

## NEW FUNCTIONALIZED DITHIA-12(13)-CROWN-4 ETHERS: SYNTHESIS, COMPLEX FORMATION, AND EXTRACTION CAPACITY

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*1,4-Dioxa-7,10-dithiacyclododecane-8-carbonitrile, 1,4-dioxa-7,11-dithiacyclotridecan-9-one, its 2,4-dinitrophenylhydrazone, and unsubstituted 7,10-dithia-12-crown-4 were synthesized. The complexing ability of the four synthesized dioxadithiacrown compounds toward Ag(I), Pb(II), Hg(II), and Cd(II) ions was assessed by <sup>1</sup>H NMR. The extracting ability of the three dioxadithiacrown compounds with respect to the Sn(II) ion from aqueous solutions was studied. The thermal stability of 1,4-dioxa-7,10-dithia-cyclododecane and the corresponding 8-carbonitrile was investigated.*

**Keywords:** dithia-12(13)-crown-4 ethers, Ag(I), Pb(II), Hg(II), Sn(II) ions, complexing, synthesis, thermal stability, extraction, <sup>1</sup>H NMR spectroscopy, X-ray crystallographic analysis.

Crown ethers and their hetero analogs have been the subjects of intensive study for the last 30 years [1]. A special position among such substances is occupied by sulfur macrocycles and their linear analogs, called podands, on account of their unique ability to serve as ligands for selective complex formation with "soft" cations, i.e., the ions of low-valence transition and heavy metals. The aim of the present work was to develop methods for the synthesis of new oxathiacrown ethers with various functional groups and also to evaluate the complex-forming characteristics of these compounds.

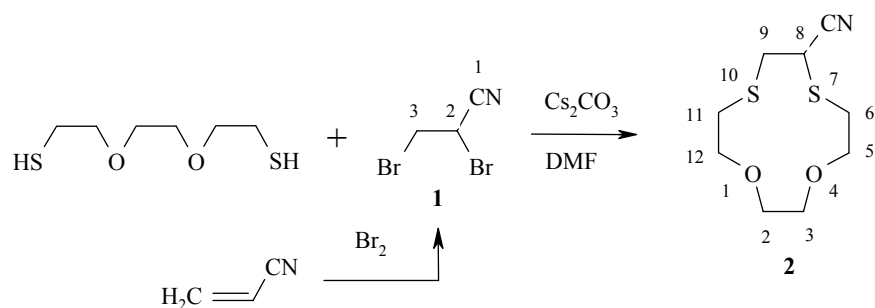
The following dithia-12(13)-crown-4 ethers were chosen as subjects for investigation: 1,4-Dioxa-7,10-dithia-cyclododecane-8-carbonitrile (**2**), 1,4-dioxa-7,11-dithiacyclotridecan-9-one (**3**), and the 2,4-dinitrophenylhydrazone **4**. The previously described [2] unsubstituted 1,4-dioxa-7,10-dithiacyclododecane (**5**) was synthesized for comparison of the complexing properties.

The 12-membered nitrile **2** was obtained with a yield of 15% by the cyclization of commercial 1,8-dimercapto-3,6-dioxaoctane and 2,3-dibromopropionitrile (**1**), synthesized by the bromination of acetonitrile with bromine at 0°C. The cyclization was conducted in DMF under conditions of high dilution and with cesium carbonate as template reagent according to the method in [3].

The synthesized macrocycle **2** was a solid, from which single crystals suitable for X-ray crystallographic analysis could be obtained by crystallization from acetonitrile (Fig. 1, Table 1).

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The bond lengths and the bond angles in the molecule do not in fact differ from the standard values. The nitrile group is in the pseudoaxial orientation in relation to the macrocyclic system.

