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SYNTHESIS OF DICYCLOHEPTANO- AND DICYCLOOCTANOTHIACROWN ETHERS THEIR PROPERTIES AS EXTRACTANTS

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12- and 15-Membered thia- and oxathiacrown ethers and podands containing cycloheptane and cyclooctane fragments have been synthesized. The properties of the synthesized compounds as extractants for Ra^{2+} and Pd^{2+} ions have been studied.

Keywords: oxathiacrown compounds, thiacrown compounds, thiacrown ethers, extraction.

The intensive development of the chemistry of crown ethers and their heteroanalogs has led to the creation of a large number of macrocycles which possess powerful complexing properties, which are increased by the such electron donating units as aliphatic or cycloaliphatic fragments [1]. For example, the previously prepared thiacrowns containing cyclohexane units are excellent extracting agents for Pb(II) and Ag(I) ions, which indicates a potential use for this type of macroligand [3].

In the present work thiacrown compounds containing cycloheptane and cyclooctane fragments have been synthesized from the corresponding β,β'-dichlorodicycloalkyl sulfides, which in turn were prepared by the addition of sulfur dichloride to cycloalkenes [4].

The dichloro sulfides **1** and **2** were obtained in 75 and 85% yields respectively by the reaction of cycloheptene and cyclooctene with sulfur dichloride in a molar ratio of cycloalkene–SCl_2 of 2:1 in methylene chloride at -40°C.

In the ^{13}C NMR spectrum of compound **1** the signal of each carbon atom appears as a doublet, which indicates that, as in the case of the reaction of cyclohexene with SCl_2, two diastereoisomeric bis(2-chlorocycloheptyl) sulfides **1a** and **1b** were formed in the ratio of ~1:1.

The ^{13}C NMR spectrum of the sulfide **2** also indicates that the two stereoisomers **2a** and **2b** were formed in the reaction of cyclooctene with SCl_2. The uniformity of the reaction of sulfur dichloride with cycloalkenes and the values of the coupling constants in the ^1H NMR spectrum for the protons of the –CHCl– and –CHS– fragments (J = 9.22 and 8.13 Hz respectively) provides the basis for the conclusion that the substituents in the dichlorosulfides **1** and **2** (Cl and S), as in the dichlorodicyclohexyl sulfides [2], are in *trans*-diequatorial positions.

