1 gives the main geometric parameters of the substituted benzene rings in compounds **4**—**7**. In all these structures, the C(2)—C(7) bonds shared by the benzene ring and the macrocycle and the C(3)—C(4) and C(5)—C(6) bonds are substantially elongated (the average bond lengths are 1.418(4), 1.404(5), and 1.402(5) Å, respectively) compared to the other three bonds, C(2)—C(3), C(4)—C(5), and C(6)—C(7) (aver., 1.378(4), 1.372(5), and 1.385(5) Å, respectively), which is indicative of a considerable degree of the bond alternation in the benzene ring. This is the difference between compounds **4**—**7** and dyes **1** and **2**, in which a pronounced bond alternation is observed only in one half of the benzene ring, C(7)—C(2)—C(3)—C(4), of the benzodithiacrown system, whereas the bonds in another half of the benzene ring, C(4)—C(5)—C(6)—C(7), are delocalized. Undoubtedly, this difference is a consequence of the ab-

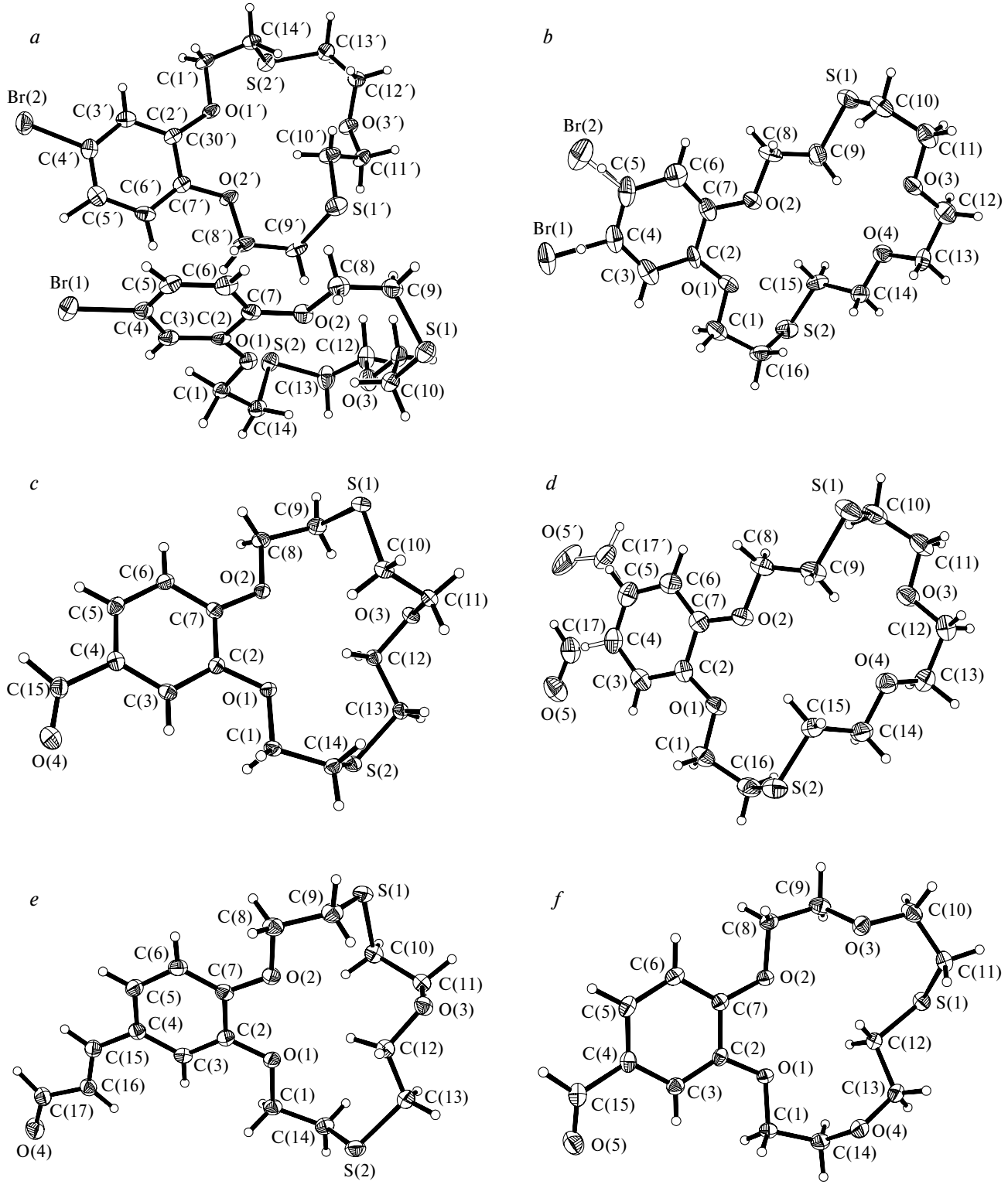


Fig. 1. Structures of compounds **4a** (two crystallographically independent molecules) (*a*), **4b** (the disordered bromine substituent) (*b*), **5a** (*c*), **5b** (the disordered formyl substituent) (*d*), **6** (*e*), and **7** (*f*). The atoms are represented by displacement ellipsoids drawn at the 50% probability level.

sence of a long conjugation chain in molecules **4**—**7** characteristic of styryl and butadienyl chromophores.