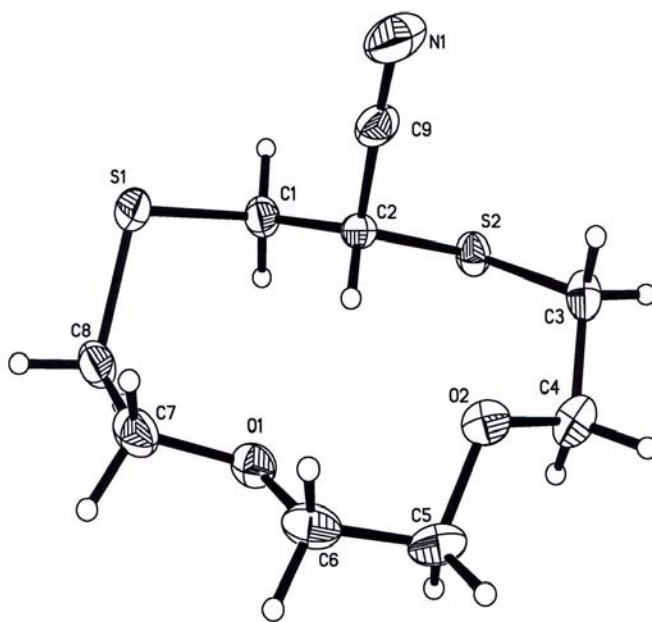


Fig. 1. The molecular structure of the carbonitrile **2**.

TABLE 1. The Individual Bond Lengths ( $d$ ) and Bond Angles ( $\omega$ ) in the Molecule of **2**

Bond	$d$ , Å	Bond	$d$ , Å	Angle	$\omega$ , deg
$\text{S}_{(1)}-\text{C}_{(1)}$	1.814(1)	$\text{O}_{(2)}-\text{C}_{(5)}$	1.421(2)	$\text{C}_{(1)}-\text{S}_{(1)}-\text{C}_{(8)}$	103.87(6)
$\text{S}_{(1)}-\text{C}_{(8)}$	1.821(1)	$\text{N}_{(1)}-\text{C}_{(9)}$	1.142(2)	$\text{C}_{(2)}-\text{S}_{(2)}-\text{C}_{(3)}$	102.24(6)
$\text{S}_{(2)}-\text{C}_{(2)}$	1.831(1)	$\text{C}_{(9)}-\text{C}_{(2)}$	1.468(2)	$\text{C}_{(6)}-\text{O}_{(1)}-\text{C}_{(7)}$	113.3(1)
$\text{S}_{(2)}-\text{C}_{(3)}$	1.814(1)	$\text{C}_{(1)}-\text{C}_{(2)}$	1.530(2)	$\text{C}_{(4)}-\text{O}_{(2)}-\text{C}_{(5)}$	114.93(9)
$\text{O}_{(1)}-\text{C}_{(6)}$	1.425(2)	$\text{C}_{(3)}-\text{C}_{(4)}$	1.514(2)		
$\text{O}_{(1)}-\text{C}_{(7)}$	1.428(2)	$\text{C}_{(5)}-\text{C}_{(6)}$	1.502(2)		
$\text{O}_{(2)}-\text{C}_{(4)}$	1.426(1)	$\text{C}_{(7)}-\text{C}_{(8)}$	1.506(2)		

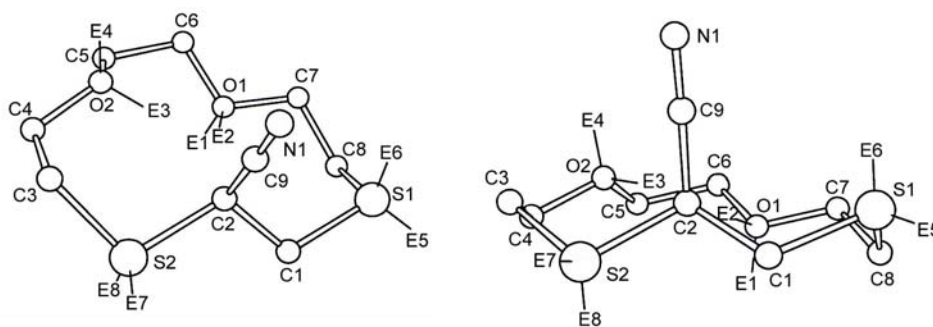


Fig. 2. The orientation of the unshared electron pairs (E1-E8) of the heteroatoms in the macrocycle **2**.

The bond angles at the oxygen and sulfur heteroatoms correspond to their  $sp^3$ -hybrid state, which enables us to judge the orientation of the unshared electron pairs of these atoms from in relation to the crown ether macrocycle. In Fig. 2 the molecule of compound **2** is shown in two different projections. The electron pairs of the sulfur and oxygen atoms are represented by segments 0.8 Å in length, denoted by the letter E with a number. The O<sub>(1)</sub> and O<sub>(2)</sub> oxygen atoms have unshared pairs E1, E2 and E3, E4, and the S<sub>(1)</sub> and S<sub>(2)</sub> atoms have pairs E5, E6 and E7, E8.

