# The Crystal Structures of 10-Oxa-1,4,7-trithiacyclododecane, 7,10,13-Trioxa-1,4-dithiacyclopentadecane, 7,10,13,16-Tetraoxa-1,4-dithiacyclooctadecane and 4,7,13,16-Tetraoxa-1,10-dithiacyclooctadecane (1)

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The structures of four macrocyclic polyether sulfides have been determined by single crystal x-ray diffraction methods. The compounds studied were 1,4,7-trithia-12-crown-4, 1,4-dithia-15-crown-5, 1,4-dithia-18-crown-6 and 1,10-dithia-18-crown-6. In all four compounds the potential donor sulfur atoms point out of the ring. This causes the rings to be irregularly shaped.

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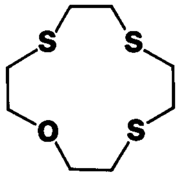
## Introduction.

The coordination chemistry of cyclic polyethers and their derivatives has created considerable interest because of the cation specificities shown by these molecules. The interactions of various polyether molecules with different ions have been studied by many investigators, and are the subject of several reviews (2). It has been shown that replacement of oxygen donor atoms by sulfur atoms changes the cation selectivity pattern. Thus, the stability of alkali and alkaline earth complexes decreases and the stability of mercury(II) and silver(I) complexes increases (3). In this study, we have investigated the structures of four thia polyether molecules in an attempt to understand the coordination chemistry of this type of molecule. Included in the study are: 1,4,7-trithia-12-crown-4 (**1**) 1,4-dithia-15-crown-5 (**2**), 1,4-dithia-18-crown-6 (**3**), and 1,10-dithia-18-crown-6 (**4**).



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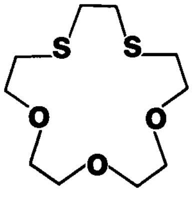

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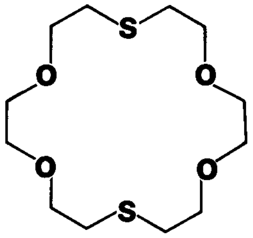

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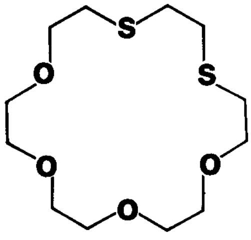

3

The compounds are named using an extension of Pedersen's nomenclature for crown compounds (4).

It is the purpose of this study to determine important structural features of the potential ligands such as bond lengths and angles, torsion angles and the arrangement of the potential donor atoms. This information will be important when studying the conformational changes which take place upon complexation of these ligands with cations. These particular compounds (**1-4**) were chosen for x-ray structure investigations because they have ring sizes similar to crown-5 and crown-6 polyethers which have been studied extensively, both thermodynamically and structurally.

## Crystal and Intensity Data.

The synthesis of the four thiaethers have been discussed (5). Preliminary crystallographic data were obtained from precession camera photographs. Suitable crystals of the compounds were mounted on a quarter circle orienter which had been fitted on a General Electric XRD-5 diffractometer. Nickel filtered Cu K$\alpha$ radiation was used for all data sets. Lattice parameters for the four compounds were obtained by least-squares refinements for $2\theta$ values. Data for compounds **2**, **3**, and **4**, were collected using a moving crystal, moving counter technique while data for **1** were collected using a stationary crystal, stationary counter technique. The data for **1** were corrected for $\alpha_1$, $\alpha_2$ splitting using a plot of I peak/I scan *vs.* $2\theta$. Data for all the crystals were collected manually. Standard reflections which were measured throughout the experimental procedures indicated that the crystals were stable and not affected by x-radiation. No absorption corrections were applied to the intensity data of **1** and **3** in as much as the crystals of these materials were made approximately spherical with a sphere grinder. However, the crystals of **2** and **4** were not equidimensional so absorption corrections, which were a function of $\phi$, were applied to those data sets. The crystal data for the compounds are summarized in Table 1.