Deformations of the bond angles at the C(2) and C(7) atoms exocyclic with respect to the benzene ring in com-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in benzothiacrown compounds **4a** (two independent molecules), **4b**, **5a,b**, **6**, and **7**

Parameter	**4a**	**5a**	**6**	**7**	**4b**	**5b**
Bond			*d*/Å			
O(1)—C(2)	1.366(5), 1.363(5)	1.371(2)	1.377(2)	1.371(2)	1.361(9)	1.352(3)
O(2)—C(7)	1.360(5), 1.374(4)	1.355(2)	1.361(2)	1.359(2)	1.361(7)	1.346(3)
C(2)—C(3)	1.375(5), 1.391(5)	1.379(2)	1.379(3)	1.377(2)	1.368(9)	1.375(4)
C(3)—C(4)	1.400(6), 1.388(6)	1.409(2)	1.421(3)	1.407(2)	1.396(12)	1.410(4)
C(4)—C(5)	1.355(6), 1.362(6)	1.385(3)	1.386(3)	1.383(3)	1.363(12)	1.369(4)
C(5)—C(6)	1.395(6), 1.403(6)	1.390(3)	1.396(3)	1.402(2)	1.434(10)	1.394(5)
C(6)—C(7)	1.384(6), 1.376(6)	1.385(2)	1.382(3)	1.390(2)	1.387(10)	1.392(4)
C(2)—C(7)	1.419(5), 1.408(5)	1.418(2)	1.424(3)	1.421(2)	1.418(10)	1.420(4)
Angle			ω/deg			
O(1)—C(2)—C(3)	125.9(3), 124.9(4)	125.6(2)	125.4(2)	125.2(2)	124.7(7)	126.8(3)
O(1)—C(2)—C(7)	114.5(3), 116.2(3)	114.5(2)	114.8(2)	115.1(2)	113.8(5)	113.7(2)
O(2)—C(7)—C(2)	115.0(3), 113.9(3)	115.1(2)	115.2(2)	114.9(2)	114.0(6)	114.1(2)
O(2)—C(7)—C(6)	125.5(3), 125.5(4)	124.5(2)	124.9(2)	125.2(2)	125.1(6)	125.4(3)

pounds **4**—**7** are typical, as can be seen from a comparison with all derivatives of benzocrown compounds, which we have studied earlier. For example, the O(1)—C(2)—C(3) and O(2)—C(7)—C(6) angles are increased, on the average, to 125.5(3)°, whereas the O(1)—C(2)—C(7) and O(2)—C(7)—C(2) angles are decreased, on the average, to 114.6(3)°. Such deformations result in the arrangement of the O(1) and O(2) atoms at distances smaller than the sum of their van der Waals radii (~2.8 Å) and are attributed to conjugation of LEPs of these oxygen atoms on the *p* orbitals with the π system of the benzene ring. This conjugation in molecules **4**—**7** is favored also by a flattened conformation of the C(1)—O(1)—C(2)—C(3) and C(8)—O(2)—C(7)—C(6) fragments (the torsion angles are small and vary from −9.2 to 11.2°). The O(1)...O(2) distances in thiacrown compounds **2a**, **4a**, **5a**, **6**, and **7** vary in a narrower range (2.561—2.583 Å) than those in 18- and 21-membered compounds **1b**,**c**, **2b**, **3b**,**c**, **4b**, and **5b** (2.512—2.606 Å), which is apparently, evidence of a greater steric strain in the benzodithia-15-crown-5 macrocycles.

The conformational features of macrocycles containing sulfur atoms are of particular interest. Figure 2 shows the superposition of the fragments of the benzodithia-15-crown-5 systems of compound **2a** and two independent molecules of **4a**, **5a**, and **6** based on the benzene rings and the analogous superposition of the fragments of the benzodithia-18-crown-6 systems of compounds **1b**—**5b** and **1c**. It can be seen that, in spite of the presence of different substituents in the benzene rings, the conformations of the macrocyclic fragments in these compounds are approximately identical in the chain between the S(1) and S(2) atoms, including the annulated benzene ring. The conformations of the second halves of the macrocycles

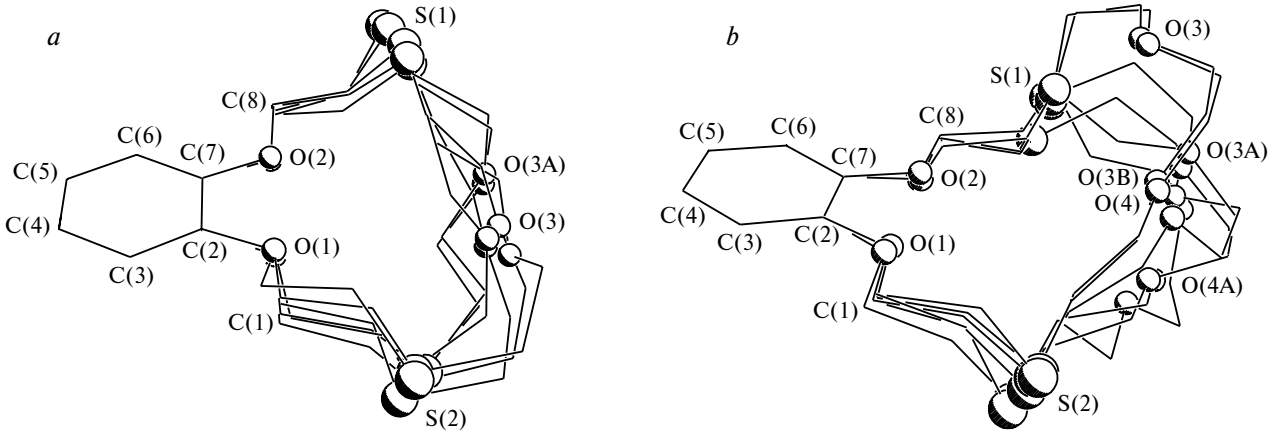


Fig. 2. Superposition of fragments of the benzodithia-15-crown-5 systems of compounds **2a** (two disordered conformations), **4a** (two independent molecules), **5a**, and **6** (*a*) and the benzodithia-18-crown-6 systems of compounds **1b**, **1c**, **2b**, **3b**, **4b**, and **5b** (*b*) based on the benzene rings. The substituents in the benzene rings and the hydrogen atoms are omitted.