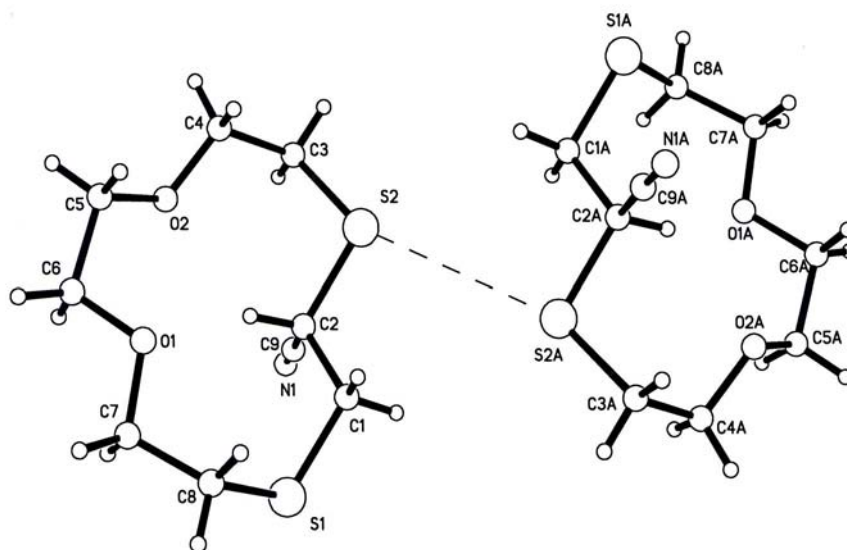


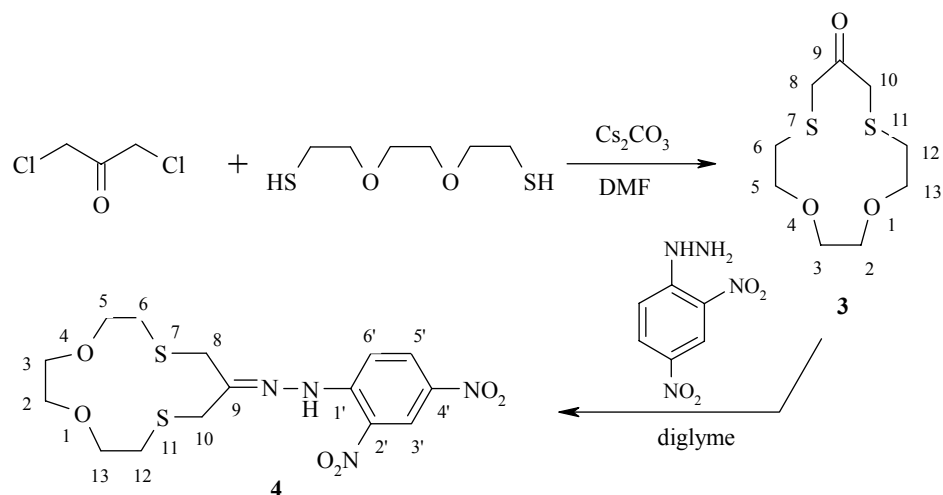
Fig. 3. The structure of the centrosymmetric dimer.

It is seen that the unshared electron pairs E2 and E3 of the two oxygen atoms are directed toward the center of the macrocycle, while the other two are directed toward different sides from the plane of the macrocycle. The unshared electron pair E6 at the S<sub>(1)</sub> atom is directed toward the same side of the plane of the macrocycle as E4 of the O<sub>(2)</sub> atom. Thus, with a certain small change in the conformation of the macrocycle it can be supposed that a chelate effect arises on account of the participation of these unshared electron pairs in interaction with the metal cation. The same situation can be proposed for the unshared electron pairs E1 of the O<sub>(1)</sub> atom and E8 of the S<sub>(2)</sub> atom, directed toward the opposite side of the average plane of the crown ether. The remaining unshared electron pairs at the sulfur atoms E5 and E7 are directed away from the macrocycle, and their participation in bonding with the metal cations requires a more radical change in its conformation.

