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SYNTHESIS, COMPLEX-FORMATION, AND EXTRACTING ABILITY OF NEW DERIVATIVES OF DITHIA-13(16)-CROWN-4(5) ETHERS

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Various methods of synthesizing functional derivatives of dithia-13(16)-crown-4(5) ethers are proposed. Complex-formation of the obtained compounds with Ag^+ and Pb^{2+} ions has been studied using ^1H NMR. A radiometric method was used to investigate the extracting ability of substituted dithia-13(16)-crown-4(5) ethers in relation to Ag^+ and Cd^{2+} ions from aqueous solution in the presence of anions of various degree of hardness, with determination of the metal content.

Keywords: dithia-13(16)-crown-4(5) ethers, Ag^+, Pb^{2+}, Cd^{2+} ions, complex-formation, synthesis, ^1H NMR spectroscopy, extraction.

Sulfur macrocycles occupy a special place among crown ethers and their hetero analogs due to their unique ability to serve as ligands for selective complex-formation with ions of heavy and transition metals. Such properties of these compounds offer the possibility of modeling biological processes linked with the transport of ionic particles and molecules *in vivo*, the creation of efficient ion-selective electrodes, selective extractants, unique receptors, and components of photochromic systems [1, 2]. The introduction into the crown ether molecule of substituents of various nature may significantly change their activity and selectivity in complex-formation with various metal cations. For example, the presence of electron-donating substituents containing long chain alkyl groups improves selectivity and adds lipophilicity to the crown ether molecule, which in turn promotes an increase in the rate of transfer of metals through lipid membranes [3].

Only a small number of methods exist for the further conversion of functional groups in macrocyclic sulfur compounds, in which the desired compounds as a rule are obtained in very low yield and with a high probability of side reactions [4-6]. The present work is devoted to the development of various methods of transforming 1,4-dioxa-7,11-dithiacyclotridecan-9-ol (**4**) and 1,4,7-trioxa-10,14-dithiacyclohexadecan-12-ol (**5**), and to the study of the complex-forming and extracting properties of the derivatives obtained.

Although it has been reported previously that compounds **4** and **5** may be obtained from 1,3-dimercaptopropan-2-ol and α,ω-dichlorides of tri- and tetraethylene glycol [7, 8] under conditions of high dilution, we have proposed a somewhat different synthetic scheme. The advantage of the proposed scheme is as follows: rejection of the use of the poorly available 1,3-dimercaptopropan-2-ol, and combination of the high dilution method with the template method, which enables an increase in the yield of oxathiacrown ethers. Synthesis of the macrocyclic compounds **4** and **5** was effected on interacting 2,3-dibromopropanol (**1**) with

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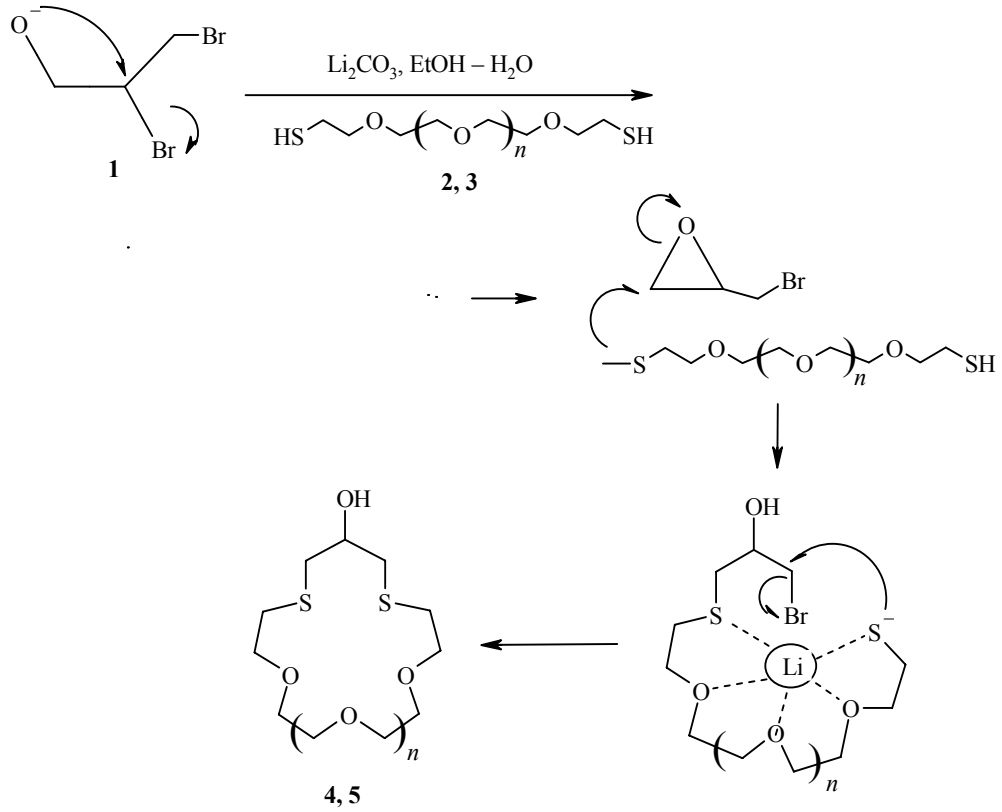
dithiols **2** and **3**. In an alkaline medium compound **1** forms an oxirane, which as a result of nucleophilic attack by thiolate ions **2** and **3** opens from the less hindered side, which in turn leads to the formation of symmetrical 13(16)-membered crown ethers.