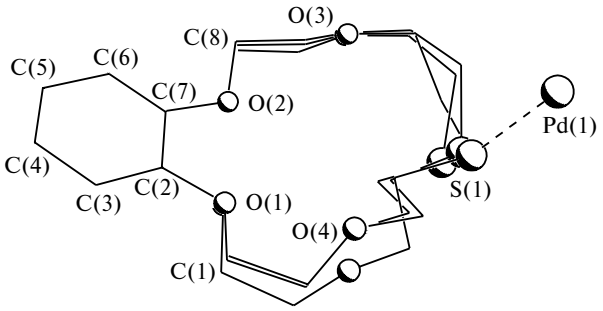


Fig. 3. Superposition of fragments of the benzomonothia-15-crown-5 systems of compounds **7**, **8**, and **9** (the complex with $PdCl_2$) based on the benzene rings. The substituents in the benzene rings and the hydrogen atoms are omitted.

are substantially different due to larger flexibility of the polyoxaalkane fragments.

Figure 3 shows the superposition of the benzene rings of benzomonothia-15-crown-5 compounds **7**—**9**. In these structures, the conformations of the macrocycles are distributed in a very narrow range. Even in compound **9**, which is the complex with palladium(II) chloride, the sulfur atoms also point outside the macrocyclic fragment. Apparently, due to low affinity of oxygen atoms for Pd^{2+} ions, no substantial rearrangement of the macroheterocycle in **9** is required for coordination of palladium by only the S(1) atom.

Evidently, the conformations of the thiacrown ether fragments in all the above-considered compounds are unfavorable for coordination of the metal cation by all heteroatoms. Figure 4 shows the orientations of LEPs of all heteroatoms in the macrocycles of formyl derivatives **5a** and **5b** on the assumption that the O(1) and O(2) atoms and both sulfur atoms are sp^2-hybridized, whereas the O(3) atom in **5a** and the O(3) and O(4) atoms in **5b** are sp^3-hybridized. It can be seen that LEPs of both sulfur atoms in **5a**,**b** point away from the center of the macrocycle. Only in compound **5a**, LEP E(3B) of the O(3) atom points approximately to the same region as LEP E(2) of the S(1) atom. These two LEPs are the only lone pairs capable of providing bidentate coordination of the metal ion with the involvement of sulfur atoms in the conformation observed in the crystal. Due to the *ortho* arrangement at the benzene ring, LEPs of the O(1) and O(2) atoms, as well as LEPs of the O(3) and O(4) atoms in **5b**, are also preorganized for bidentate coordination. However, LEPs of the O(1) and O(2) atoms are involved in conjugation with the benzene ring, which should decrease the donor ability of these atoms and, consequently, weaken the ion-dipole interaction with the metal cation. It should be noted that, on the assumption of the sp^3-hybridized state of the sulfur atoms, there is a lower possibility of even bidentate coordination of the metal cation in the macrocycle adopting this conformation.

An approximately the same situation is characteristic of the conformations of the macrocycles in the other benzodithiacrown compounds. Therefore, all the compounds under consideration, in which the macrocycles have the conformations observed in the crystals, are virtually incapable of providing polydentate coordination of the metal cation. Evidently, this coordination would require a considerable conformational rearrangement of the macrocycles. Analogous rearrangements of the macrocyclic fragments were observed in the crystalline complexes of dithia-15-crown-5 compound **4a** with $AgClO_4$ and of dithia-18-crown-6 compound **5b** with $Pb(ClO_4)_2$.

The structure of complex **4a**·$AgClO_4$ is shown in Fig. 5. Selected geometric parameters are given in Table 2. The silver cation is located in the center of the macrocyclic cavity and is coordinated by all five heteroatoms of the macrocycle and by one of the oxygen atoms of the perchlorate anion. The deviation of the Ag(1) atom from the mean plane passing through all heteroatoms of the macrocycle is 0.83 Å. The coordination polyhedron of the Ag(1) atom is irregular, which is typical of singly

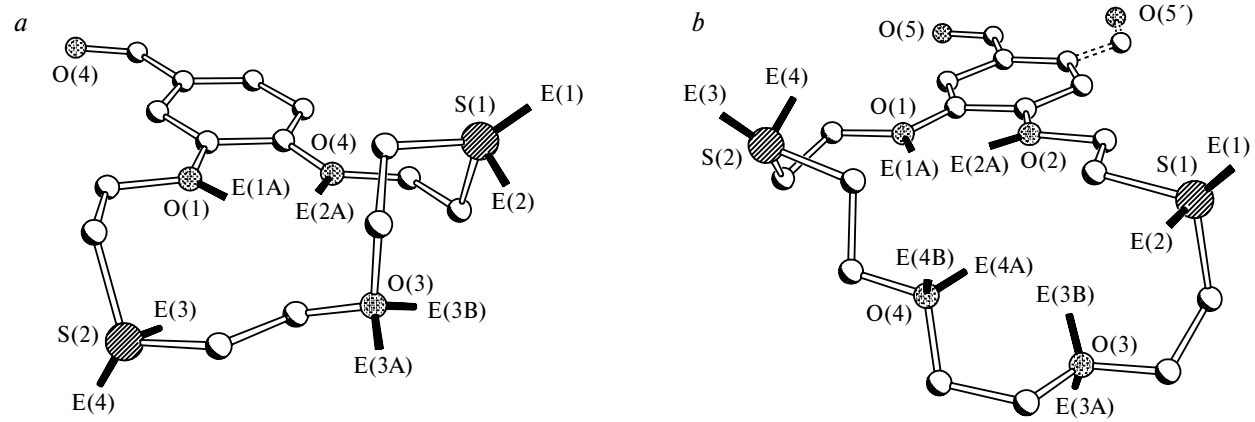


Fig. 4. Molecules **5a** (*a*) and **5b** (*b*) with the directions of LEPs of the heteroatoms (shown by solid lines); LEPs of the O(1) and O(2) atoms on the p orbitals conjugated with the benzene ring are omitted.