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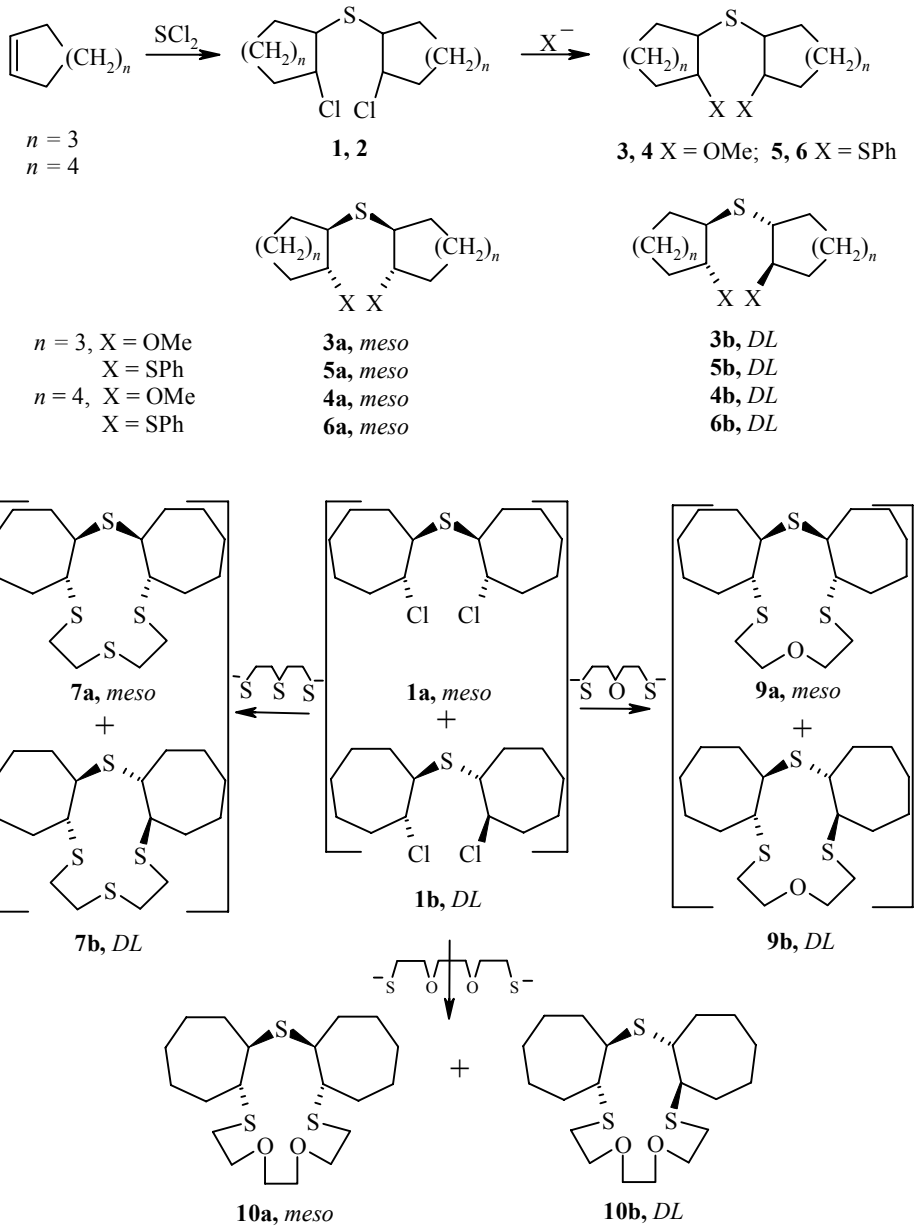
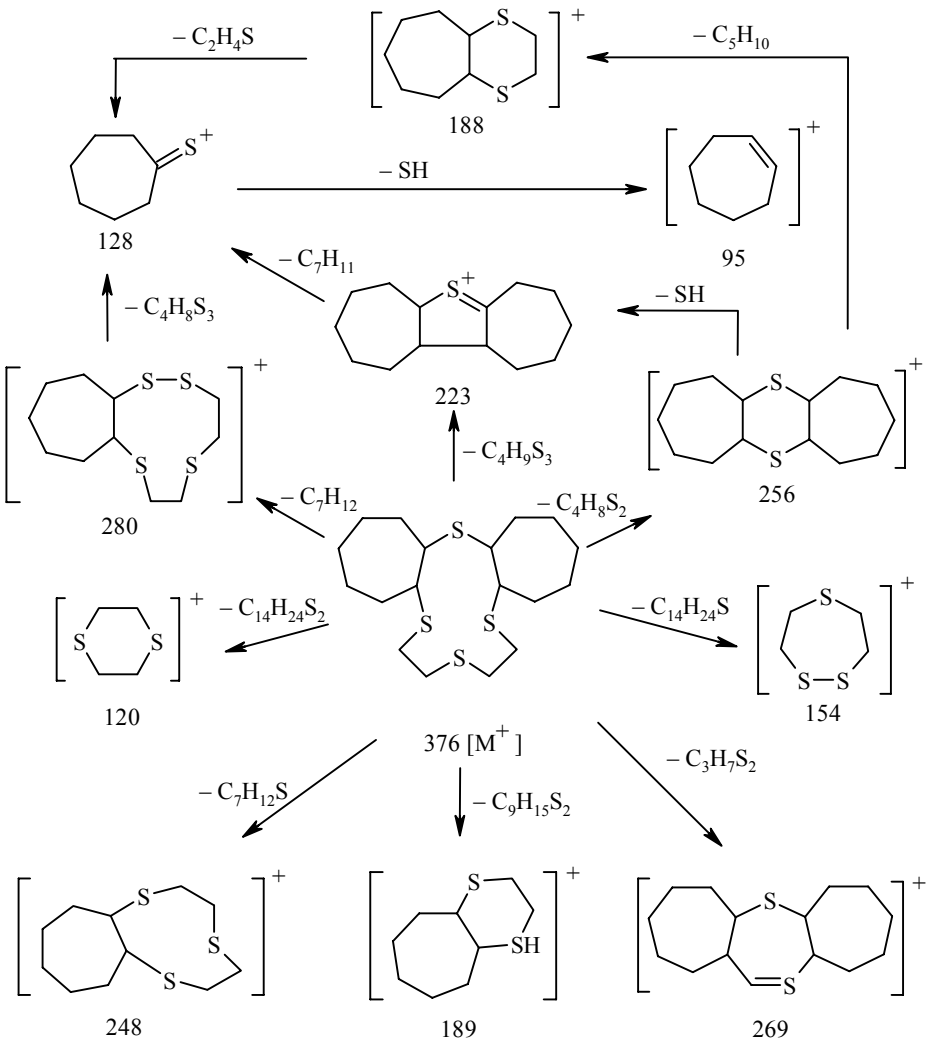


Considering that the stereochemical results of the reaction of dichlorodicycloalkyl sulfides with binucleophiles (dithiols and glycols) and mononucleophiles could be the same, in the first stage we investigated the reactions of the dichloro sulfides **1** and **2** with sodium methoxide and sodium thiophenoxide. Furthermore, introduction into the molecules of the dichloro sulfides **1** and **2** of such nucleophilic centers as methoxy and thiophenoxy with very different flexibility provided the possibility of forming the podands **3-6**, which, like the macrocycles, can form complexes with metals.

According to the NMR spectroscopic results a mixture of two diastereoisomeric dimethoxy- and diphenylthio-substituted compounds **3-6** in a 1:1 ratio was formed by the interaction of the dichloro sulfides **1** and **2** with sodium methoxide and thiophenoxide, just as was observed with the corresponding cyclohexane derivatives [2, 5].

The reaction of bis(2-chlorocycloheptyl) sulfide (**1**) with 2,2'-dimercaptodiethyl sulfide was carried out in ethanol under high dilution conditions.

The mass spectrum of the compound isolated, show to be pure by TLC, showed a molecular ion* (376) which corresponded to the molecular mass of 5,6,8,9-dicycloheptano-1,4,7,10-tetrathiacyclododecane (**7**). The mass spectrum also contains peaks at 280, 269, 256, 248, 223, 189, 188, 154, 128, 120, and 95 which can be interpreted by the following mass spectroscopic decomposition scheme:

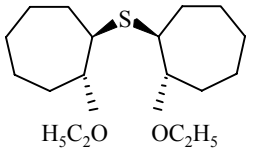


The presence of these ions in the mass spectrum of the macrocyclic compound obtained indicates that the product of the reaction of dichlorosulfide **1** with 2,2'-dimercaptodiethyl sulfide is indeed compound **7**.

