X-Ray Crystal Structures of Three Cyclic Thioethers

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Summary The structures of three macrocyclic thioethers with ring sizes varying from 12 to 18 atoms have been determined by X-ray diffraction and the donor atoms have been found to be nearly coplanar with the sulphur atoms directed out of the ring.

Recently, several compounds which resemble the macrocyclic polyethers synthesized by Pedersen[1] have been prepared in which one or more oxygen atoms have been replaced by sulphur atoms.[2] Like the cyclic ethers the cyclic thioethers form complexes with metal ions but the thermodynamic stabilities of the complexes may differ considerably from those of the all oxygen compounds. For example, when sulphur replaces oxygen as the donor atom in crown-5 and crown-6 ligands the stability of the silver complexes increases while that of the potassium complexes decrease.[3]

We have begun a study of the conformational changes which occur when oxygen atoms of the cyclic polyethers are replaced by sulphur atoms. The structures of the three compounds investigated are shown in the Figure. We use an extension of the nomenclature proposed by Pedersen.[1]

Crystal data: 1,4,7-trithio-(12-crown-4),[4] $C_8H_{16}OS_3$, (I). Space group $P2_1/a$, $a = 8{\cdot}230(1)$, $b = 17{\cdot}120(1)$, $c = 8{\cdot}705(1)$ Å, $\beta = 115{\cdot}44(2)°$, $Z = 4$; 1377 independent reflections were measured on a diffractometer with Ni-filtered Cu-K_α radiation; current R 0·078.

The trial structure of (I) was obtained by heavy-atom methods and was refined by full-matrix least-squares procedures. The donor atoms are nearly coplanar with the sulphur atoms directed out of the cavity. A projection of the molecule down the b axis resembles a heart with the oxygen atom O(4) pointing into the cavity. The shortest distance across the ring of 4·46 Å is from O(4) to S(2) at the point of the heart.

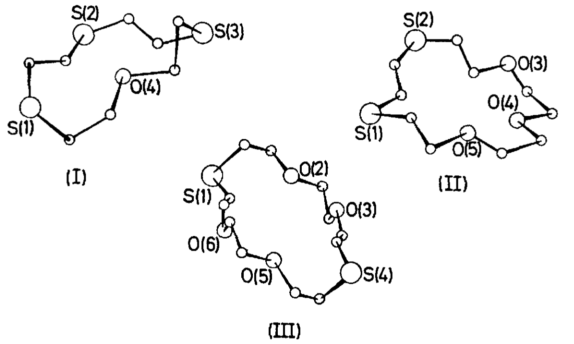

FIGURE. Structures of 1,4,7-trithio-(12-crown-4), (I); 1,4-dithio-(15-crown-5), (II), and 1,10-dithio-(18-crown-6), (III).

Crystal data: 1,4-dithio-(15-crown-5), $C_{10}H_{20}O_3S_2$, (II). Space group $P\bar{1}$ $a = 9{\cdot}170(7)$, $b = 10{\cdot}148(7)$, $c = 7{\cdot}328(6)$Å, $\alpha = 87{\cdot}47(2)$, $\beta = 106{\cdot}04(2)$, $\gamma = 99{\cdot}47(2)°$, $Z = 2$; 2422 independent reflections were measured on a diffractometer with Ni-filtered Cu-K_α radiation; current R 0·11.

The two sulphur atoms of (II) were located in a Patterson map. Phases determined by the sulphur atoms were expanded by symbolic addition methods and the resulting E map yielded the remaining atoms. This model was refined by full-matrix least-squares procedures. The donor atoms of (II) are nearly coplanar with $S(1)$ and $S(2)$ and one oxygen atom, O(3), directed out of the cavity. The distances across the ring between two donor atoms not connected by the same carbon bridge range from 4·83 Å between O(3) and O(5) to 6·44 Å from $S(1)$ to O(3).

Crystal data: 1,10-dithio-(18-crown-6), $C_{12}H_{24}O_4S_2$, (III). Space group $P2_1/n$, $a = 8{\cdot}561(1)$, $b = 13{\cdot}330(2)$, $c = 7{\cdot}050(1)$ Å, $\beta = 104{\cdot}08(1)°$, $Z = 2$; 1459 independent reflections were measured on a diffractometer with Ni-filtered Cu-K_α radiation. Current R 0·079.

The trial model of (III) was obtained by heavy-atom methods and the model was refined by full-matrix least-squares procedures. The molecule is located about a centre of symmetry. The heteroatoms are nearly coplanar and they form an elliptical cavity. The shortest distance across the cavity, 4·6 Å, is between symmetry-related oxygen atoms. The sulphur atoms are directed out of the cavity.

The consistent feature of the three structures is that all sulphur atoms of all three compounds are directed out of the cavities. The oxygen atoms are directed into the cavities with the exception of one oxyygen atom in the crown-5 compound. By way of comparison with cyclic ethers containing only oxygen donor atoms, in both the *cis-syn-cis* and *cis-anti-cis* isomers (isomers A and B′, respectively) of dicyclohexyl-18-crown-6 the two axial oxygen atoms are directed out of their respective cavities.[5] This feature causes the cavities of both isomers to be more elliptical than that of (III). In all three sulphur-substituted crown compounds the average C–C distances in the ring [(I), 1·49; (II), 1·51; (III), 1·50 Å] appear to be shorter than the expected C–C distance (1·54 Å).[6] The shortening of C-C bonds is also observed in crown compounds containing only oxygen as the donor atom.[7]

It seems unlikely that a metal ion could be located in the cavity of (I) from size considerations. As the size of the ring cavity increases, metal complexation within the cavity seems more likely. It remains now to determine structures of metal complexes of the larger sulphur ligands to learn the effect of the metal ion on the ligand conformation. The effect of metal complexation in cyclic polyethers is to cause the cavity to become more circular with the donor atoms directed toward the metal ion in the centre of the cavity.[5,8]

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