The preparation of the hydroxy-substituted macrocycles **4** and **5** represents a convenient opportunity for their further conversion into compounds with a carbonyl group by selective oxidation, which has not been effected until now for sulfur-containing macrocyclic ligands [9].

In this connection we studied the action on macrocycle **4** of various mild oxidation systems, not affecting the C–S–C bond. Oxidation of compound **4** in the system DMSO–acetic anhydride [10] leads, according to data of ^{1}H NMR and mass spectrometry, to a complex mixture of products, the identification of which was not possible.

The most convenient proved to be oxidation according to Swern [11], on carrying out which it was established that DMSO, alcohol **4**, and oxalyl chloride react in methylene chloride at low temperatures with the formation of an alkoxysulfonium salt. Treatment of this salt with triethylamine forms 1,4-dioxo-7,11-dithiacyclotridecan-9-one (**6**) in 40% yield.

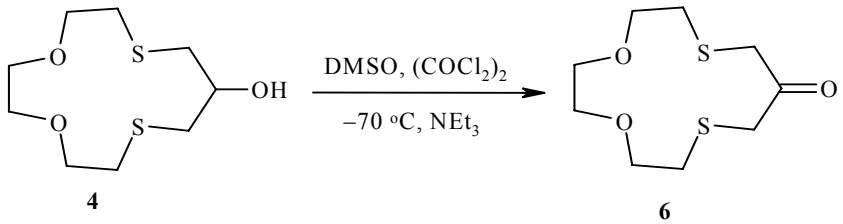
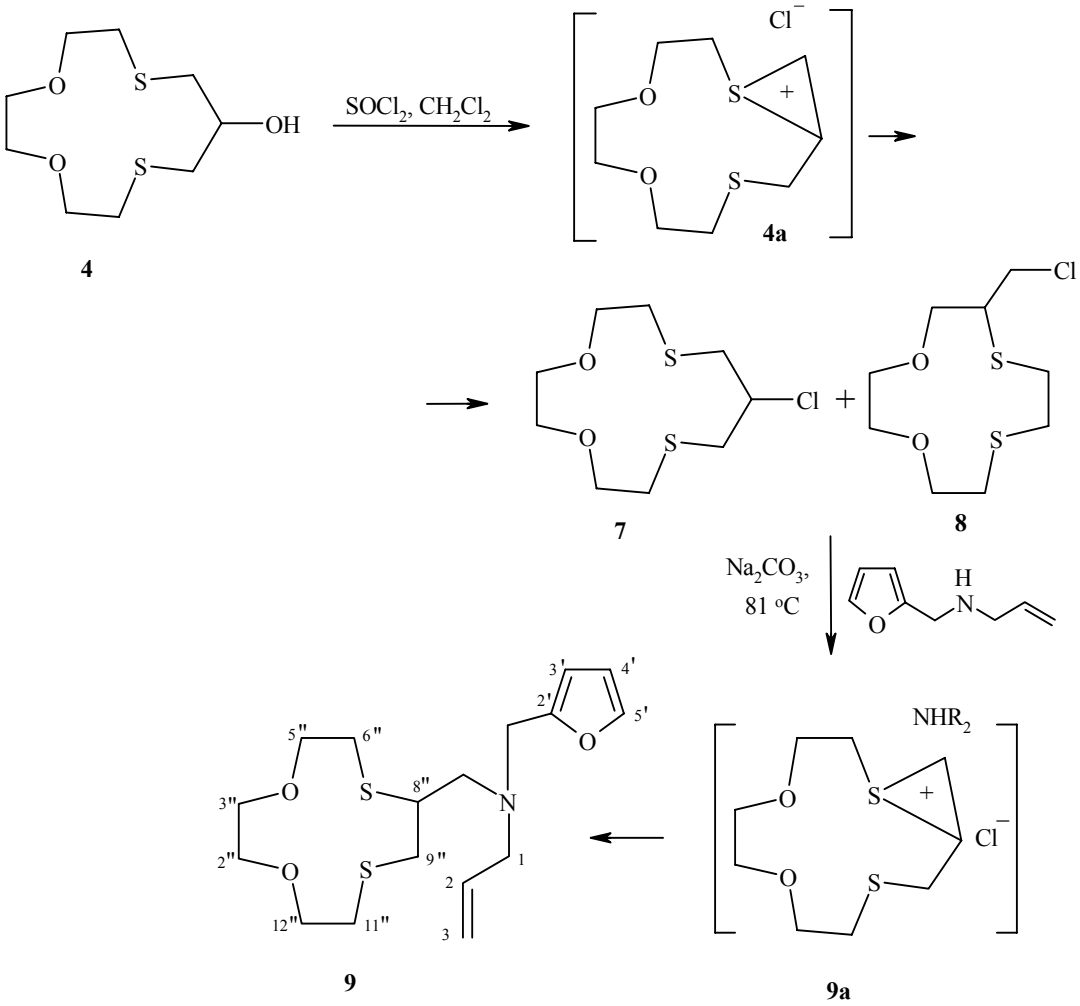