## Structure Determinations and Refinement.

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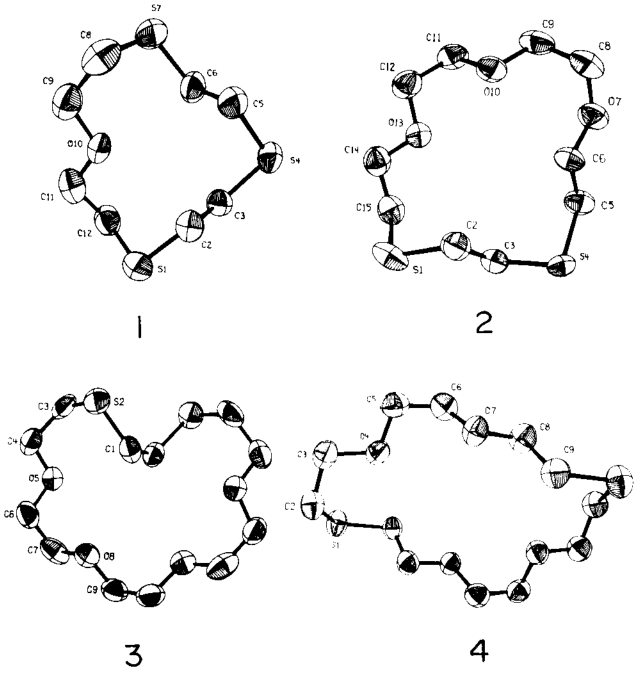
Details of the crystal structure solutions and the refinements of these structures are summarized in Table 2. Trial structures for **1**, **3** and **4** were obtained using conventional heavy atom and Fourier procedures. In each case the positions for the sulfur atoms were obtained from Patterson maps and the lighter non-hydrogen atoms were located in Fourier maps phased by the sulfur positions. The sulfur atom positions for **2** were also located in a Patterson map. However, because positions for other atoms were difficult to locate in subsequent Fourier maps the rest of the structure was obtained using statistical methods. It was possible to phase 135 of the reflections with large $|E|$ and $|F|$ values using the sulfur positions. These data were expanded to a set of 400 $|E|$ values with the symbolic addition procedure. The carbon and oxygen atoms were located in the resulting E map.

All data sets were refined using ORFLS (6), a full-matrix least-squares program. The atomic scattering factors for C, O and S were taken from Cromer and Waber (7) while those for H were taken from the International Tables for X-ray Crystallography (8). Weights for the data sets of the four molecules were based on counting statistics with allowances for some instrumental error (9). Refinement for all four compounds was continued until the shifts in the individual parameters were considerably less than their uncertainties. The difference maps of the four compounds which were calculated when refinements were completed showed no spurious peaks (10).



1 2

3 4

Figure 1. ORTEP (11) drawings of the four sulfur containing polyether molecules.

Discussion.

The conformations of the four molecules as drawn by ORTEP (11) along with the atom labels are shown in Figure 1. The labels used for the atoms in **3** and **4** do not coincide with the numbering in the nomenclature due to the presence of a two-fold axis in **3** and a center of inversion in **4**. Because of these symmetries only one-half of the atoms are labeled. Positional parameters for the atoms are given in Table 3. The bond lengths, bond angles and torsion angles for the structures are listed in Table 4. Chemically similar bond lengths and angles for the four different structures agree well. The average bond lengths and standard deviations for chemically similar bonds calculated for the four structures are C-C, 1.498(15) Å; C-S, 1.806(13) Å; and C-O, 1.418(8) Å. Only one bond length, a C-S bond in **3**, differs by more than two standard deviations from the average value. The short C-C and C-O bond lengths are typical of those found in cyclic polyethers (12). The C-S bond lengths agree well with the results reported for 1,4,8,11-tetrathiacyclotetradecane (13), the sulfur analog of cyclam. The four molecules have other structural similarities in addition to bond lengths and angles. In all the molecules the sulfur atoms and usually some of the oxygen atoms point out of the ring. This causes the ring of **1** to be heart shaped, the one oxygen pointing into the ring, and the rings of **2**, **3** and **4** to be irregularly shaped.

One interesting conformational feature which is unique to **3** is the magnitude of the S-C-C-S torsion angle. This torsion angle has a value close to 60° while the chemically similar torsion angles in **1** and **2** have values close to 180° (See Table 4). As a result of the gauche conformation, the two sulfur atoms are in contact (the S-S interatomic distance is 3.48 Å) and are in a position so that the molecule can function as a bidentate ligand. The ethylene bridge between the two sulfur atoms and the attached H atoms are in the interior of the ring restricting the size of the cavity of the molecule. This is in contrast to the situation in **1** and **2** where the S-S interatomic distance between adjacent sulfur atoms is at least 4.5 Å and where there are no atoms restricting the space in the cavity. It is interesting to note that **3** does act as a bidentate ligand when it forms a complex with mercury(II) chloride; the conformation of the ligand is essentially unchanged in the complexation process (14).