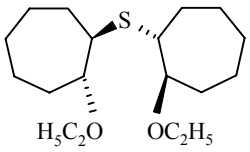
All the signals of the carbon atoms in the ^{13}C NMR spectrum of thiacrown **7** appear as doublets with an intensity ratio (~1:1) corresponding to that of the initial sulfur dichloride **1**. From this and the fact that nucleophilic substitution in dichlorodicyclohexyl sulfide occurs with retention of configuration at the atom attacked [4], it may be concluded that the thiacrown **7** is a mixture of two stereoisomers, **7a** and **7b**.

Bis(2-ethoxycycloheptyl) sulfide (**8**) is formed along with thiacrown **7** as a by-product when the reaction is carried out in ethanol. Compound **8** is also a mixture of two stereoisomers to judge from its ^{13}C NMR spectrum in which the signal for each carbon atom appears as a doublet. The identity of the ^{1}H and ^{13}C NMR signals for the diethoxy derivative **8** and bis(2-methoxycycloheptyl) sulfide **3** provides a basis for the conclusion that mixture of the diastereoisomers **8a** and **8b** has been formed:

* Here and below values of *m/z* are given for the ion peaks.



8a



8b

The structure of compound was confirmed by the presence of the molecular ion peak (313) in its mass spectrum.

We also used the template method for the synthesis of the thiacrown ether **7** using cesium carbonate in DMF. This method permits the synthesis of macrocycles in sufficiently high yield (up to 90%) [8-10], but in this case the yield of thiacrown **7** only reached 28%, which was lower than using the high dilution technique (40%). Therefore we used the traditional method of macrocyclization in ethanol solution for the synthesis of the other twelve-membered thiacrowns.

The reaction of the dichloro sulfide **1** with 2,2'-dimercaptodiethyl ether was carried under conditions analogous to those for the synthesis of thiacrown **7**. Mass spectroscopic data (molecular ion peak at 360 and a fragmentation pattern consistent with the structure) and the ^{13}C NMR spectrum indicated that the main product of the reaction was 5,6,8,9-dicycloheptano-1-oxa-4,7,10-trithiacyclododecane (**9**). As was the case with thiacrown **7**, the signals of all of the carbon atoms appeared as doublets with intensity ratios (~1:1) corresponding to those of the dichlorosulfide **1**. This gave the basis for the conclusion that the oxathiacrown **9**, just like the thiacrown **7**, can be formed as a mixture of the two diastereoisomers **9a** and **9b** with configurations corresponding to those of the stereoisomers of thiacrown **7**.

TABLE 1. Distribution Coefficients of Radium(II) and Palladium (II) in the Presence of Picrate (D_1) and Nitrate Ions (D_2) with Macrocyclic and Open Chain*

Ion extracted	Extractant, S	c_S, mol/l	Solvent	D_1 (Counter ion Pic^-)*[2]	D_2 (Counter ion NO_3^-)*[3]
Ra^{2+}	**3**	1.0×10^{-2}	$CHCl_3$	0.1000	0.0180
	5	3.4×10^{-3}	$CHCl_3$	0.1300	0.0080
	7	7.1×10^{-3}	$CHCl_3$	0.0065	0.0670
	9	4.2×10^{-3}	$CHCl_3$	0.0090	0.0700
	DB-24-C-8	5.0×10^{-3}	$CHCl_3$	0.1400	0.0770
Pd^{2+}	**7**	5.0×10^{-3}	$CHCl_3$	—	1.5100
	7	5.0×10^{-3}	CH_2ClCH_2Cl	18.6000	16.6000
	10	5.0×10^{-3}	$CHCl_3$	—	2.0000
	10	5.0×10^{-3}	CH_2ClCH_2Cl	4.8000	2.4000
	18-C-6	1.0×10^{-2}	CH_2ClCH_2Cl	0.0680	0.0900
	15-C-5	1.0×10^{-2}	CH_2ClCH_2Cl	0.0170	0.2200

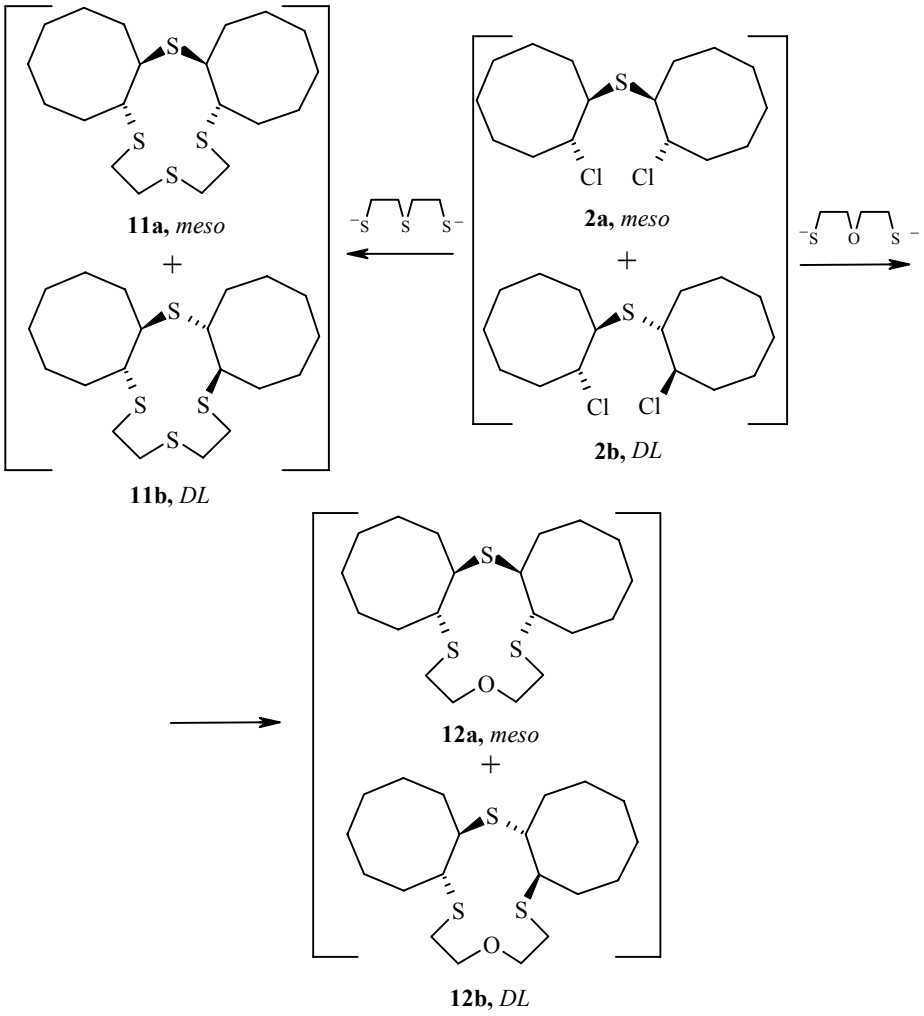
* The distribution coefficients for the extraction of palladium from aqueous solution into chloroethane with thiacrowns **7** and **9** in the presence of ClO_4^- (1M $LiClO_4$) as counterion were 5.00 and 5.85 respectively.