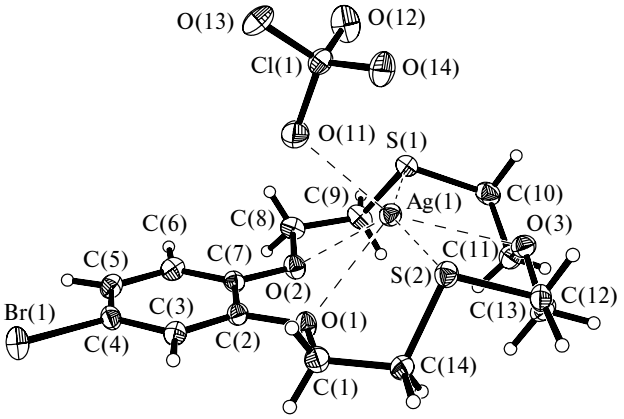


Fig. 5. Structure of **4a** · $AgClO_4$. The atoms are represented by displacement ellipsoids drawn at the 50% probability level.

charged silver cations. The Ag^+ ion forms two stronger coordination bonds with the sulfur atoms; the angle between these bonds is 149.09(3)°. The Ag—S distances are 2.4960(8) and 2.5194(7) Å; the Ag—O distances are 2.662(2)—2.766(2) Å. These geometric characteristics directly confirm the data obtained earlier[15,18] by ^{1}H NMR spectroscopy providing evidence that the sulfur atoms are more involved in binding of silver cations compared to the oxygen atoms of the macrocycles of styryl dyes **1**. Undoubtedly, this feature characterizes higher affinity of the soft Ag^+ ion for soft sulfur atoms compared to hard oxygen atoms.

The high accuracy of the determination of this structure allowed us to compare the geometric characteristics of free ligand **4a** and this ligand in the complex. The bond length distribution in the benzene ring C(2)...C(7) in the complex is analogous to that found in free ligand **4a** (see Table 1). The angles at the C(2) and C(7) atoms exocyclic

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **4a** · $AgClO_4$

Bond	*d*/Å	Angle	ω/deg
Ag(1)—S(1)	2.4960(8)	Ag(1)—S(1)—C(9)	104.8(1)
Ag(1)—S(2)	2.5194(7)	Ag(1)—S(1)—C(10)	101.9(1)
Ag(1)—O(1)	2.662(2)	Ag(1)—S(2)—C(13)	104.3(1)
Ag(1)—O(2)	2.766(2)	Ag(1)—S(2)—C(14)	102.1(1)
Ag(1)—O(3)	2.717(2)	S(1)—Ag(1)—S(2)	149.09(3)
Ag(1)—O(11)	2.552(2)	Ag(1)—O(1)—C(1)	112.9(2)
O(1)—C(2)	1.371(3)	Ag(1)—O(1)—C(2)	114.1(1)
O(2)—C(7)	1.374(4)	C(1)—O(1)—C(2)	117.1(2)
C(2)—C(3)	1.384(4)	O(1)—C(2)—C(3)	124.6(2)
C(2)—C(7)	1.405(4)	O(1)—C(2)—C(7)	114.4(3)
C(3)—C(4)	1.392(4)	Ag(1)—O(2)—C(7)	110.5(2)
C(4)—C(5)	1.383(4)	Ag(1)—O(2)—C(8)	111.4(2)
C(5)—C(6)	1.396(5)	C(7)—O(2)—C(8)	117.6(2)
C(6)—C(7)	1.386(4)	O(2)—C(7)—C(2)	115.0(2)
		O(2)—C(7)—C(6)	125.4(3)
		C(11)—O(3)—C(12)	112.9(2)

with respect to the benzene ring are distorted in the same way as in all known benzothiacrown compounds. The O(1) and O(2) atoms are sp^2-hybridized, which is confirmed by the characteristic bond angles at these atoms (~117.4°). The Ag(1)—O(1)—C and Ag(1)—O(2)—C angles (110.5(2)—114.1(1)°) are not quite suitable for efficient interactions between LEPs of these oxygen atoms on the sp^2-hybridized orbitals and the silver cation. The geometry observed in the crystal structure of the complex allows the second LEPs of the O(1) and O(2) atoms occupying the p orbitals to be partially involved in coordination to the cation. This should lead to a decrease in the degree of their involvement in conjugation with the π system of the benzene ring. Our studies of chromogenic compounds **1** and **2** confirmed their ability to serve as optical molecular sensors for Ag^+, Hg^{2+}, and Pb^{2+} ions based on the above-described weakening of conjugation between LEPs of the O(1) and O(2) atoms occupying the p orbitals and the chromophoric system of the dye upon coordination of the metal cation.[12—15,18]

The structure of the complex of formyl derivative **5b** with $Pb(ClO_4)_2$ is shown in Fig. 6. This complex crystallizes as a solvate with benzene and water molecules. The Pb(1) atom is coordinated by all heteroatoms of the macrocycle and is located deeply inside its cavity. The deviation of the Pb(1) atom from the mean plane of the hexagon formed by the heteroatoms of the macrocycle is only 0.19 Å. The O(11) and O(21) atoms of two perchlorate anions located on the opposite sides of the plane of the macrocycle and the water molecule O(1W) lead to an increase in the coordination number of the lead cation to 9. The coordination polyhedron of the Pb(1) atom is irregular, which is typical of this metal. Selected geometric parameters of this complex are given in Table 3.