In the crystal the molecules are linked into centrosymmetric dimers (Fig. 3) on account of weak interaction (a secondary bond) of the  $S_{(2)}\cdots S_{(2A)}$  type. The distance corresponding to this secondary bond 3.657(1) Å is appreciably shorter than twice the van der Waals radius of this atom ( $\sim 4$  Å). This secondary interaction may be realized by a  $n \rightarrow \sigma^*$  mechanism with the participation of E7 with the antibonding orbital of the  $S_{(2)}-C_{(3)}$  bond. This conclusion does not contradict the overall geometry of the dimer since the secondary bond  $S_{(2)}\cdots S_{(2A)}$  lies almost on an extension of the  $S_{(2)}-C_{(3)}$  bond. In fact, the  $C_{(3)}-S_{(2)}\cdots S_{(2A)}$  angle amounts to  $157.51(2)^\circ$ , and the  $C_{(2)}-S_{(2)}\cdots S_{(2A)}$  angle to  $98.32^\circ$ .

Such a T-shaped configuration of the sulfur atoms is typical of  $S\cdots S$  interaction. The participation of this sulfur atom in weak interaction is probably caused by its bond with the  $C_{(2)}$  atom carrying an electron-withdrawing substituent – the nitrile group.

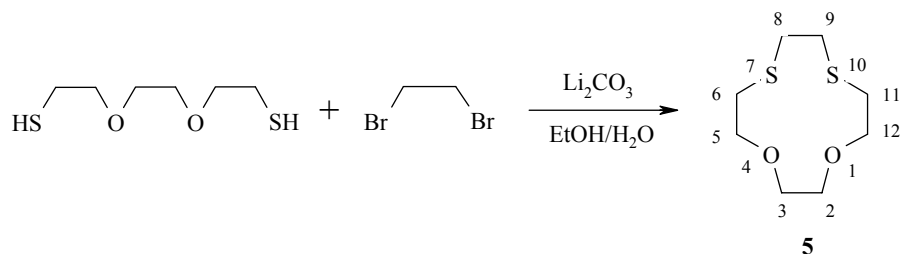
1,4-Dioxa-7,11-dithiacyclotridecan-9-one (**3**) was obtained by the cyclization of 1,8-dimercapto-3,6-dioxaoctane and 1,3-dichloroacetone by the method in [4].



The desired crown ether **3** was isolated with a yield of 11% in the form of colorless crystals.

The corresponding 2,4-dinitrophenylhydrazone **4** was obtained from the ketone **3** with a yield after crystallization of 75%.

1,4-Dioxa-7,10-dithiacyclododecane (**5**) was obtained by the cyclization of 1,8-dimercapto-3,6-dioxaoctane and 1,2-dibromomethane in a 1:1 mixture of alcohol and water under conditions of high dilution and with lithium carbonate as template reagent:



The crown ether **5** was isolated in the form of a yellow oil with a yield of 27%. Earlier this macrocycle was obtained with a lower yield (19%) from 1,2-ethanedithiol and 1,2-bis(2-chloroethoxy)ethane [2].

Complexes of oxathiacrown ethers **2** and **5** with Ag(I), Pb(II), and Cd(II) cations were prepared using the corresponding perchlorates with a metal–ligand ratio of 1:1. The complexes were analyzed by  $^1\text{H}$  NMR spectroscopy, and in order to estimate the complexing characteristics the obtained spectra were compared with the  $^1\text{H}$  NMR spectra of the initial oxathiacrown ethers (Tables 2 and 3). For ease of comparison the parameter  $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$  was calculated.

For the complexes of the macrocycles **2** and **5** with the Ag(I) and Pb(II) cations changes were observed in the chemical shifts of the protons of the methylene groups attached to both the sulfur and the oxygen atoms. However, they are significantly larger for the former, and complexing with the lead ion has a larger effect on the  $\Delta\delta$  value, indicating the formation of more stable complexes. During comparison of the changes in the chemical shifts of the protons ( $\Delta\delta$ ) for the complexes of crown ethers **2** and **5** with Ag(I) and Pb(II) it is seen that these values are larger for the unsubstituted ligand **5** than for the ligand **2** containing the electron-withdrawing nitrile group. This indicates that the macrocycle **5** forms more stable complexes than the carbonitrile **2** with the investigated cations.