*[2] $c_{LiPic} = 10^{-2}$ mol/l.

*[3] $c_{HNO_3} = 3$ mol/l.

2,2'-Dichlorodicycloheptyl sulfide (**1**) was also used to obtain the 15-membered oxathiacrown 8,9,11,12-dicycloheptano-1,4-dioxa-7,10,13-trithiacyclopentadecane (**10**) by reaction with 1,8-dimercapto-3,6-dioxaoctane. The reaction was carried out by the template method using a suspension of Cs_2CO_3 in DMF. According to published results [8-10], the maximum yields with this method were achieved in the synthesis of fifteen membered thiamacrocycles. The spectroscopic results for this compound (a molecular ion peak at 404 in the mass spectrum) and the character of the ^{13}C NMR spectrum (the signal for each carbon atom appeared as a doublet) indicated the possibility of the formation of a mixture of two diastereoisomers **10a** and **10b** in approximately equal amounts.

The reactions of bis(2-chlorocyclooctyl) sulfide (**2**) with 2,2'-dimercaptodiethyl sulfide and 2,2'-dimercaptodiethyl ether were carried out under conditions analogous to those with the dichloro sulfide **1**. As in the case with the sulfide **1**, the mass spectroscopic data (general agreement of the fractionation pattern with those for compounds **7** and **9**) and the ^{13}C NMR spectra (signals of all carbon atoms were doublets) indicate that the products of the reaction in each case are a pair of diastereoisomers (compounds **11a** and **11b**, and **12a** and **12b** respectively):



So the interaction of dichlorodicycloalkyl sulfides **1** and **2** with dithiols gave mixtures of the corresponding diastereoisomers of thia- and oxathiacrown compounds in yields of 35-40% (compounds **7**, **9**, **11**, **12**) and 61% (**10**) in ratios of ~1:1, which agrees well with results obtained previously for cyclohexane derivatives [2, 5].

Radium and palladium ions and the use of a radiometric method of control were chosen to estimate the extraction properties and to study the complex forming properties of some synthesized sulfur containing macrocycles and open chain compounds. The radium ion was chosen for the following reasons. Firstly, radium is a typical "hard" cation for which sulfur containing macrocycles appear to have negligible affinity, whereas excellent extraction results may be expected with the dimethoxy derivative **1** because it contains a "hard" oxygen atom. Secondly, the compounds synthesized in this work might be suitable for the separation of the mixture of radium and actinium isotopes formed as the result of decay of the thorium radioactive series.

DB-24-C-8 was used as the standard for the study of the extraction properties with respect to radium and 18-C-6 and 15-C-5 with respect to palladium. As the investigations showed, radium was extracted best by DB-24-C-8, which is explained by its large cavity in comparison with DCHT-12-thiacrown-4 (**7**) and DCHT-12O-1S3 (**9**) and the absence of "soft" sulfur atoms from its ring. It is interesting that the podands **3** and **5** show better extraction results in the presence of the picrate ion than the macroligands **7** and **9**. An estimate of the complexing abilities of DCHT-12-thiacrown-4 (**7**) and the oxathiacrown **10** with respect to Pd^{2+} ions was carried out. The results of our studies of the extraction of radium and palladium ions from aqueous solutions are shown in Table 1.

EXPERIMENTAL

^{1}H NMR spectra of 25% solutions in $CDCl_3$ with TMS as internal standard were recorded with a Varian VXR-400 (400 MHz) spectrometer. ^{13}C NMR spectra of 30-50% solutions in $CDCl_3$ or DMSO-d_6 were recorded with a WH-90 impulse spectrometer (90 MHz). ^{13}C chemical shifts were measured relative to TMS.

Chromato-mass spectrometric analysis was carried out with a Finnigan MAT-112S machine (electron impact, ionizing voltage 80 eV) with a glass capillary column (l = 30 m, d = 0.25 mm) with OV-101 as stationary phase, and temperature programming from 100 to 250°C at a rate of 5-15°/min, and with helium as the carrier gas.