A poor quality of the crystals of complex **5b** · $Pb(ClO_4)_2$ allowed us to estimate only the differences in the coordination of the Pb^{2+} ion by the heteroatoms of the macrocycle and the conformational changes caused by the complex formation. The Pb(1)—S bonds (aver., 3.049(4) Å) and the bonds of the Pb(1) atom with the O(1) and O(2) atoms (aver., 2.89(1) Å) are comparable in length, whereas the Pb(1)—O(3) and Pb(1)—O(4) bonds are much shorter (aver., 2.65(1) Å). Therefore, the lead cation is stronger coordinated by the sp^3-hybridized O(3) and O(4) atoms than by the O(1) and O(2) atoms, whose LEPs on the p orbitals are involved in conjugation with the benzene ring, and only their LEPs on the sp^2-hybridized orbitals are involved in coordination of the Pb(1) atom (the Pb(1)—O(1)—C and Pb(1)—O(2)—C angles are in the range of 111.6(8)–120.7(9)°). Since the van der Waals radius of the sulfur atom is approximately 0.4 Å larger than the van der Waals radius of the oxygen atom, the observed Pb—S distances are indicative of the approximately equal interactions of the lead cation with the S(1), S(2), O(3), and O(4) atoms. This conclusion is

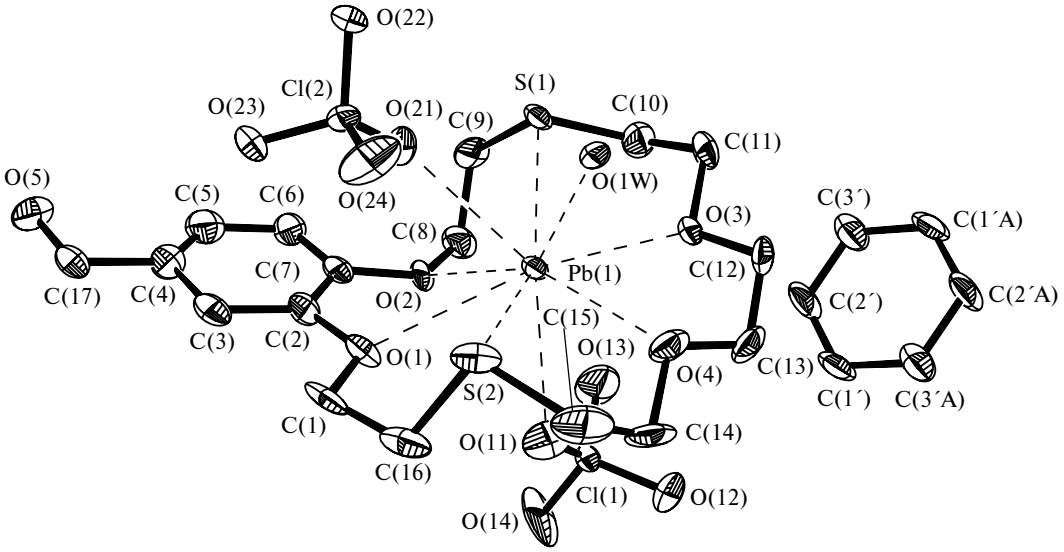


Fig. 6. Structure of **5b** · $Pb(ClO_4)_2$ (the solvate with benzene and water). The hydrogen atoms are omitted. The atoms are represented by displacement ellipsoids drawn at the 50% probability level.

consistent with the conclusion, which we have drawn based on the spectroscopic data[14,19] as to the approximately equal binding of the Pb^{2+} ions by the sulfur and oxygen atoms in the macrocycles of dyes **1** and **2**.

Particular attention should be given to a considerable conformational rearrangement of the dithiacrown fragment in compounds **4a** and **5b** upon complexation. As mentioned above, the extended conformation is typical of free dithia-15(18)-crown-5(6) compounds in the crystalline state. In this conformation, the sulfur atoms are located outside the macrocyclic cavity. For efficient binding of the metal cation by all heteroatoms of the macrocycle, the sulfur atoms and some oxygen atoms should substantially change their positions and their LEPs should point toward the center of the macrocyclic cavity. Such changes are actually observed in complexes **4a** · $AgClO_4$ and **5b** · $Pb(ClO_4)_2$, as can be seen in Fig. 7. In both complexes, the macrocycles of the dithiacrown compounds have a nearly crown conformation, which is more typical of crown ethers. In this conformation, all heteroatoms of the macrocycle are in the equatorial plane about the coordinated metal cation so that their LEPs point toward this atom. Steric strains that appear in this conformation of the macrocycle are apparently compensated by ion-dipole interactions between both sulfur atoms and the heavy metal cation.

Therefore, the conformations of the macroheterocycles observed in the crystals of derivatives of benzothiacrown compounds are characterized by the common structural feature, that is by the preferable location of the sulfur atoms outside the macrocyclic cavity. These conformations are unfavorable for the formation of inclusion complexes with metal cations because LEPs of the sulfur atoms point away from the center of the cavity. However, this fact does not hinder the formation of complexes of benzodithiacrown compounds with Ag^+ and Pb^{2+} ions due to high conformational flexibility of the macrocycles and high affinity of sulfur atoms for heavy metal cations.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in complex **5b** · $Pb(ClO_4)_2$

Bond	*d*/Å
Pb(1)—S(1)	3.116(4)
Pb(1)—S(2)	2.981(4)
Pb(1)—O(1)	2.929(11)
Pb(1)—O(2)	2.858(9)
Pb(1)—O(3)	2.669(10)
Pb(1)—O(4)	2.633(11)
Pb(1)—O(11)	2.893(13)
Pb(1)—O(21)	2.777(11)
Pb(1)—O(1W)	2.489(10)