Since the radii of the silver (1.13) and lead (1.32 Å) cations are large for the cavity size of 12- and 13-membered oxathiacrown ethers, complex formation probably takes place through the formation of "sandwich" structures with two ligands to one metal cation. It should be noted that the most appreciable change in the chemical shifts during complex formation with crown ether **2** appears at the protons of the tertiary carbon atom attached to the nitrile group:  $\Delta\delta = -0.25$  for Ag(I) and  $\Delta\delta = -0.42$  ppm for Pb(II). The negative values of  $\Delta\delta$  confirm the formation of the sandwich structure, in which the protons at the tertiary carbon atom of one of the ligands is close to the nitrile group of the second macrocycle, leading to an anisotropic effect and to an upfield shift. We note that a similar anisotropic effect for the protons at the tertiary carbon atoms was observed in previously investigated complexes of substituted dithia-13-crown-4 ethers [5]. The very small changes of the chemical shifts of the protons in the oxathiacrown ether (**2**)–Cd(II) complex indicates weak complex formation with this cation.

During complex formation between the ligand **2** and the Ag(I) there is also a shift of the absorption band for the CN group in the IR spectrum of the complex. Thus,  $\nu_{\text{CN}}$  for the initial carbonitrile **2** is at  $2246\text{ cm}^{-1}$ , whereas in the complex (**2**)·Ag(I) it is at  $2256\text{ cm}^{-1}$ . A similar shift was observed earlier [6] for the complexes of dithia-12-crown-4 with the dithiamaleonitrile fragment with a silver cation. Here the  $\nu_{\text{CN}}$  frequency was 2229 and 2216 in the complex and 2222 and  $2208\text{ cm}^{-1}$  in the free ligand.

Complexes with Ag(I), Pb(II), and Hg(II) ions were obtained for the ketone **3**. As for the nitrile **2**, the largest changes in the chemical shifts were observed for the protons of the methylene groups attached to the sulfur atoms, and these changes were most significant for the mercury and lead cations (Table 2). At the same time for the lead and mercury ions the chemical shifts of the methylene groups attached to the oxygen atoms change.

The complex with the Ag(I) ions was investigated for compound **4**. It should be noted that in the obtained complex, together with the significant change in the chemical shifts for the protons of the methylene groups attached to the sulfur atoms, there are also appreciable changes in the chemical shifts of the protons in the  $\text{CH}_2\text{--O}$  fragments in the ring and NH in the substituent.

TABLE 2. The Changes in the Chemical Shifts for the Protons of Compound **2** during Complex Formation with  $\text{AgClO}_4$ ,  $\text{Pb}(\text{ClO}_4)_2$ , and  $\text{Cd}(\text{ClO}_4)_2$ \*

Cation	$\Delta\delta$ , ppm			
	H-6,9,11	H-2,3,12	H-5	H-8
Ag(I)	0.07-0.24	0.03-0.06	0.09	-0.25
Pb(II)	0.12-0.35	0.18	0.04	-0.42
Cd(II)	0.04-0.13	0.05-0.06	0	0

\* In a solution in  $\text{CD}_3\text{CN}$ ,  $30^\circ\text{C}$ ,  $c_{\text{lig}} = c_{\text{m}} = 7.13 \cdot 10^{-2}\text{ M}$  (here and in Tables 3 and 4).

TABLE 3. The Changes in the Chemical Shifts of the Protons in Compound **5** during Complex Formation with AgClO<sub>4</sub> and Pb(ClO<sub>4</sub>)<sub>2</sub>

Cation	$\Delta\delta$ , ppm			
	H-5,12	H-8,9	H-2,3	H-6,11
Ag(I)	0.11	0.04	0.12	0.26
Pb(II)	0.58	0.63	0.39	0.33

TABLE 4. The Changes in the Chemical Shifts of the Protons in Compounds **3** and **4** during Complex Formation with AgClO<sub>4</sub>, Pb(ClO<sub>4</sub>)<sub>2</sub>, and Hg(ClO<sub>4</sub>)<sub>2</sub>

Com- pound	Cation	$\Delta\delta$ , ppm							
		H-2,3	H-5,13	H-6,12	H-8,10	H-3'	H-5'	H-6'	NH
<b>3</b>	Ag(I)	0.04	0.03	0.20	0.06	—	—	—	—
	Pb(II)	0.17	0.25	0.34	0.2	—	—	—	—
	Hg(II)	0.24	0.18	0.57	0.21	—	—	—	—
<b>4</b>	Ag(I)	0.11	0.01	0.24	0.11	0	0.05	0.01	0.11

TABLE 5. The Distribution Coefficients of Tin(II) (*D*) during Extraction of Sn(NO<sub>3</sub>)<sub>2</sub>\* by Compounds (**2**), (**3**), and (**5**) in Dichloroethane

Extractant	$c_{\text{extract}}$ , mol/l	<i>D</i>
<b>2</b>	$4 \cdot 10^{-3}$	0.008
<b>3</b>	$1.3 \cdot 10^{-2}$	0.013
<b>5</b>	$5.9 \cdot 10^{-3}$	0.100

\*  $c_{\text{Sn(NO}_3)_2} = 10^{-5}$  mol/l,  $c_{\text{LiPi}} = 3.8 \cdot 10^{-3}$  mol/l.