TABLE 1. ^{13}C NMR Spectra of the Synthesized Compounds

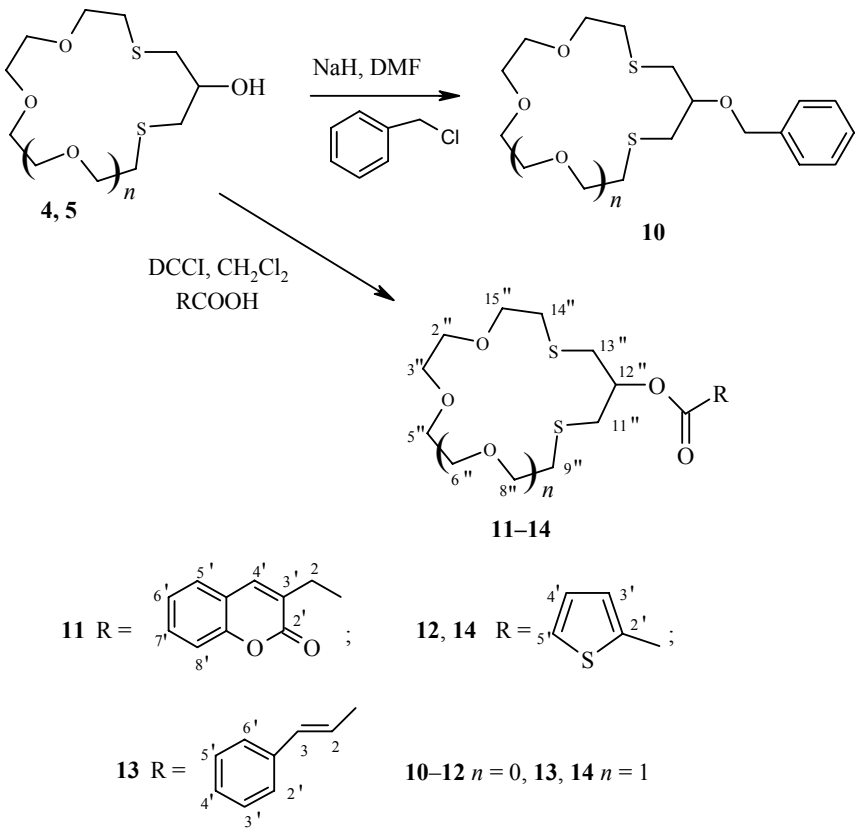
Compound	Chemical shifts, δ, ppm*					
	$\underline{C}H_2O$	$\underline{C}HO$	$S\underline{C}H_2CH_2O$	$CH\underline{C}H_2S$	$\underline{C}$=O	R
4	69.95; 72.62	71.29	32.91	39.71	—	—
5	70.06; 70.57; 72.51	69.80	31.33	38.69	—	—
7	70.09; 71.87	63.26	33.61	41.23	—	—
8	70.29; 70.48; 73.50; 74.35	46.33 ($CH_2\underline{C}HS$)	31.47; 35.93	47.41; 48.25 $CH\underline{C}H_2R$)	—	—
9	70.33; 70.42; 72.96; 73.82	44.59 ($CH_2\underline{C}HS$)	31.04; 35.91	37.56	—	44.59 (Fur$\underline{C}H_2$); 57.23, 57.36 ($C_{(13)}$, $C_{(1'')}$); 108.55, 109.88 ($C_{(3')}$, $C_{(4')}$); 117.47 ($C_{(3'')}$); 135.77 ($C_{(2'')}$); 141.65 ($C_{(5')}$); 152.47 ($C_{(2')}$)
10	70.26; 71.61	72.46	33.44	37.59	—	79.23 ($\underline{C}H_2$–C_6H_5); 127.49 (*p*-C_6H_5); 127.95, 128.20 (*o*-, *m*-C_6H_5); 138.55 (*ipso*-C_6H_5)
11	70.09; 71.56	74.77	33.22	36.29	169.81	116.46 ($C_{(8')}$); 119.14, 122.56 ($C_{(3')}$, $C_{(4a')}$); 124.34, 127.61, 131.19 ($C_{(5')}$, $C_{(6')}$, $C_{(7')}$); 141.43 ($C_{(4')}$); 153.42 ($C_{(8a')}$); 161.18 ($C_{(2')}$)
12	70.90; 73.21	75.00	33.24	37.05	162.15	128.73 ($C_{(4')}$); 133.48, 134.00 ($C_{(3')}$, $C_{(5')}$); 135.05 ($C_{(2')}$)
13	71.55; 72.06; 74.61	72.10	31.98	36.93	167.21	119.64 ($C_{(2')}$); 129.61, 130.33 (*o*-, *m*-C_6H_5); 131.70 (*p*-C_6H_5); 135.92 (*ipso*-C_6H_5); 146.06 ($C_{(3)}$)
14	71.16; 71.66 74.40	72.56	31.50	36.52	162.31	128.98 ($C_{(4')}$); 134.00, 134.45 ($C_{(3')}$,$C_{(5')}$); 134.92 ($C_{(2')}$)

* Spectra were taken in $CDCl_3$ (compounds **4**, **5**, **7-11**) and in acetone-d_6 (compounds **12-14**).