While the conformational changes of a molecule in the complexation process may be small as in the case of mercury(II) chloride-**3** this is often not the case. For example, in the palladium(II) chloride-**4** complex the molecule "bows" around the palladium atom bringing the two sulfur atoms which are at opposite ends of the molecule into contact distance, the S-S interatomic distance being

Table 1

Crystal Data for the Four Molecules

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Space Group | $P2_1/a$ | $P\bar{1}$ | $C2/c$ | $P2_1/n$ |
| a (Å) | 8.230(1) | 9.170(7) | 15.905(4) | 8.561(1) |
| b (Å) | 17.120(1) | 10.148(7) | 9.513(3) | 13.330(2) |
| c (Å) | 8.705(1) | 7.328(6) | 12.514(3) | 7.050(1) |
| α (°) | 90 | 87.47(2) | 90 | 90 |
| β (°) | 115.44(2) | 106.04(2) | 124.31(1) | 104.08(1) |
| γ (°) | 90 | 99.47(2) | 90 | 90 |
| 2θ values used in lattice parameter refinement | (a) | 29 | 55 | 15 |
| Z | 4 | 2 | 4(b) | 2(c) |
| Crystal Size (mm) | approximate 0.23 diameter | 0.4 × 0.4 × 0.2 | approximate 0.24 diameter | 0.4 × 0.3 × 0.2 |
| Dm $gcm^{-3}$ | 1.34 | 1.27 | 1.26 | 1.24 |
| Dx $gcm^{-3}$ | 1.34 | 1.29 | 1.26 | 1.26 |
| Sin θ/λ Limit | 0.53 | 0.61 | 0.61 | 0.61 |
| Total Data | 1377 | 2437 | 1490 | 1459 |
| Unobserved Data | 108 | 59 | 745 | 14 |
| $\mu$ $cm^{-1}$ | 55 | 34.9 | 31.6 | 31.6 |
| Abs. Coefficient Range | | 1-2.1 | | 1-1.4 |

(a) Not available but ≥ 12. (b) Molecule located about a 2 fold axis. (c) Molecule located about a center of inversion.

Table 2

Summary of Structure Solutions and Refinements

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Method of Solution | heavy atom | combination of heavy atom and statistical methods | heavy atom | heavy atom |
| Hydrogen Positions | located in ΔF map, refined | calculated not refined | calculated, refined | located in ΔF map, refined |
| Temperature Factors | | | | |
| Non-Hydrogen Atoms | anisotropic | anisotropic | anisotropic | anisotropic |
| Hydrogen Atoms | refined | set at 2.0<br>not refined | refined | refined |
| Unweighted $R_1$ (a) | 0.071 | 0.114 | 0.128 | 0.084 |
| Weighted $R_2$ (b) | 0.049 | 0.114 | 0.045 (c) | 0.064 |

(a) $R_1 = \Sigma |k|F_o| - |F_c|| / \Sigma k|F_o|$. (b) $R_2 = [\Sigma w(k|F_o| - |F_c|)^2/(\Sigma w|F_o|^2)]^{1/2}$. (c) The large difference between $R_1$ and $R_2$ was caused by the exclusion of the reflections which had zero weight in the weighted refinement. These included one reflection which was misset, four reflections which were affected by extinction and 198 reflections which had intensity values of zero or less.

3.17 Å (15). Such a major conformational change is reflected in large changes in torsion angle values. The absolute values of the torsion angles about S-C bonds in 4 range from 68 to 71° while the palladium(II) chloride-4 these angles range from 165-171°. These two examples illustrate the difficulties in predicting types of conformational changes that occur during complexation. Nevertheless, since conformational changes are related to structural features such as flexibility or rigidity of the potential ligand ring and the geometry of potential donor atoms, the structural parameters of these uncomplexed ligands provide a data base that is valuable in understanding the complexation process.