The synthesized oxathiacrown compounds **2**, **3**, and **5** contain oxygen atoms and sulfur atoms in the macrocycle. It must therefore be expected that they can occupy, according to Pearson's principle, an intermediate position between "soft" and "hard" ligands. The "intermediate" Sn(II) cation was used to study their extracting ability. Extraction was conducted from solutions of lithium picrate (LiPi).

The distribution coefficient was determined by a radiometric method as the ratio of the radioactivity recorded in the organic phase to that in the aqueous phase (after subtraction of the background):  $D = I_{\text{org}}/I_{\text{aq}}$ .

According to the data in Table 5, the extraction ability of the crown ether with a nitrile group **2** and the ketone (**3**) is lower than the extracting ability of the unsubstituted crown ether **5**. In the case of the synthesized oxathiacrown compounds it can be concluded that the introduction of an electron-withdrawing group has a negative effect on the extraction characteristics of the macrocycles. The distribution coefficients *D* obtained for Sn(II) during extraction with the macrocycles **2**, **3**, and **5** correlate with the changes in the chemical shifts  $\Delta\delta$  in the NMR spectra of the complexes of the same compounds with the isoelectronic Pb(II) cation.

The thermal stability of oxathiacrown ethers **2** and **5** was determined in order to work out a procedure for depositing oxathiacrown compounds on the surface of solid mineral supports such as SnO<sub>2</sub> with the subsequent production of multisensor systems. Thermogravimetric methods showed that the introduction a nitrile group into the macrocycle increases its thermal stability. Thus, a strong weight loss occurs in the nitrile (**2**) at 130-440°C and in its unsubstituted analog at 75-260°C.

## EXPERIMENTAL

The  $^1\text{H}$  NMR spectra were recorded on a Varian XR-400 spectrometer (400 MHz) for 25% solutions in  $\text{CDCl}_3$  or  $\text{CD}_3\text{CN}$  with HMDS as internal standard ( $\delta$  0.05 ppm). The  $^{13}\text{C}$  NMR spectra were recorded for 30-35% samples in deuterated solvents on a Varian XR-400 spectrometer (100 MHz). The mass spectra were obtained on a Finnigan MAT-112S instrument with electron impact and 70 eV ionizing electrons. Analysis by TLC was conducted on Silufol plates in various solvent systems. Merck silica gel and Acros silica gel were used as sorbents, and the composition of the eluants was selected individually for each mixture being analyzed.

The distribution coefficients ( $D$ ) of Sn(II) were determined radiometrically on a Canberra-Packard-2700 liquid scintillation counter, using the  $^{117}\text{Sn}$  isotope according to the procedure in [8]. The thermal stability of the oxathiacrown compounds **2** and **5** was determined on a Q-1500 derivatograph.

**X-Ray Crystallographic Analysis.** A single crystal of compound **2**, coated with perfluorinated oil, was placed in a Bruker SMART CCD diffractometer. The collection of experimental reflections was measured at  $-150^\circ\text{C}$ . The structure was interpreted by the direct method and refined in full-matrix anisotropic approximation in  $F^2$  for all the non-hydrogen atoms. The hydrogen atoms were revealed in a Fourier difference synthesis and refined in isotropic approximation. All the calculations were made by the SHELXTL Plus software [7]. Crystallographic data, experimental details, and structural refinements of compound **2**:  $M$  233.34, monoclinic system, space group  $P2_1/c$ ,  $a = 8.2429(7)$ ,  $b = 13.860(1)$ ,  $c = 10.8154(9)$  Å,  $V = 1165.3(2)$  Å<sup>3</sup>,  $\beta = 109.430(2)^\circ$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.330$  g/cm<sup>3</sup>,  $F(000)$  496,  $\theta = 2.48$ – $28.00$ ,  $\rho(\text{MoK}\alpha) = 0.433$  mm<sup>-1</sup>, crystal size  $0.52 \times 0.48 \times 0.44$  mm, ranges of reflection indices  $-9 \leq h \leq 10$ ;  $-7 \leq k \leq 18$ ;  $-13 \leq l \leq 10$ , measured reflections 4808, unique reflections 2536 ( $R_{\text{int}} = 0.0171$ ), reflections with  $I > \sigma 2(I)$  2507, absorption correction with SADABS, transmission min/max 0.8062/0.8323, refinement variables 187,  $R$  factors in  $I > \sigma 2(I)$   $R_1 = 0.0240$ ,  $wR_2 = 0.0629$ ; in all reflections  $R_1 = 0.0275$ ,  $wR_2 = 0.0650$ , quality factor in  $F^2$  1.024, residual electron density min/max, e/Å<sup>3</sup> -0.150/0.292.