Nucleophilic substitution of the secondary hydroxyl group in alcohol **4** by chlorine was carried out using thionyl chloride in methylene chloride at room temperature. Data of ^{1}H and ^{13}C NMR spectra of the compound obtained indicated the presence of two isomers **7** and **8**, the separation of which by adsorption chromatography was unsuccessful due to the close R_f values. Nucleophilic substitution in compound **4** occurs through the formation of an episulfonium ion (Appel reaction) due to the anchimeric cooperation of the sulfur atom located in the position β to the reaction center in accordance with an S_Ni mechanism [12]. Probably the presence of a contacting ion pair in **4a,** and consequently the absence of complete dissociation of the S–Cl bond, hinders the directed formation in methylene chloride of only the rearrangement product. This leads to the preparation of a mixture of the two isomers **7** and **8** in a ratio of 6:1, according to data of ^{13}C NMR spectra, with a predominance of the thermodynamically more stable isomer **7**. On boiling a mixture of the isomeric chlorides with various amines in acetonitrile reaction products are formed having the rearranged skeleton of macrocycle **8**. The dipolar aprotic solvent acetonitrile stabilizes the solvate-divided ion pair **9a** with the possible exchange of chloride anion by amine. For example, on carrying out the reaction with N-allyl-N-(2-furylmethyl)amine the N-(1,4-dioxa-7,10-dithiacyclododecan-8-ylmethyl)-N-(2-furylmethyl)prop-2-enylamine (**9**) (unsymmetrical product) was obtained in 98% yield.



Ether **10** was obtained in 37% yield from alcohol **4** and benzyl chloride in DMF in the presence of sodium hydride. Esters **11-14** were obtained by the interaction of compounds **4** and **5** with carboxylic acids in the presence of dicyclohexylcarbodiimide (DCCI).



The ^{1}H NMR spectra of oxathiacrown ethers **11-14** in the presence of Ag(I) and Pb(II) cations were analyzed to study the complex-forming ability of these compounds. The changes of proton chemical shift of compounds **11-14** on complex formation with these cations are given in Table 2.

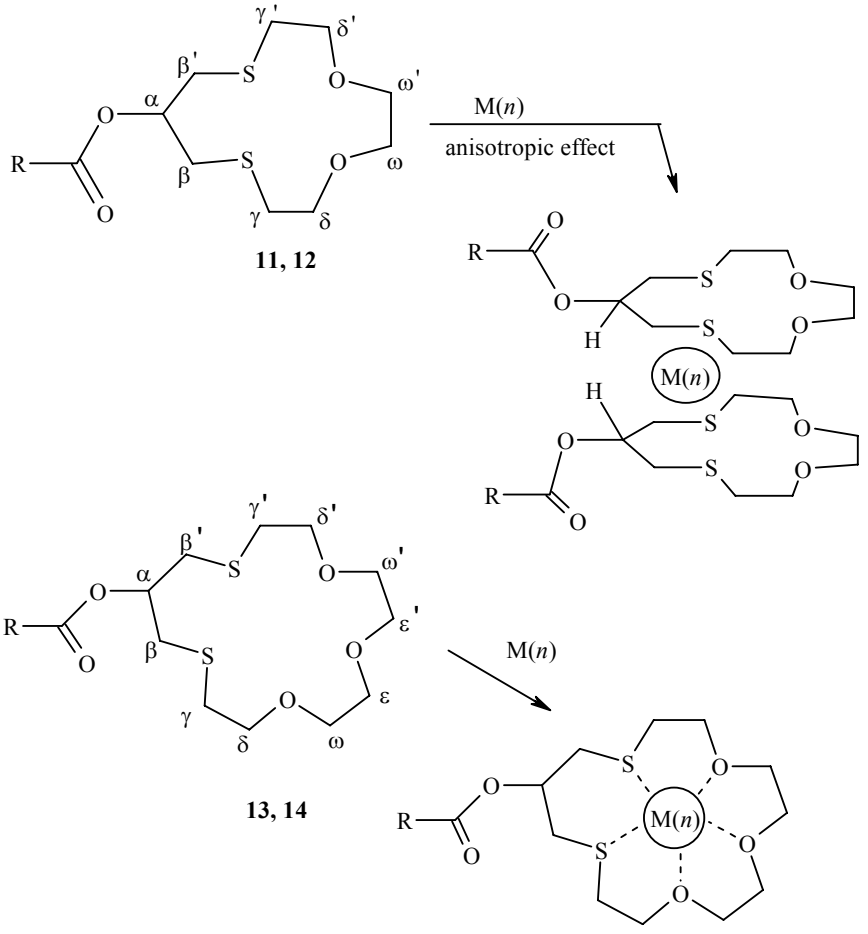
TABLE 2. Change of Proton Chemical Shifts (Δδ*) for Compounds **11-14** on Adding $AgClO_4$ and $Pb(ClO_4)_2$*[2]