Course of the reactions and purity of compounds were controlled by TLC on Silufol plates with various systems of eluents. Starting materials and products were isolated by preparative TLC with loose sorbent layers and by liquid column chromatography. Merck and L40/100 silica gels were used as absorbents. The eluents were chosen separately for each mixture to be analyzed.

Extraction of radium was carried out with ^{228}Ra ($T_{1/2}$ = 6.3 y, E_β-max = 0.053 meV). ^{228}Ra is in equilibrium with ^{228}Ac ($T_{1/2}$ = 6.13 h, E_β-max = 1 meV) and these isotopes were not separated during the experiment. Recording of the radium samples was carried after equilibrium between ^{228}Ra and ^{228}Ac had been established (2-3 d). ^{228}Ra, which is obtained as the result of natural decay of ^{232}Th ($T_{1/2}$ =$1.4\cdot10^{10}$ y), was separated from the parent nucleus by precipitation of thorium as peroxide with subsequent washing out of the radium from the precipitate with water [11]. Distribution coefficients of ^{228}Ra were determined with a Canberra-Packard 2700 liquid scintillation counter. Analysis of spectra of the ^{228}Ra–^{228}Ac couple showed that the spectra of the mother and daughter products did not overlap and that ^{228}Ra can be detected in the tritium channel (up to 18.6 keV) on account of the shift of the radium spectrum to this channel. ^{228}Ac and the other nuclides are counted basically at much higher energies. To confirm the correctness of this approach to recording and the choice of standard, we randomly checked the distribution coefficients from results obtained after equilibrium had been established between the pair of isotopes.

The distribution coefficients for palladium were also determined radiometrically using the radionuclide ^{103}Pd. The basic type of decay of ^{103}Pd is electron capture accompanied by characteristic X-rays which we also recorded with the Canberra-Packard 2700 liquid scintillation counter.

Cycloheptene was obtained by a known method [12], starting from suberone (Merck). **Cyclooctene** was obtained commercially (Merck). **2,2'-Dimercaptodiethyl sulfide** was obtained commercially (Aldrich).

Bis(2-chlorocycloheptyl) Sulfide (1). A solution of dry cycloheptene (10 g, 0.104 mol) in dry methylene chloride (50 ml) was cooled to -40°C and then a solution of freshly distilled (bp 56-58°C) sulfur dichloride in methylene chloride (20 ml) was added over 1 h with intense stirring. The reaction mixture was then stirred for a further hour at -40°C and for 4 h at room temperature. After removal of the solvent, the product, a mixture of crystals and a yellow sticky oil, was recrystallized four times at -70°C from a 1:1 mixture of diethyl ether and hexane to give a white crystalline substance, yield 12 g (75%); mp 67-67.5°C. ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 22.18, 22.28 (d, $C_{(5)}$); 24.38, 24.48 (d, $C_{(6)}$); 27.66, 27.80 (d, $C_{(4)}$); 30.56, 30.60 (d, $C_{(7)}$); 34.37, 34.44 (d, $C_{(3)}$); 54.03, 54.41 (d, $C_{(1)}$–CHS); 66.76, 67.08 (d, $C_{(2)}$–CHCl). Mass spectrum, *m/z* (I_{rel}, %): 294 [M^+] (2), 288 (60), 259 (2), 223 (12), 192 (50), 163 (3), 127 (20), 96 (15), 95 (100), 67 (30). Found, %: C 57.37; H 8.45; Cl 23.84; S 11.00. $C_{14}H_{24}Cl_2S$. Calculated, %: C 56.95; H 8.10; Cl 24.10; S 10.85.

Bis(2-chlorocyclooctyl) Sulfide (2) was obtained by a method analogous to sulfide **1** from cyclooctene (6 g, 0.054 mol) and sulfur dichloride (2.8 g, 0.027 mol) as a light yellow oil. Yield 7.4 g (85%). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 23.94, 24.48 (d, $C_{(6)}$); 25.55, 25.86 (d, $C_{(5)}$); 26.04, 26.73 (d, $C_{(7)}$); 29.10, 29.60 (d, $C_{(4)}$); 30.54, 31.12 (d, $C_{(8)}$); 32.40, 33.17 (d, $C_{(3)}$); 53.15, 54.60 (d, $C_{(1)}$–CHS); 67.48, 68.93 (d, $C_{(2)}$–CHCl). Mass spectrum, *m/z* (I_{rel}, %): 322 [M^+], 287 (1), 250 (1), 210 (1), 177 (12), 142 (10), 109 (53), 67 (100), 41 (75). Found, %: C 59.80; H 8.87; Cl 22.10; S 9.23. $C_{16}H_{28}Cl_2S$. Calculated, %: C 59.44; H 8.67; Cl 21.98; S 9.91.

Bis(2-methoxycycloheptyl) Sulfide (3). Sodium (0.16 g, 6.8 mmol) was dissolved in methanol (50 ml) and then a solution of **1** (1 g, 3.4 mmol) in hexane (20 ml) was added with stirring, after which the mixture was boiled for 5 h. The solvent was evaporated and a mixture of ether (50 ml) and water (50 ml) was added to the residue. The water layer was extracted twice with ether. The combined ether extracts were dried over $MgSO_4$. After removal of the ether the chromatographically pure product was obtained as light yellow oil. Yield 0.6 g (70%). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 21.92, 21.99 (d, $C_{(5)}$); 25.61, 25.64 (d, $C_{(6)}$); 29.03, 29.09 (d, $C_{(4)}$); 29.46, 29.47 (d, $C_{(7)}$); 31.07 (s, $C_{(3)}$); 49.96, 50.20 (d, $C_{(1)}$–CHS); 56.66, 56.78 (d, CH_3O); 85.77, 85.94 (d, $C_{(2)}$–CHO). Mass spectrum, *m/z* (I_{rel}, %): 286 [M^+] (1), 255 (1), 254 (6), 159 (2), 128 (8), 126 (100), 95 (80), 45 (81). Found, %: C 67.62; H 11.00; O 11.00; S 10.38. $C_{16}H_{30}O_2S$. Calculated, %: C 67.13; H 10.49; O 11.19; S 11.19.