Angle	ω/deg
Pb(1)—S(1)—C(9)	103.3(5)
Pb(1)—S(1)—C(10)	96.3(6)
Pb(1)—S(2)—C(15)	101.9(6)
Pb(1)—S(2)—C(16)	95.8(6)
S(1)—Pb(1)—S(2)	151.1(1)
Pb(1)—O(1)—C(1)	118.2(10)
Pb(1)—O(1)—C(2)	116.0(9)
C(1)—O(1)—C(2)	117.0(13)
O(1)—C(2)—C(3)	124.9(16)
O(1)—C(2)—C(7)	116.6(14)
Pb(1)—O(2)—C(7)	120.7(9)

Angle	ω/deg
Pb(1)—O(2)—C(8)	111.6(8)
C(7)—O(2)—C(8)	119.3(13)
O(2)—C(7)—C(2)	114.3(15)
O(2)—C(7)—C(6)	122.8(17)
Pb(1)—O(3)—C(11)	120.4(9)
Pb(1)—O(3)—C(12)	111.5(9)
Pb(1)—O(4)—C(13)	112.4(9)
Pb(1)—O(4)—C(14)	116.3(10)
C(11)—O(3)—C(12)	111.5(12)
C(13)—O(4)—C(14)	113.7(12)

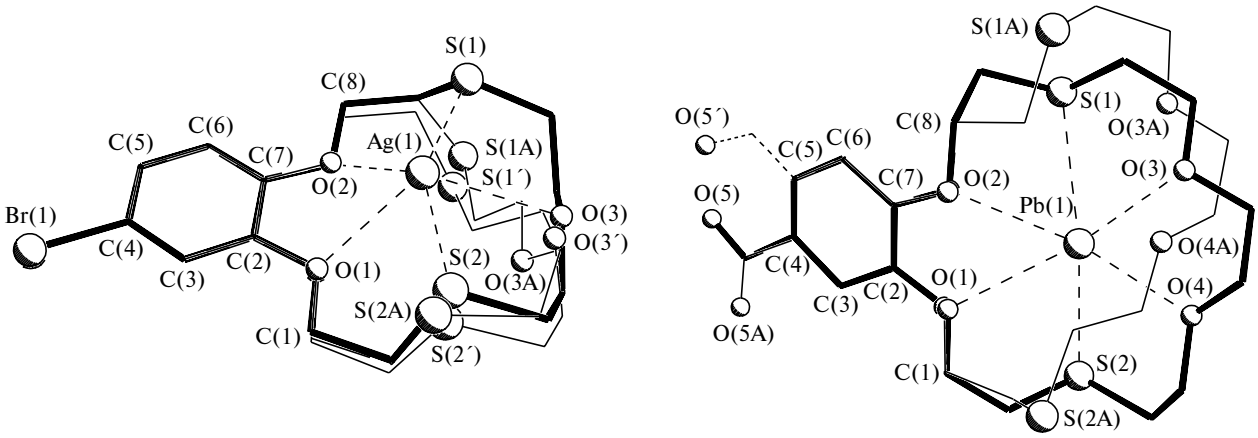


Fig. 7. Superposition of complex **4a**·$AgClO_4$ and two independent molecules of free **4a** (*a*) and the superposition of complex **5b**·$Pb(ClO_4)_2$ and free **5b** (*b*) based on the benzene rings.

Table 4. Crystal parameters and the X-ray diffraction data collection and refinement statistics for compounds **4a**, **4b**, **5a**, and **5b**

Compound	**4a**	**4b**	**5a**	**5b**
Molecular formula	$C_{14}H_{19}BrO_3S_2$	$C_{16}H_{23}BrO_4S_2$	$C_{15}H_{20}O_4S_2$	$C_{17}H_{24}O_5S_2$
Molecular weight/g mol^{-1}	379.32	423.37	328.43	372.48
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$	$Pccn$	$Pna2_1$
a/Å	8.8100(5)	16.772(2)	14.5425(9)	16.5800(14)
b/Å	12.5927(7)	12.2412(13)	26.9389(17)	12.2753(10)
c/Å	15.3724(9)	8.9805(12)	7.8381(5)	8.9266(7)
α/deg	102.005(2)	90	90	90
β/deg	90.302(2)	90	90	90
γ/deg	105.615(2)	90	90	90
V/Å^3	1603.17(16)	1843.7(4)	3070.6(3)	1816.8(3)
Z	4	4	8	4
ρ_{calc}/g cm^{-3}	1.572	1.525	1.421	1.362
F(000)	776	872	1392	792
μ(MoK_α)/mm^{-1}	2.828	2.472	0.359	0.316
Crystal dimensions/mm	0.32×0.28×0.12	0.36×0.24×0.08	0.2×0.08×0.06	0.32×0.14×0.08
T/K	120.0(2)	120.0(2)	120.0(2)	120.0(2)
Radiation/Å	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Scan mode	ω	ω	ω	ω
θ-Scanning range/deg	1.95—29.00	2.43—29.00	1.51—29.00	2.06—29.00
Ranges of reflection indices	$-12 \le h \le 11$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-18 \le h \le 22$, $-15 \le k \le 15$, $-12 \le l \le 12$	$-19 \le h \le 17$, $-21 \le k \le 36$, $-10 \le l \le 9$	$-22 \le h \le 10$, $-15 \le k \le 16$, $-12 \le l \le 11$
Number of measured reflections	11974	9630	18980	8358
Number of independent reflections (R_{int})	8045 0.0484	4699 0.0918	4083 0.0457	4365 0.0624
Number of reflections with $I > 2\sigma(I)$	5003	2664	3258	3515
Number of refinement variables	513	218	270	324
R Factors based on reflections with $I > 2\sigma(I)$				
R_1	0.0535	0.0736	0.0465	0.0447
wR_2	0.1227	0.1805	0.0969	0.1015
R Factors based on all reflections				
R_1	0.1014	0.1456	0.0624	0.0606
wR_2	0.1359	0.2042	0.1028	0.1092
Goodness-of-fit on F^2	0.944	1.050	1.057	1.047
Residual electron density (ρ_{min}/ρ_{max})/e Å^{-3}	−0.919/1.336	−0.946/2.206	−0.229/0.419	−0.224/0.398

The above-described structural features of benzothiacrown-containing fragments provide an explanation of high efficiency and selectivity of such structures, when being involved in chromoionophoric compounds, and elucidate the factors responsible for the optical response upon coordination of heavy metal cations.