Com-pound	Cation M	Δδ, ppm								
		H-α	H-β,β'	H-γ,γ'	H-δ,δ'	H-ω,ω'	H-ε,ε'	R		
11	Ag(I)	-0.23	0.19	0.10	0.00	0.02		0.03	0.02	0.00
	Pb(II)	-0.32	0.44	0.41, 0.65	0.34	0.04	—	0.04	0.03	0.03
12	Ag(I)	-0.15	0.09	0.12	0.06	0.00		0.01	0.02	0.01
	Pb(II)	-0.21	0.25	0.12, 0.23	0.18	0.18	—	0.02	0.04	— 0.06
13	Ag(I)	0.03	—	0.23	0.00	0.07	0.07	0.02	0.01	0.02
	Pb(II)	0.20	0.02, 0.38	0.4	0.33	0.36	0.36	0.02	0.04	0.00
14	Ag(I)	0.03	—	0.18	0.06	0.06	0.66	0.02	0.04	0.03
	Pb(II)	0.21	0.03, 0.39	1.39, 0.77	0.36	0.36	0.36	0.04	0.07	0.04

* $\Delta\delta = \delta_{compl} - \delta_{lig}$.

*[2] In CD_3CN solution, 25°C, $c_{lig} = 10^{-3}$ M; $c_{compl} = 10^{-3}$ M.

The most clearly expressed changes of the chemical shifts were for the protons at tertiary carbon atoms in the fragments of oxathiacrown compounds **11-14**. The shifts of the signals of the aromatic protons in the cinnamic acid derivative **13**, having no heteroaromatic atom free to coordinate a metal cation, and of the derivatives of thiophene **12** and **14**, and coumarin **11** were close in size. This indicates that the heterocyclic portion of the molecule does not take part in coordination with the metal cation. For complexes with silver cations the greatest changes were observed for the chemical shifts of protons of the methylene groups linked to sulfur atoms. For the complexes with lead cations the changes of position of the proton signals of the methylene groups linked both with sulfur atoms and with oxygen were close. Negative values of the proton shifts at tertiary carbon atoms of the crown ether enabled the suggestion that compounds **11** and **12** form sandwich structures on complex formation with composition two ligand to one metal cation. Evidently in the dimeric complex the α-protons are disposed close to the oxycarbonyl grouping, which may lead to an anisotropic effect and displacement towards high field. In the case of compounds containing the 16-crown-5 ether fragment **13** and **14** the size of the crown ether cavity enables the metal cation to be located within the cavity of the macrocycle and a complex of composition one ligand to one metal cation is formed.



M(*n*) = Ag(I), Pb(II)

To investigate the extracting ability of the synthesized 13-crown-4 ethers **4** and **10** we used the soft cations Ag(I) and Cd(II). Extraction was carried out from solutions of nitric acid and lithium picrate (LiPi) (Tables 3 and 4). From the data obtained it is seen that the macrocyclic compounds **4** and **10** preferentially extract the silver cation from picrate solutions. Unlike silver, cadmium is extracted poorly. The relatively small

TABLE 3. Distribution Coefficients of Cd(II)*

Extractant	*c* extractant, mol/l*[2]	Composition of aqueous phase		
		$c_{Cd(II)}$ = = 2.0×10^{-4} mol/l/ 3 mol/l HNO_3	3.84×10^{-3} mol/l LiPi	1×10^{-4} mol/l LiPi
4	3×10^{-3}	3.0×10^{-2}	4.0×10^{-3}	4.0×10^{-3}
10	1.1×10^{-3}	6.0×10^{-3}	5.0×10^{-3}	3.0×10^{-3}

* $c_{Cd(II)} = 10^{-5}$ to 10^{-4} M.
*[2] Measured in CH_2Cl_2 (compound **4**) and $CHCl_3$ (compound **10**).

TABLE 4. Distribution Coefficients of Ag(I)*

Extractant	*c* extractant, mol/l*[2]	Composition of aqueous phase		
		$c_{Ag(I)} = 1.0 \times 10^{-3}$ mol/l / 3 mol/l HNO_3	$c_{Ag(I)} = 2.0 \times 10^{-4}$ mol/l / 3 mol/l HNO_3	3.84×10^{-3} mol/l LiPi
4	3.0×10^{-3}	4.3×10^{-2}	6.0×10^{-2}	3.0×10^{-2}
10	1.1×10^{-3}	4.5×10^{-1}	3.3×10^{-1}	1.0×10^{-1}

* $c_{Ag(I)} = 10^{-5}$ to 10^{-3} M.
*[2] Measured in CH_2Cl_2 (compound **4**) and $CHCl_3$ (compound **10**).

values for the distribution coefficients for extractants **4** and **10** is probably linked both with the electron-withdrawing properties of the OCH_2Ph group and with the reduction of the effective charge in the cavity of the macrocycle in compound **10**, and also with the inability of the Cd(II) ion with a filled 4d sublevel to chemically interact additionally.