Bis(2-methoxycyclooctyl) Sulfide (4) was made analogously to sulfide **3**. A solution of sulfide **2** (0.64g, 2 mmol) in hexane (20 ml) was added to a solution of sodium (1 g, 4 mmol) in methanol (50 ml). As a result an oily substance was isolated (yield 0.5 g, 80%). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 19.08, 19.12 (d, $C_{(6)}$); 22.04, 22.07 (d, $C_{(5)}$); 23.05, 23.11 (d, $C_{(7)}$); 25.87, 26.04 (d, $C_{(4)}$); 28.11, 28.16 (d, $C_{(8)}$); 29.30, 29.42 (d, $C_{(3)}$); 53.98, 54.23 (d, $C_{(1)}$–CHS); 56.47, 56.84 (d, CH_3O); 77.65, 78.02 (d, $C_{(2)}$–CHO). Mass spectrum, *m/z* (I_{rel}, %): 314 [M^+] (2), 283 (4), 234 (1), 217 (1), 171 (1), 169 (3), 149 (4), 142 (1), 141 (2), 138 (18), 109 (62), 67 (100), 43 (57), 41 (50). Found, %: C 69.32; H 11.11; O 9.57; S 10.00. $C_{18}H_{34}O_2S$. Calculated, %: C 68.79; H 10.83; O 10.19; S 10.19.

Bis(2-phenylthiocycloheptyl) Sulfide (5). Sodium (0.14 g, 6 mmol) was dissolved in ethanol (50 ml) and thiophenol (0.63 g, 6 mmol) was added. The reaction mixture was stirred with gentle heating for 3 h. Sulfide **1** (0.85 g, 3 mmol) in ether (15 ml) was added with stirring over 15 min. The reaction mixture was stirred with heating for a further 3 h and then for 5 h at room temperature. The reaction was carried out under an inert atmosphere. When the reaction had ended, most of the ethanol was evaporated, then ether (50 ml) and water (50 ml) were added to the residue, and the water layer was extracted twice with ether. The ether extracts were washed with alkali and then water. The ether extracts were then combined and dried over magnesium sulfate. After evaporation of the ether a yellow oil was obtained which was purified by passage of an ether solution through a layer of silica gel. Yield 1.16 g (87%). ^{13}C NMR spectrum, ($CDCl_3$, TMS), δ, ppm: 24.57, 24.99 (d, $C_{(4)}$); 25.43, 25.87 (d, $C_{(5)}$); 26.08, 26.19 (d, $C_{(6)}$); 34.65, 34.92 (d, $C_{(7)}$); 36.24, 37.32 (d, $C_{(3)}$); 52.97, 53.56 (d, $C_{(1)}$); 54.30, 55.12 (d, $C_{(2)}$); 125.12, 126.03 (d, $C_{(4\text{-}Ar)}$); 127.97, 128.79 (d, $C_{(3\text{-}Ar)}$); 129.42, 129.46 (d, $C_{(2\text{-}Ar)}$); 136.59, 137.05 (d, $C_{(1\text{-}Ar)}$). Mass spectrum, *m/z* (I_{rel}, %): 442 [M^+] (1), 332 (1), 269 (1), 254 (1), 237 (2), 223 (3), 205 (50), 145 (2), 123 (20), 95 (100) 45 (10). Found, %: C 71.20; H 8.58; S 20.22. $C_{26}H_{34}S_3$. Calculated, %: C 70.59; H 7.69; S 21.72.

Bis(2-phenylthiocyclooctyl) Sulfide (6) was prepared as for compound **5**. Sodium (0.14 g, 6 mmol) was dissolved in ethanol (50 ml), thiophenol (0.63 g, 6 mmol) was added to this solution, followed a solution of sulfide **2** (0.92 g, 3 mmol) in ether (10 ml). Yield 1.2 g (85%). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 23.20, 23.50 (d, $C_{(5)}$); 24.42, 24.80 (d, $C_{(6)}$); 26.20, 26.62 (d, $C_{(4)}$); 26.80, 27.12 (d, $C_{(7)}$); 34.88, 35.20 (d, $C_{(8)}$); 36.99, 37.60 (d, $C_{(3)}$); 55.22, 55.60 (d, $C_{(1)}$); 56.30, 56.98 (d, $C_{(2)}$); 125.12, 126.01 (d, $C_{(4\text{-Ar})}$); 127.93, 128.79 (d, $C_{(3\text{-Ar})}$); 129.42, 129.46 (d, $C_{(2\text{-Ar})}$); 136.20, 136.85 (d, $C_{(1\text{-Ar})}$). Mass spectrum, *m/z* (I_{rel}, %): 470 [M^+] (1), 436 (1), 434 (2), 393 (1), 359 (2), 326 (2), 252 (3), 249 (14), 219 (30), 141 (36), 109 (100), 67 (98), 45 (37). Found, %: C 72.24; H 8.22; S 19.54. $C_{28}H_{38}S_3$. Calculated, %: C 71.49; H 8.08; S 20.43.