The crystal structure data for this compound were deposited at the Cambridge Crystallographic Center (CCDC-609525)\*.

**2,3-Dibromopropionitrile (1).** To acetonitrile (10 g, 180 mmol) cooled to  $0^\circ\text{C}$  we added dropwise bromine (30 g, 180 mmol) at  $0^\circ\text{C}$  over 4 h with stirring. The mixture was left at  $40^\circ\text{C}$  for 2 h and was then distilled under vacuum. We isolated the dibromide **1** (31.6 g). Yield 78%; bp  $90$ – $95^\circ\text{C}$  (20 mm Hg),  $n_D^{20}$  1.5450 (bp  $92$ – $93^\circ\text{C}$ , 14 mm Hg [9]).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 3.78 (2H, m, H-3); 4.55 (H, dd,  $J_1 = 9.1$ ,  $J_2 = 6.3$ , H-2).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 29.75 ( $\text{C}_{(3)}$ ), 40.84 ( $\text{C}_{(2)}$ ), 115.3 ( $\text{C}_{(1)}$ ).

**Synthesis of 1,4-Dioxo-7, 10-Dithiacyclododecane-8-carbonitrile (2) and 1,4-Dioxo-7,11-dithiacyclotridecan-9-one (3) (General Method).** To a stirred solution of cesium carbonate (50 mmol) in anhydrous DMF (500 ml) at  $55$ – $60^\circ\text{C}$  in a stream of argon we added dropwise the dibromide **1** or 1,3-dichloroacetone (10 mmol) and 1,8-dimercapto-3,6-dioxaoctane (10 mmol), each dissolved in DMF (200 ml). The mixture was then stirred at the same temperature for 25 h. The solvent was distilled, and the residue was extracted with ether. The extract was dried with magnesium sulfate. The solvent was distilled, and the residue was chromatographed on a column of silica gel with 1:3 ethyl acetate–hexane as eluant.

**1,4-Dioxo-7,10-dithiacyclododecane-8-carbonitrile (2).** Yield 15%; mp  $93^\circ\text{C}$ . IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2246 ( $\text{C}\equiv\text{N}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 2.75–2.84 (6H, m, H-6,9,11); 3.53–3.77 (6H, m, H-2,3,12); 3.83 (H, ddd,  $J_1 = 9.9$ ,  $J_2 = 4.9$ ,  $J_3 = 2.2$ , H-5); 4.08 (1H, dt,  $J_1 = 10.1$ ,  $J_2 = 3.0$ , H-5); 5.23 (1H, dd,  $J_1 = 9.5$ ,  $J_2 = 7.0$ , H-8).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 32.23 ( $\text{C}_{(6)}$ ), 34.52 ( $\text{C}_{(11)}$ ), 35.91 ( $\text{C}_{(9)}$ ), 36.71 ( $\text{C}_{(8)}$ ), 70.02, 70.94 ( $\text{C}_{(2)}$ ,  $\text{C}_{(3)}$ ), 73.80, 74.84 ( $\text{C}_{(5)}$ ,  $\text{C}_{(12)}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 233 [ $\text{M}]^+$  (44), 200 (4), 173 (17), 145 (8), 112 (86), 99 (30), 61 (98), 45 (92). Found, %: C 46.38; H 6.42; N 6.10; S 27.56.  $\text{C}_9\text{H}_{15}\text{NO}_2\text{S}_2$ . Calculated, %: C 46.32; H 6.48; N 6.00; S 27.48.