In the present work methods have therefore been demonstrated for the conversion of a hydroxyl group in oxathia-13(16)-crown-4(5) ethers. In particular, the possibility has been shown of selectively oxidizing the hydroxyl group in the oxathiacrown ethers without affecting the skeleton of the macrocycle. An assessment has been carried out of the extracting and complex-forming abilities of certain of the derivatives obtained.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian XR 400 (400 MHz) spectrometer. Solutions (25%) of samples in $CDCl_3$, acetone-d_6, or CD_3CN were used, internal standard was HMDS (δ 0.05 ppm). The ^{13}C NMR spectra for 30-50% solutions in deuterium-containing solvents were recorded on a Varian XR 400 (100 MHz) spectrometer. Measurement of ^{1}H chemical shift (Δδ) was recorded in CD_3CN after adding metal salts to the crown ether in a 1:1 ratio. The mass spectra were obtained on a Finnigan MAT 112S instrument in electron impact mode, energy of ionizing electrons was 70 eV.

Preparation of 1,4-Dioxa-7,11-dithiacyclotridecan-9-ol (4) and 1,4,7-Trioxa-10,14-dithiacyclohexadecan-12-ol (5) (General Procedure). Solutions of dibromide **1** (2.12 g, 10 mmol) and dithiol **2** or **3** (2.26 g, 10 mmol) in ethanol (50 ml) were added simultaneously with stirring to a boiling solution of cesium carbonate (3.57 g, 11 mmol) in 1:1 aqueous alcohol (500 ml). The reaction mixture was refluxed for 50 h, evaporated, and dilute HCl solution added to the residue to pH 7. The mixture was then extracted with ethyl acetate. The extract was dried over $CaCl_2$, evaporated, and the residue chromatographed on a column (silica gel, eluent EtOAc–hexane, 3:2).

Compound 4. Yield 67%; mp 64-65°C. Mass spectrum, found: *m/z* 238.3687 $[M]^+$. $C_9H_{19}O_3S_2$. Calculated: M 238.3694; *m/z* (I_{rel}, %): 238 (52) $[M]^+$, 220 (6), 194 (3), 161 (7), 122 (8), 103 (44), 75 (100), 61 (30), 45 (35). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.79-2.89 (8H, m, H-6, 8, 10, 12); 3.57-3.81 (9H, m, H-2, 3, 5, 13, OH); 4.08 (1H, m, H-9).

Compound 5. Yield 58%. Mass spectrum, found: *m/z* 282.4218 $[M]^+$. $C_{11}H_{22}O_4S_2$. Calculated: M 282.4220; *m/z* (I_{rel}, %): 282 (44) $[M]^+$, 264 (9), 191 (6), 130 (9), 103 (52), 75 (100), 45 (56). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.71-3.25 (8H, m, H-9, 11, 13, 15); 3.7 (8H, m, H-2, 3, 5, 6); 3.75-3.89 (4H, m, H-8, 16); 4.08 (1H, m, H-12).

1,4-Dioxa-7,11-dithiacyclotridecan-9-one (6). A solution of oxalyl chloride (0.064 g, 0.504 mmol) in dry dichloromethane (5 ml) was cooled to -70°C in a stream of argon. A mixture of DMSO (0.085 g, 1.092 mmol) in dichloromethane (5 ml) was slowly added dropwise while stirring the mixture at -70°C. A solution of alcohol **4** (0.100 g, 0.42 mmol) in dichloromethane (2 ml) (at < -60°C) was then added dropwise, and the mixture stirred at -70°C for 30 min. Triethylamine (0.212 g, 2.1 mmol) was added such that the temperature did not rise above -60°C. The temperature of the reaction mixture was then raised to room temperature and water (10 ml) was added with stirring. The aqueous solution was extracted with two portions of dichloromethane. The organic phase was dried over Na_2SO_4. The solvent was distilled in vacuum, and the residue chromatographed on silica gel, eluting with EtOAc–hexane, 1:4. A colorless oil (0.040 g) was isolated. Mass spectrum, found: *m/z* 236.3540 $[M]^+$. $C_9H_{16}O_3S_2$. Calculated: M 236.3535; *m/z* (I_{rel}, %): 236 (87) $[M]^+$, 192 (5), 174 (18), 148 (11), 146 (11), 120 (22), 115 (38), 75 (48), 61 (88), 45 (100). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.72 (4H, m, H-6, 12); 3.52 (4H, s, H-8, 10); 3.68-3.74 (8H, m, H-2, 3, 5, 13).

9-Chloro-1,4-dioxa-7,11-dithiacyclotridecane (7) and 6-Chloromethyl-1,4-dioxa-7,10-dithiacyclododecane (8). A solution of crown ether **4** (0.307 g, 1.29 mmol) in dichloromethane (5 ml) was added dropwise at room temperature to a solution of freshly distilled $SOCl_2$ (0.19 ml) in dry dichloromethane (10 ml). The reaction mixture was stirred for 6 h, then methanol (1 ml) was added. The solvent was distilled off, and the residue chromatographed on silica gel, eluting with acetone. A yellow oil (0.277 g) was isolated. The substance was a mixture of the isomeric chlorides **7** and **8**. Mass spectrum, *m/z* (I_{rel}, %): 256 (100) $[M]^+$, 220 (25), 196 (11), 161 (41), 135 (39), 99 (67), 61 (35), 45 (49). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.74-2.95 (2H, m, CH_2S); 3.61-4.08 (2H, m, CH_2O); 4.64 (1H, m, $CH_2C\underline{H}ClCH_2$).