2,2'-Dimercaptodiethyl Ether was prepared by a known method [6,7] from diethylene glycol *via* 2,2'-dibromodiethyl ether. 2,2'-Dibromodiethyl ether; bp 87-90°C (7 mm Hg). Yield 55.3 g (56%). 2,2'-Dimercaptodiethyl ether; bp 80-81°C (8 mm Hg). Yield 23 g (70%). Mass spectrum: M^+ 138.

1,8-Dimercapto-3,6-dioxaoctane was prepared analogously to 2,2'-dimercaptodiethyl ether, starting from triethyleneglycol.

1,8-Dibromo-3,6-dioxooctane. Pyridine (80 g) and commercial triethyleneglycol (90 g, 0.6 mol) were added to phosphorus tribromide (115.2 g, 0.4 mol). Yield 97.2 g (63%); bp 120-122°C (5 mm Hg). Thiourea (53.2 g, 0.7 mol) was added to solution of the dibromide (97.2 g, 0.35 mol) in ethanol (200 ml), followed by 40% aqueous KOH (120 ml). Yield 40.95 g (64.3 %); bp 117-119°C (2 mm Hg). Mass spectrum: M^+ 182.

5,6,8,9-Dicycloheptano-1,4,7,10-tetrathiacyclododecane (7). A. Sodium (0.46 g, 0.02 mol) was dissolved in ethanol (300 ml). 2,2'-Dimercaptodiethyl sulfide (1.54 g, 0.01 mol) was added under an atmosphere of argon. Then a solution of sulfide **1** (2.95 g, 0.01 mol) in ethanol (50 ml) was added to the reaction mixture over 10 h. The reaction mixture was stirred at 60°C for 5 h and then at 20°C for 3 h. The reaction mixture was cooled, filtered, the ethanol was evaporated, and ether and 20% NaOH were added to the residue. The ether layer was extracted with water and the water layer extracted with ether. The ether extract was dried and the ether evaporated. The residue was dissolved in a 1:8 mixture of ether and hexane and purified by preparative thin layer chromatography on silica gel. Yield 1.53 g (40%).

B. Finely divided cesium carbonate (3.9 g, 0.012 mol) was dispersed in DMF (200 ml) and dimercaptodiethyl sulfide (1.54 g, 0.01 mol) was added to the solution. The dichloro sulfide **1** (2.95 g, 0.01 mol) dissolved in DMF (50 ml) was then added over 15 h with gentle heating. At the end of the addition the mixture was stirred for a further 12 h. It was then filtered, most of the solvent was removed in vacuum, and water and ether added to the residue. The water layer was separated and washed twice with ether. The ether extracts were shaken with 20% sodium hydroxide solution (100 ml), then water, and dried over magnesium sulfate. The solvent was evaporated and the reaction product purified chromatographically (1:8 ether:hexane). Yield 1 g (28%). ^{13}C NMR spectrum (DMSO-d_6, TMS), δ, ppm: 21.57, 21.65, 24.60, 24.68, 24.77, 24.90, 30.58, 30.73, 33.80, 33.89 (d, d, d, d, d - carbon atoms of the cycloheptane ring); 39.27, 38.99 (d, $C_{(3)}$ and $C_{(11)}$); 39.54, 39.82 (d, $C_{(2)}$ and $C_{(12)}$); 49.57, 49.68 (d, $C_{(6)}$ and $C_{(8)}$); 52.46, 52.58 (d, $C_{(5)}$ and $C_{(9)}$). Mass spectrum, *m/z* (I_{rel}, %): 376 [M^+] (6), 269 (2), 280 (1), 256 (5), 248 (8), 223 (1), 189 (7), 188 (7), 154 (12), 128 (21), 120 (10), 95 (100), 67 (45), 41 (43). Found, %: C 58.04; H 8.09; S 33.87. $C_{18}H_{32}S_4$. Calculated, %: C 57.45; H 8.51; S 34.04.

Bis(2-ethoxycycloheptyl) Sulfide (8). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 15.68, 15.71 (d, CH_3); 22.23, 22.25 (d, CH_2O); 25.33, 25.40, 29.01, 29.12, 30.25, 30.36, 31.19, 31.30 (d, d, d, d - carbon atoms of the cycloheptane ring); 50.40, 50.77 (d, $C_{(1)}$–CHS); 64.35, 64.45 (d, $C_{(8)}$–CH_2O); 84.03, 84.21 (d, $C_{(2)}$–CHO). Mass spectrum, *m/z* (I_{rel}, %): 313 [M^+] (1), 269 (1), 253 (1), 207 (1), 190 (3), 161 (1), 159 (1), 128 (3), 113 (24), 95 (100), 59 (51), 43 (22). Found, %: C 69.00; H 10.45; O 10.53; S 10.02. $C_{18}H_{34}O_2S$. Calculated, %: C 68.79; H 10.83; O 10.19; S 10.19.

5,6,8,9-Dicycloheptano-1-oxa-4,7,10-trithiacyclododecane (9) was synthesized as for **7** by method A. Sodium (0.46 g, 0.02 mol) was dissolved with stirring in ethanol (300 ml), 2,2'-dimercaptodiethyl ether (1.38 g, 0.01 mol) was added to the solution, and then the dichloro sulfide **1** (2.95 g, 0.01 mol) in ethanol (50 ml) was added over 10 h. After removal of the ethanol and ether, the residue was purified on silica gel (1:8 ether–hexane).