\*A copy of these data can be obtained free on application to: CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

**1,4-Dioxa-7,11-dithiaclotridecan-9-one (3).** Deliquescent colorless crystals. Yield 11%.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 2.73 (4H, t,  $J = 5.1$ , H-6,12); 3.53 (4H, s, H-8,10); 3.69 (4H, t,  $J = 5.1$ , H-5,13); 3.78 (4H, s, H-2,3).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 32.60 ( $\text{C}_{(6)}$ ,  $\text{C}_{(11)}$ ), 42.38 ( $\text{C}_{(8)}$ ,  $\text{C}_{(9)}$ ), 70.13 ( $\text{C}_{(5)}$ ,  $\text{C}_{(12)}$ ), 72.48 ( $\text{C}_{(2)}$ ,  $\text{C}_{(3)}$ ), 192.72 ( $\text{C}=\text{O}$ ).

**1,4-Dioxa-7,10-dithiaclo-dodecane (5).** To a stirred solution of lithium carbonate (3.7 g, 50 mmol) in a 1:1 mixture of alcohol and water (500 ml) at 55–60°C in a stream of argon we added dropwise dibromoethane (1.87 g, 10 mmol) and 1,8-dimercapto-3,6-oxaoctane (1.82 g, 10 mmol), each dissolved in alcohol (200 ml). The reaction mixture was stirred at the same temperature for a further 25 h. The solvent was distilled, the residue was extracted with ether, and the extract was dried with magnesium sulfate. The solvent was distilled, and the residue was chromatographed on a column of silica gel with a 1:1 mixture of ethyl acetate and hexane as eluant. We obtained 0.58 g (27%) of compound **5** in the form of a yellow oil.  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ),  $\delta$ , ppm ( $J$ , Hz): 2.65 (4H, t,  $J = 5.1$ , H-6,11); 2.92 (4H, s, H-8,9); 3.54 (4H, s, H-2,3); 3.73 (4H, t,  $J = 4.8$ , H-5,12).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 31.08 ( $\text{C}_{(6)}$ ,  $\text{C}_{(11)}$ ), 32.96 ( $\text{C}_{(8)}$ ,  $\text{C}_{(9)}$ ), 70.45 ( $\text{C}_{(5)}$ ,  $\text{C}_{(12)}$ ), 74.19 ( $\text{C}_{(2)}$ ,  $\text{C}_{(3)}$ ).

**1,4-Dioxa-7,11-dithiaclotridecan-9-one 2,4-Dinitrophenylhydrazone (4).** 2,4-Dinitrophenylhydrazine (0.167 g, 2.8 mmol) was dissolved by heating in diglyme (5 ml), and a cooled solution of the crown ether **3** (0.1 g, 0.4 mmol) in toluene (1 ml) was added. The mixture was heated at 100°C for 30 min, and three drops of hydrochloric acid were added. The solvent was distilled. After recrystallization from chloroform of compound **4** (0.119 g) was obtained. Yield 75%; mp 290°C (decomp., chloroform).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 2.73–2.78 (4H, m, H-6,12); 3.62 (4H, s, H-2,3); 3.77–3.81 (4H, m, H-5,13); 3.90, 4.03 (4H, 2s, H-8,10); 7.88 (2H, d,  $J = 9.6$ , H-6'); 8.29 (2H, ddd,  $J_1 = 9.6$ ,  $J_2 = 2.5$ ,  $J = 0.8$ , H-5'); 8.95 (2H, d,  $J = 2.5$ , H-3'); 11.48 (H, s, NH). Found, %: C 43.26; H 4.84; N 13.45; S 15.40.  $\text{C}_{15}\text{H}_{20}\text{N}_4\text{O}_6\text{S}_2$ . Calculated, %: C 43.31; H 4.80; N 13.49; S 15.46.

**Preparation of the Complexes of the Crown Ethers.** In order to investigate the  $^1\text{H}$  NMR spectra of the crown ether ( $4.28 \cdot 10^{-5}$  mol) and of the perchlorate ( $4.28 \cdot 10^{-5}$  mol) of the respective metal were placed in a 5-ml flask, and 0.6 ml of  $\text{CD}_3\text{CN}$  was added. The solution was placed in a tube, and the  $^1\text{H}$  NMR spectrum was recorded.

**Complex (2)·Ag(I).** A solution of the carbonitrile **2** (0.05 g, 8 mmol) and of  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  (0.044 g, 8 mmol) in methanol (3 ml) was left to cool at 0°C. After 24 h crystals of the complex **2**·Ag(I) separated. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2256 ( $\text{C}\equiv\text{N}$ ).

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