Experimental

The salts $AgClO_4 \cdot H_2O$ and $Pb(ClO_4)_2 \cdot 3H_2O$ (Aldrich) were used without additional purification. Compounds **4a**,**b**,[8] **5a**,**b**,[8,9] **6**,[23] and **7** [24] were prepared according to known procedures.

Single crystals of all free benzothiacrown compounds were grown by slow evaporation of solutions of **4**—**7** in a CH_2Cl_2—hexane mixture at room temperature. Single crystals of complexes **4a** · $AgClO_4$ and **5b** · $Pb(ClO_4)_2$ were grown by slow saturation of equimolar mixtures of the ligand and metal perchlorate in acetonitrile with benzene vapor at room temperature.

Single crystals of benzothiacrown compounds or their metal complexes coated with perfluorinated oil were mounted on a Bruker SMART-CCD diffractometer under a flow of cooled nitrogen. The experimental X-ray data sets were collected from single crystals using the ω-scanning technique and Mo-Kα radiation. The reflections were processed with the use of the Bruker SAINT software.[25] All structures were solved by direct methods

Table 5. Crystal parameters and the X-ray diffraction data collection and refinement statistics for compounds **6**, **7**, **4a** · $AgClO_4$, and **5b** · $Pb(ClO_4)_2 \cdot 0.5C_6H_6 \cdot H_2O$

Compound	**6**	**7**	**4a** · $AgClO_4$	**5b** · $Pb(ClO_4)_2 \cdot 0.5C_6H_6 \cdot H_2O$
Molecular formula	$C_{17}H_{22}O_4S_2$	$C_{15}H_{20}O_5S$	$C_{14}H_{19}AgBrClO_7S_2$	$C_{20}H_{29}Cl_2O_{14}PbS_2$
Molecular weight/g mol^{-1}	354.47	312.37	586.64	835.64
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	*Pccn*	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	14.7252(9)	18.5922(7)	9.6305(2)	17.039(3)
b/Å	29.3814(19)	9.8018(4)	9.6390(2)	9.4922(15)
c/Å	7.9467(5)	8.1676(3)	12.3600(3)	17.848(3)
α/deg	90	90	112.6840(10)	90
β/deg	90	92.349(2)	91.1330(10)	105.464(4)
γ/deg	90	90	112.0220(10)	90
V/Å^3	3438.1(4)	1487.19(10)	963.08(4)	2782.2(8)
Z	8	4	2	4
ρ_{calc}/g cm^{-3}	1.370	1.395	2.023	1.995
F(000)	1504	664	580	1636
μ(MoK_α)/mm^{-1}	0.327	0.237	3.510	6.473
Crystal dimensions/mm	0.34×0.26×0.18	0.34×0.24×0.08	0.40×0.40×0.06	0.42×0.24×0.06
T/K	120.0(2)	120.0(2)	120.0(2)	120.0(2)
Radiation/Å	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Scan mode	ω	ω	ω	ω
θ-Scanning range/deg	1.39—29.00	2.19—29.00	2.32—29.00	2.36—28.00
Ranges of reflection indices	$-19 \le h \le 20$, $-35 \le k \le 39$, $-10 \le l \le 10$	$-25 \le h \le 25$, $-9 \le k \le 13$, $-11 \le l \le 10$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-16 \le l \le 16$	$-22 \le h \le 21$, $-12 \le k \le 12$, $-23 \le l \le 17$
Number of measured reflections	28039	8143	8392	16495
Number of independent reflections	4563	3766	5020	6611
R_{int}	0.0654	0.0302	0.0281	0.0625
Number of reflections with $I > 2\sigma(I)$	3257	2830	4216	5332
Number of refinement variables	296	270	311	352
R Factors based on reflections with $I > 2\sigma(I)$				
R_1	0.0472	0.0459	0.0329	0.0991
wR_2	0.1106	0.0965	0.0843	0.2574
R Factors based on all reflections				
R_1	0.0785	0.0706	0.0413	0.1153
wR_2	0.1212	0.1034	0.0875	0.2666
Goodness-of-fit on F^2	1.098	1.029	1.015	1.101
Residual electron density (ρ_{min}/ρ_{max})/e Å^{-3}	—0.375/0.435	—0.218/0.383	—0.912/1.542	—8.160/8.854

and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were placed geometrically and refined isotropically for **4a**, **5a**, **6**, **7**, and **4a**·$AgClO_4$ or using a riding model for **4b** and **5b**·$Pb(ClO_4)_2$. In the structure of **5b**, all hydrogen atoms were refined isotropically, except for the hydrogen atoms of the disordered fragment, for which the riding model was used.

For complexes **4a**·$AgClO_4$ and **5b**·$Pb(ClO_4)_2$, absorption corrections were applied using the SADABS method. Low quality of single crystals did not allow us to precisely refine the latter structure. Additional difficulties in the case of **5b**·$Pb(ClO_4)_2$ were associated with a thin-plate shape of the single crystal, which hinders the accurate measurement of its thickness, thus increasing the error in the absorption correction. As a result, residual electron densities were high; however, the highest peaks were located about the heavy atoms at distances smaller than 1.5 Å. In spite of the low accuracy of the determination of **5b**·$Pb(ClO_4)_2$, we believe that it is correct to discuss the conformational changes of the macrocycle of free crown compound **5b** upon coordination to the metal cation.