Yield 1.33 g (38%). ^{13}C NMR spectrum (DMSO-d_6, TMS), δ, ppm: 22.02, 22.13, 26.32, 26.73, 27.01, 27.07, 39.21, 39.49, 40.32, 40.66 (d, d, d, d, d - carbon atoms of the cycloheptane ring); 29.61, 29.68 (d, $C_{(3)}$, $C_{(11)}$); 61.42, 61.49 (d, $C_{(6)}$, $C_{(8)}$); 63.45, 63.47 (d, $C_{(5)}$, $C_{(9)}$); 73.48, 73.66 (d, $C_{(2)}$, $C_{(12)}$). Mass spectrum, *m/z* (I_{rel}, %): 360 [M^+] (1), 330 (1), 313 (3), 269 (1), 223 (2), 204 (1), 189 (3), 172 (1), 138 (2), 128 (1), 95 (100), 67 (30), 43 (67). Found, %: C 60.92; H 8.54; O 5.08; S 25.46. $C_{18}H_{32}OS_3$. Calculated, %: C 60.00; H 8.88; O 4.45; S 26.67.

8,9,11,12-Dicycloheptano-1,4-dioxa-7,10,13-trithiacyclopentadecane (10) was prepared analogously to compound **7** by method B. Finely divided cesium carbonate (3.9 g, 0.012 mol) was dispersed in DMF (200 ml) and 1,8-dimercapto-3,6-dioxooctane (1.82 g, 0.01 mol) was added to the reaction mixture. Then a solution of the dichlorosulfide **1** (2.95 g, 0.01 mol) in DMF (50 ml) was added. The reaction product was purified chromatographically (1:9 ethanol–hexane). Yield 2.46 g (61%). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ, ppm: 24.47, 25.16, 25.88, 25.90, 26.05, 26.15, 35.06, 35.14, 35.77, 36.18 (d, d, d, d, d - C atoms of the cycloheptane ring); 28.30, 28.73 (d, $C_{(6)}$, $C_{(14)}$), 50.34, 51.07 (d, $C_{(9)}$, $C_{(11)}$), 52.30, 52.89 (d, $C_{(8)}$, $C_{(12)}$), 68.90, 69.27 (d, $C_{(2)}$, $C_{(3)}$), 70.92, 71.45 (d, $C_{(5)}$, $C_{(15)}$). Mass spectrum, *m/z* (I_{rel}, %): 404 [M^+] (5), 371 (1), 340 (1), 309 (1), 277 (11), 256 (3), 216 (8), 181 (5), 128 (32), 95 (100), 67 (50).

5,6,8,9-Dicyclooctano-1,4,7,10-tetrathiacyclododecane (11) was synthesized analogously to the thiacrown **7** (method A). Sodium (0.23 g, 0.01 mol) was dissolved in ethanol (200 ml) and 2,2-dimercaptodiethyl sulfide (0.77 g, 0.005 mol) was added. Then a solution of the sulfide **2** (1.62 g, 0.005 mol) in ethanol (50 ml) was added. An oil was obtained which was purified chromatographically (1:8 ether–hexane). Yield 0.8 g (39%). ^{13}C NMR spectrum (DMSO-d_6, TMS), δ, ppm: 22.27, 23.45, 24.57, 24.82, 25.03, 25.32, 29.05, 29.82, 30.69, 30.94, 32.92, 33.12 (d, d, d, d, d, d - C atoms of the cyclooctane ring); 39.01, 39.28 (d, $C_{(3)}$, $C_{(11)}$); 39.54, 39.84 (d, $C_{(2)}$, $C_{(12)}$); 40.40, 41.02 (d, $C_{(6)}$, $C_{(8)}$), 55.5 (s, $C_{(5)}$, $C_{(9)}$). Mass spectrum, *m/z* (I_{rel}, %): 299 (1), 285 (1), 251 (1), 203 (2), 167 (5), 154 (2), 141 (25), 109 (60), 67 (100), 41 (87). Found, %: C 60.37; H 9.41; S 30.22. $C_{20}H_{36}S_4$. Calculated, %: C 59.41; H 8.91; S 31.68.

5,6,8,9-Dicyclooctano-1-oxa-4,7,10-trithiacyclododecane (12) was obtained using the method in ethanolic solution. 2,2'-Dimercaptodiethyl ether (0.69 g, 0.005 mol) was added to a solution of sodium ethoxide (0.23 g, 0.01 mol) in ethanol (200 ml). Then a solution of sulfide **2** (1.62 g, 0.005 mol) in ethanol (50 ml) was added over 10 h. An oil was obtained which was purified chromatographically (1:8 ether:hexane). Yield 0.68 g (35%). ^{13}C NMR spectrum (DMSO-d_6, TMS), δ, ppm: 22.29, 22.50, 23,32, 23.99, 28.46, 28.79, 29.11, 29.62, 39.93, 39.60, 40.77, 41.06 (d, d, d, d, d, d - C atoms of the cyclooctane ring); 29.88, 30.06 (d, $C_{(3)}$, $C_{(11)}$); 60.09, 60.74 (d, $C_{(6)}$, $C_{(8)}$); 62.60, 63.94 (d, $C_{(5)}$, $C_{(9)}$); 71.81, 75.03 (d, $C_{(2)}$, $C_{(12)}$). Mass spectrum, *m/z* (I_{rel}, %): 328 (1), 279 (42), 204 (2), 186 (1), 167 (60), 149 (100), 142 (12), 138 (5), 109 (58), 67 (43), 43 (70).

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