N-(1,4-Dioxa-7,10-dithiacyclododecan-8-ylmethyl)-N-(2-furylmethyl)prop-2-enylamine (9). A solution of the mixture (0.180 g, 0.73 mmol) of the two isomeric chlorides **7** and **8** in dry acetonitrile (5 ml) was added to a solution of allylfurylamine (0.096 g, 0.73 mmol) in acetonitrile (10 ml), and Na_2CO_3 (0.116 g, 0.73 mmol) was added. The reaction mixture was boiled for 2 days, the solvent evaporated, and the residue purified by chromatography (silica gel, eluting with $CHCl_3$–CH_3OH, 10:1). A yellow oil (0.234 g) was isolated. Mass spectrum, found: *m/z* 357.5327 $[M]^+$; $C_{17}H_{27}NO_3S_2$; calculated: M 357.533; *m/z* (I_{rel}, %): 389 (23) $[M]^+$, 208 (4), 182 (100), 104 (9), 77 (11). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.50-2.81 (8H, m, H-6", 9", 11", NCH_2); 3.02 (1H, m, H-8"); 3.17 (2H, d, *J* = 6.3, H-1); 3.55-3.95 (10H, m, H-2", 3", 5", 12", $FurCH_2$); 5.10-5.24 (2H, m, H-3); 5.77-5.94 (1H, ddt, *J* = 17, 10.3, 6.3, H-2); 6.22, 6.29 (2H, 2 m, H-3', 4'); 7.34 (1H, m, H-5').

9-Benzyloxy-1,4-dioxa-7,11-dithiacyclotridecane (10). A solution of 13-crown-4 ether **4** (0.200 g, 0.84 mmol) in DMF (10 ml) was added slowly during 1 h to sodium hydride (0.024 g, (1 mmol) dispersed in DMF (15 ml) in an atmosphere of argon. Benzyl chloride (0.106 g, 0.84 mmol) was added dropwise to the reaction mixture, previously cooled to 0°C, then the mixture was stirred at room temperature for 4 h, and poured into water (50 ml). The aqueous phase was extracted with three portions of dichloromethane, and the extract dried over Na_2SO_4. The solvent was distilled off, and the residue chromatographed on silica gel, eluting with ethyl acetate–hexane, 1:3. A colorless oil (0.102 g) was isolated. Mass spectrum, found: *m/z* 328.5013 $[M]^+$; $C_{16}H_{24}O_3S_2$; calculated: M 328.4920; *m/z* (I_{rel}, %):328 (44) $[M]^+$, 255 (7), 220 (14), 161 (9), 103 (57), 91 (100), 75 (94), 45 (25). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.65, 2.78 (6H, 2m, H-6, 12, 8a, 10a); 2.89 (2H, dd, *J* = 13.6, *J* = 6.3, H-8b, 10b); 3.55-3.79 (8H, m, H-2, 3, 5, 13); 3.97 (1H, dd, *J* = 12.1, *J* = 6.0, H-9); 4.72 (2H, s, $C\underline{H}_2Ph$); 7.25 (1H, dd, *J* = 7.1, *p*-C_6H_5); 7.31 (2H, t, *J* = 7.1, *m*-C_6H_5); 7.41 (1H, d, *J* = 7.2, *o*-C_6H_5).

Preparation of 1,4-Dioxa-7,11-dithia-9-cyclotridecanyl 2-Oxo-3(2H)-chromenylacetate (11), 1,4-Dioxa-7,11-dithia-9-cyclotridecanyl Thiophene-2-carboxylate (12), 1,4,7-Trioxa-10,14-dithia-12-cyclohexadecanyl (2*E*)-3-Phenylacrylate (13), 1,4,7-Trioxa-10,14-dithia-12-cyclohexadecanyl Thiophene-2-carboxylate (14) (General Procedure). Dicyclohexylcarbodiimide (0.173 g, 0.84 mmol), N,N-dimethylaminopyridine (0.012 g, 0.01 mmol), and the appropriate acid (0.084 mmol) were added sequentially to a solution of compound **4** or **5** (0.84 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred for 2 h, EtOAc (10 ml) was added, and the dicyclohexylurea was filtered off. The filtrate was washed sequentially with dilute acetic acid, water, 5% sodium carbonate solution, and dried over Na_2SO_4. The solvent was distilled off, and the residue chromatographed on silica gel eluting with EtOAc–hexane, 1:4.

Compound 11. Yield 42%. Mass spectrum, found: *m/z* 424.5325 $[M]^+$; $C_{20}H_{24}O_6S_2$; calculated: M 424.5330; *m/z* (I_{rel}, %): 424 (47) $[M]^+$, 353 (2), 308 (3), 220 (73), 159 (100), 132 (44), 99 (88), 73 (51), 45 (55). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.60-2.76 (6H, m, H-8a", 10a", 6", 12"); 2.93 (1H, dd, *J* = 14.2, *J* = 4.0, H-8b", 10b"); 3.63 (2H, s, H-2); 3.68-3.82 (8H, m, H-2", 3", 5", 13"); 5.48 (1H, br. s, H-9"); 7.28, 7.47 (4H, 2m, H-5', 6', 7', 8'); 7.78 (1H, s, H-4').