Table 3

Fractional Atomic Coordinates ($\times 10^4$) for the Non-hydrogen Atoms of the Four Compounds

| Molecule | Atom | x | y | z |
|---|---|---|---|---|
| **1** | S(1) | 9326(2) | 1323(1) | 259(2) |
| | C(2) | 7171(7) | 1643(4) | 155(7) |
| | C(3) | 5811(7) | 1007(3) | −359(7) |
| | S(4) | 3712(2) | 1298(1) | −297(2) |
| | C(5) | 4469(9) | 1550(4) | 1921(7) |
| | C(6) | 5300(9) | 894(4) | 3154(7) |
| | S(7) | 6180(2) | 1173(1) | 5359(2) |
| | C(8) | 8041(10) | 1822(4) | 5660(8) |
| | C(9) | 9664(9) | 1422(4) | 5626(7) |
| | O(10) | 9243(4) | 1193(2) | 3940(4) |
| | C(11) | 10748(9) | 886(5) | 3717(9) |
| | C(12) | 10055(9) | 588(4) | 1907(8) |
| **2** | S(1) | 9414(1) | 8897(1) | 2574(2) |
| | C(2) | 8427(5) | 8033(5) | 358(7) |
| | C(3) | 8566(5) | 6572(5) | 443(7) |
| | S(4) | 7984(1) | 5757(1) | −1840(2) |
| | C(5) | 5966(5) | 5185(5) | −2175(7) |
| | C(6) | 5004(5) | 6279(5) | −2750(7) |
| | O(7) | 3437(4) | 5682(3) | −3268(5) |
| | C(8) | 2405(6) | 6629(6) | −3828(8) |
| | C(9) | 1966(5) | 7136(6) | −2211(9) |
| | O(10) | 3223(3) | 7933(3) | −987(5) |
| | C(11) | 2917(5) | 8231(5) | 743(8) |
| | C(12) | 4304(6) | 9084(5) | 1968(9) |
| | O(13) | 5598(4) | 8403(4) | 2349(5) |
| | C(14) | 6827(7) | 9015(6) | 3844(7) |
| | C(15) | 8199(6) | 8307(6) | 4093(7) |
| **3** | C(1) | 519(3) | −70(5) | 2642(4) |
| | S(2) | 1319(1) | 1387(1) | 3576(1) |
| | C(3) | 1366(3) | 1320(6) | 5024(5) |
| | C(4) | 1932(4) | 70(6) | 5912(5) |
| | O(5) | 1277(2) | −1102(3) | 5369(2) |
| | C(6) | 1792(4) | −2393(6) | 5920(5) |
| | C(7) | 1066(4) | −3555(6) | 5193(5) |
| | O(8) | 808(2) | −3580(3) | 3909(3) |
| | C(9) | 110(4) | −4668(5) | 3154(5) |
| **4** | S(1) | 944(1) | 1519(1) | 1142(1) |
| | C(2) | 2528(5) | 2453(2) | 1825(6) |
| | C(3) | 3978(5) | 2281(3) | 1044(6) |
| | O(4) | 4819(3) | 1429(2) | 1967(3) |
| | C(5) | 6299(4) | 1261(3) | 1459(5) |
| | C(6) | 6999(4) | 287(3) | 2309(5) |
| | O(7) | 7454(3) | 360(1) | 4368(3) |
| | C(8) | 7972(5) | −566(2) | 5272(5) |
| | C(9) | 8234(4) | −418(2) | 7440(5) |

## Acknowledgment.

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Table 4

Bond Distances (Å), Bond Angles (°) and Torsion Angles (°)