All calculations were carried out with the use of the SHELXTL-Plus program package.[26] The crystallographic parameters and the X-ray diffraction data collection and refinement statistics are given in Tables 4 and 5. The atomic coordinates and other experimental data were deposited with the Cambridge Structural Database* (CSD refcodes 636349 (**4a**), 636351 (**4b**), 636352 (**5a**), 636353 (**5b**), 636355 (**6**), 636356 (**7**), 636350 (**4a**·$AgClO_4$), and 636354 (**5b**·$Pb(ClO_4)_2$)).

We thank O. V. Eshcheulova, M. S. Kapichnikova, and N. I. Sidorenko for providing benzothiacrown compounds. This study was financially supported by the Russian Foundation for Basic Research (Project Nos 06-03-32434, 06-03-32456, and 06-03-33162), the Russian Academy of Sciences (Program No. 8 of the Presidium of the Russian Academy of Sciences), and the Royal Society of Chemistry (Great Britain).

References

1. M. Takagi, H. Nakamura, and K. Ueno, *Anal. Lett.*, 1977, **10**, 1115.
2. J. P. Dix and F. Vögtle, *Angew. Chem.*, *Int. Ed. Engl.*, 1978, **17**, 857.
3. R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721.
4. W.-P. Li, X.-F. Lui, H.-S. Xu, Y.-Q. Huang, and S.-Z. Hu, *Chin. J. Chem.*, 1995, **13**, 47.
5. J. S. Bradshaw and R. M. Izatt, *Acc. Chem. Res.*, 1997, **30**, 338.
6. V. W.-W. Yam, Y.-L. Pui, K.-K. Cheung, and N. Zhu, *New J. Chem.*, 2002, **26**, 536.
7. T. Tsuchiya, T. Shimizu, K. Hirabayashi, and N. Kamigata, *J. Org. Chem.*, 2003, **68**, 3480.
8. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, N. S. Zefirov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 121 [*Russ. Chem. Bull.*, 1995, **44**, 116 (Engl. Transl.)].
9. O. A. Fedorova, A. I. Vedernikov, O. V. Eshcheulova, P. V. Tsapenko, Yu. V. Pershina, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1881 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1853].
10. A. Bilgin, B. Ertem, and Y. Gök, *Tetrahedron Lett.*, 2003, **44**, 6937.
11. O. A. Fedorova, E. N. Andryukhina, and S. P. Gromov, *Synthesis*, 2003, 371.
12. M. V. Alfimov, Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, I. K. Lednev, J. N. Moore, V. P. Oleshko, and A. I. Vedernikov, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1441.
13. M. V. Alfimov, A. I. Vedernikov, S. P. Gromov, Yu. V. Fedorov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2213 [*Russ. Chem. Bull.*, 1997, **46**, 2099 (Engl. Transl.)].
14. E. N. Ushakov, L. G. Kuz´mina, A. I. Vedernikov, M. S. Kapichnikova, J. A. K. Howard, M. Wörner, A. M. Braun, M. V. Alfimov, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 90 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 94].
15. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, O. V. Eshcheulova, Yu. V. Fedorov, and M. V. Alfimov, *Pat. RF 2176256*; *Byul. izobret.* [*Invention Bull.*], 2001, No. 33 (in Russian).
16. F. H. Allen, *Acta Cryst. B*, 2002, **58**, 380.
17. V. W.-W. Yam, Y.-L. Pui, W.-P. Li, K. K.-W. Lo, and K.-K. Cheung, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3615.
18. M. V. Alfimov, S. P. Gromov, Yu. V. Fedorov, O. A. Fedorova, A. I. Vedernikov, A. V. Churakov, L. G. Kuz´mina, J. A. K. Howard, S. Bossmann, A. Braun, M. Woerner, D. F. Sears, Jr., and J. Saltiel, *J. Am. Chem. Soc.*, 1999, **121**, 4992.
19. O. A. Fedorova, Yu. V. Fedorov, A. I. Vedernikov, O. V. Yescheulova, S. P. Gromov, M. V. Alfimov, L. G. Kuz´mina, A. V. Churakov, J. A. K. Howard, S. Yu. Zaitsev, T. I. Sergeeva, and D. Möbius, *New J. Chem.*, 2002, **26**, 543.
20. S. V. Pavlova, L. I. Budarin, V. N. Kalinin, Yu. A. Simonov, A. A. Dvorkin, and T. I. Malinovskii, *Zh. Neorg. Khim.*, 1989, **34**, 1224 [*J. Inorg. Chem. USSR*, 1989, **34** (Engl. Transl.)].
21. H.-J. Holdt, M. Muller, A. Kellina, H.-J. Drexler, T. Muller, T. Schwarze, U. Schilde, and I. Starke, *Z. Anorg. Allg. Chem.*, 2006, **632**, 114.
22. S. N. Dmitrieva, N. I. Sidorenko, A. I. Vedernikov, L. G. Kuz´mina, J. A. K. Howard, T. M. Buslaeva, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 958 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, No. 5].
23. A. I. Vedernikov and S. P. Gromov, *Synthesis*, 2001, 889.
24. O. V. Eshcheulova, Ph. D. (Chem.) Thesis, Moscow, 2001 (in Russian).
25. SAINT, Version 6.02A, Bruker AXS Inc., Madison, Wisconsin (USA), 2001.
26. SHELXTL-Plus. Version 5.10, Bruker AXS Inc., Madison, Wisconsin (USA), 1997.

* CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223 33 6033; e-mail: deposit@ccdc.cam.ac.uk). The data can also be obtained from the authors.

Received November 7, 2006;
in revised form February 9, 2007