Compound 12. Yield 68%. Mass spectrum, found: *m/z* 348.5014 $[M]^+$; $C_{14}H_{20}O_4S_3$; calculated: M 348.5042; *m/z* (I_{rel}, %): 348 (3) $[M]^+$, 272 (2), 220 (15), 161 (20), 150 (74), 111 (100), 103 (60), 82 (74), 61 (42), 41 (43). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.76 (6H, m, H-8a", 10a", 6", 12"); 3.05 (2H, dd, *J* = 14.4, *J* = 4.2, H-8b", 10b"); 3.65, 3.79 (8H, 2 m, H-2", 3", 5", 13"); 5.70 (1H, tt, *J* = 8.9, *J* = 4.2, H-9"); 7.20 (1H, m, H-4'); 7.80 (2H, m, H-3', 5').

Compound 13. Yield 85%. Mass spectrum, found: *m/z* 412.5655 $[M]^+$; $C_{20}H_{28}O_5S_2$; calculated: M 412.5653; *m/z* (I_{rel}, %): 412 (2) $[M]^+$, 264 (38), 205 (14), 148 (18), 131 (79), 117 (72), 104 (58), 103 (100), 89 (48), 72 (49), 61 (60), 56 (42). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.58, 2.86 (6H, 2m, H-9', 11a', 13a', 14'); 3.28 (2H, dd, *J* = 14.0, *J* = 3.9, H-11b', 13b'); 3.60 (8H, m, H-2', 3', 5', 6'); 3.75, 3.81 (4H, 2m, H-8', 16'); 5.36 (1H, tt, *J* = 8.1, *J* = 4.0, H-12'); 6.55 (2H, d, *J* = 16, H-2); 7.42, 7.70 (6H, 2m, *o*-, *m*-, *p*-C_6H_5, H-3).

Compound 14. Yield 65%. Mass spectrum, found: *m/z* 392.5572 $[M]^+$. $C_{16}H_{24}O_5S_3$; calculated: M 392.5568; *m/z* (I_{rel}, %): 392 (14) $[M]^+$, 264 (20), 205 (7), 130 (23), 111 (100), 103 (52), 89 (17), 73 (22), 61 (23), 45 (43). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.54-3.02 (6H, m, H-11a", 13a", 9", 15"); 3.31 (2H, dd, *J* = 14.4, *J* = 4.0, H-11b", 13b"); 3.6 (8H, m, H-2", 3", 5", 6"); 3.68-3.87 (4H, m, H-8", 6"); 5.42 (1H, tt, *J* = 8.06, *J* = 3.91, H-12"); 7.19 (1H, m, H-4'); 7.81 (2H, m, H-3', 5').

Extraction of Ag(I) and Cd(II) Cations. Determination of the distribution coefficients of Cd(II) and Ag(I) was carried out by radiometry on a "Treugolnik" γ scintillation counter with a solid crystalline NaY scintillation detector with Tl (activator). Isotopes used were ^{110m}Ag ($T_{1/2}$ = 270 days) and ^{115m}Cd ($T_{1/2}$ = 43.3 days). Samples for activity recording were stored for approximately 25 days from the time of preparation before starting counting.

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REFERENCES

1. Yu. A. Zolotov, A. A. Formanovskii, and I. V. Pletnev, *Macrocyclic Compounds in Analytical Chemistry* [in Russian], Nauka, Moscow (1993).
2. B. Valer, *Molecular Fluorescence: Principles and Applications*, Wiley-Interscience, New York (2001), p. 273.
3. M. Oue, K. Akama, K. Kimura, M. Tanaka, and T. Shono, *J. Chem. Soc., Perkin Trans. 1*, 1675 (1989).
4. S. Karabösek, K. Serbest, and N. E. M. Karabösek, *J. Heterocycl. Chem.*, **40**, 639 (2003).
5. N. R. Champness, D. W. Bruce, and M. Schwuder, *New J. Chem.*, **23**, 671 (1999).
6. V. Guyon, A. Guy, J. Toos, M. Zemaire, and M. Praye, *Tetrahedron Lett.*, **51**, 4065 (1995).

7. A. Yu. Nazarenko, V. N. Kalinin, P. I. Mikhalyuk, V. V. Sukhan, and V. M. Timoshenko, *Zh. Neorg. Khim.*, **38**, 1580 (1999).
8. J. S. Bradshaw, K. E. Krakowiak, and R. M. Izatt, *J. Heterocycl. Chem.*, **27**, 347 (1990).
9. N. Dann, A. Chies, and B. Gates, *J. Org. Chem.*, **26**, 1991 (1961).
10. H.-J. Liu, H.-K. Hune, G. L. Mhele, and D. Weinbera, *Can. J. Chem.*, **56**, 1368 (1978).
11. L. Titsay and T. Aikher, *Preparative Organic Chemistry* [Russian translation], Mir, Moscow (1999), p. 118.
12. P. Comba, A. Fath, B. Nuber, and A. Peter, *J. Org. Chem.*, **62**, 8459 (1996).