| Molecule | 1 | 2 | 3 | 4 | 1 - 2 | 1 - 2 - 3 | 1-2-3-4 |
|---|---|---|---|---|---|---|---|
| **1** | C(12) | S(1) | C(2) | C(3) | 1.806(7) | 103.5(3) | −62.7(5) |
| | S(1) | C(2) | C(3) | S(4) | 1.821(7) | 112.7(5) | 175.2(3) |
| | C(2) | C(3) | S(4) | C(5) | 1.487(8) | 113.1(5) | −60.4(5) |
| | C(3) | S(4) | C(5) | C(6) | 1.821(7) | 101.6(3) | −62.0(6) |
| | S(4) | C(5) | C(6) | S(7) | 1.808(6) | 115.3(5) | 176.0(4) |
| | C(5) | C(6) | S(7) | C(8) | 1.500(9) | 114.5(5) | −66.9(6) |
| | C(6) | S(7) | C(8) | C(9) | 1.801(6) | 104.1(3) | −70.9(5) |
| | S(7) | C(8) | C(9) | O(10) | 1.818(8) | 114.7(5) | 71.7(6) |
| | C(8) | C(9) | O(10) | C(11) | 1.512(12) | 108.8(4) | 173.3(6) |
| | C(9) | O(10) | C(11) | C(12) | 1.411(7) | 113.7(4) | 174.1(6) |
| | O(10) | C(11) | C(12) | S(1) | 1.433(9) | 107.6(5) | 70.0(7) |
| | C(11) | C(12) | S(1) | C(2) | 1.515(10) | 116.0(5) | −74.8(6) |
| **2** | C(15) | S(1) | C(2) | C(3) | 1.801(6) | 103.2(2) | −73.2(4) |
| | S(1) | C(2) | C(3) | S(4) | 1.810(5) | 112.8(3) | −166.8(3) |
| | C(2) | C(3) | S(4) | C(5) | 1.507(7) | 114.3(3) | −89.3(4) |
| | C(3) | S(4) | C(5) | C(6) | 1.802(5) | 103.1(2) | 77.0(4) |
| | S(4) | C(5) | C(6) | O(7) | 1.798(5) | 113.3(3) | 170.7(3) |
| | C(5) | C(6) | O(7) | C(8) | 1.504(7) | 108.1(4) | 179.5(4) |
| | C(6) | O(7) | C(8) | C(9) | 1.417(5) | 113.3(4) | −88.6(5) |
| | O(7) | C(8) | C(9) | O(10) | 1.427(7) | 113.2(4) | 68.3(6) |
| | C(8) | C(9) | O(10) | C(11) | 1.489(9) | 111.2(4) | −169.3(4) |
| | C(9) | O(10) | C(11) | C(12) | 1.405(5) | 112.3(4) | −179.9(4) |
| | O(10) | C(11) | C(12) | O(13) | 1.427(7) | 109.2(4) | −58.8(6) |
| | C(11) | C(12) | O(13) | C(14) | 1.500(7) | 109.9(5) | −166.0(5) |
| | C(12) | O(13) | C(14) | C(15) | 1.426(7) | 111.8(4) | −176.2(4) |
| | O(13) | C(14) | C(15) | S(1) | 1.416(6) | 109.3(5) | 85.7(5) |
| | C(14) | C(15) | S(1) | C(2) | 1.514(9) | 114.8(4) | −81.9(4) |
| **3** | S(2') | C(1') | C(1) | S(2) | | | 61.4(5) |
| | C(1') | C(1) | S(2) | C(3) | 1.479(7) | 116.2(4) | 57.9(4) |
| | C(1) | S(2) | C(3) | C(4) | 1.797(4) | 104.1(3) | 68.2(4) |
| | S(2) | C(3) | C(4) | O(5) | 1.772(7) | 116.1(5) | −77.5(6) |
| | C(3) | C(4) | O(5) | C(6) | 1.527(7) | 107.0(3) | 165.9(5) |
| | C(4) | O(5) | C(6) | C(7) | 1.411(6) | 112.5(3) | −174.2(6) |
| | O(5) | C(6) | C(7) | O(8) | 1.421(6) | 108.1(4) | 66.3(7) |
| | C(6) | C(7) | O(8) | C(9) | 1.483(7) | 109.6(6) | −179.8(7) |
| | C(7) | O(8) | C(9) | C(9') | 1.416(7) | 112.7(4) | −178.5(4) |
| | O(8) | C(9) | C(9') | O(8') | 1.419(5) | 110.4(5) | −77.9(6) |
| | C(9) | C(9') | | | 1.468(9) | | |
| **4** | C(9') | S(1) | C(2) | C(3) | 1.818(3) | 104.1(2) | 71.9(3) |
| | S(1) | C(2) | C(3) | O(4) | 1.818(4) | 115.6(3) | −68.9(3) |
| | C(2) | C(3) | O(4) | C(5) | 1.492(6) | 109.2(3) | −174.3(3) |
| | C(3) | O(4) | C(5) | C(6) | 1.415(4) | 113.4(3) | −173.4(3) |
| | O(4) | C(5) | C(6) | O(7) | 1.415(4) | 109.4(3) | −67.3(3) |
| | C(5) | C(6) | O(7) | C(8) | 1.493(5) | 109.6(3) | 173.9(3) |
| | C(6) | O(7) | C(8) | C(9) | 1.412(4) | 112.4(3) | −173.5(3) |
| | O(7) | C(8) | C(9) | S(1') | 1.410(4) | 107.3(3) | −175.6(2) |
| | C(8) | C(9) | S(1') | C(2') | 1.503(5) | 113.3(2) | −65.3(3) |