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The Structure of the 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Bis(dimethyl sulphone) Complex

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Abstract

$C_{12}H_{24}O_6.2C_2H_6O_2S$ is monoclinic, $P2_1/n$, with $a = 8{\cdot}852\ (4)$, $b = 16{\cdot}440\ (8)$, $c = 8{\cdot}389\ (2)$ Å, $\beta = 107{\cdot}39\ (2)°$, $U = 1165{\cdot}0$ Å^3, $Z = 2$, $D_m = 1{\cdot}26$, $D_c = 1{\cdot}29$ Mg m^{-3}. Final $R = 0{\cdot}049$ for 1902 observed reflections. The centrosymmetrical 18-crown-6 molecule has approximately D_{3d} symmetry; one methyl group of each dimethyl sulphone molecule yields three C—H$\cdots$O contacts of 2·47 (4), 2·48 (4) and 2·62 (4) Å to alternate O atoms.

Introduction

The macrocyclic polyether, 18-crown-6, which was first synthesized by Pedersen (Pedersen, 1967) has proved a versatile complexing agent, not only for cations of suitable radius, approximately 0·8 Å and larger, but also as an acceptor of hydrogen bonds from O—H, N—H, and even C—H groups, as in the compounds formed with the dimethyl ester of acetylenedicarboxylic acid (Goldberg, 1975) or that with malononitrile (Kaufman, Knöchel, Kopf, Oehler & Rudolph, 1977); the compound can be purified *via* its complex with acetonitrile (Gokel, Cram, Liotta, Harris & Cook, 1974). Recently, Vögtle & Müller (1980) have reported a variety of molecular complexes with this and other crown ethers observing, as had Pedersen (1971) in his investigation of thiourea/crown interactions, a variety of stoichiometries. A crystalline complex having stoichiometry (2:1) dimethyl sulphone:18-crown-6 is the subject of the present study.

It was necessary to coat the crystals in Araldite to lessen decomposition in air; even so, two crystals were required for complete collection of intensities. Observations were collected on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70926$ Å). No absorption correction was

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applied, $\mu = 0{\cdot}261$ mm^{-1}. Accurate unit-cell dimensions, obtained from high-θ reflections on crystal A ($0{\cdot}38 \times 0{\cdot}30 \times 0{\cdot}30$ mm), were used to index a Guinier powder photograph showing that there was one phase in the sample. This crystal was used to collect reflections in the range $1 \leq \theta \leq 20°$. Two intensity-control reflections ($13\bar{1}$ and 432) were measured every 3600 s. When one had fallen to 75% of its initial value, 1038 unique reflections had been measured including the systematically absent ones. A second crystal, B ($0{\cdot}46 \times 0{\cdot}56 \times 0{\cdot}41$ mm), was used to repeat 50 intensities for scaling purposes and then to cover the range $20 \leq \theta \leq 27°$. This gave a further 1754 reflections. Lorentz and polarization corrections were applied as were scaling factors and compensation for fading intensity. The systematically absent reflections had been considered weak on the criterion $\sigma(I)/I > 1{\cdot}0$ confirming the space group. Of the total of 2530 unique reflections, 628 had $4\sigma(F) > |F|$ and were not used for structure determination.

The structure was solved by Patterson synthesis, the S atom serving to phase one electron-density difference map which revealed all the C and O atoms. After isotropic refinement to $R = 0{\cdot}11$, the methyl H atoms were located in a difference map. These atoms were included in subsequent refinements with a common isotropic vibration parameter. H atoms of the 18-crown-6 molecule were included in calculated positions, C—H = 0·98 Å, with a common vibration parameter. The other atoms were allowed anisotropic vibration parameters and full-matrix least-squares refinement converged at $R = 0{\cdot}049$. The highest peak on the final difference map was 0·22 e Å^{-3}. Scattering factors were calculated using the analytical approximation coefficients in *International Tables for X-ray Crystallography* (1974). A good weighting analysis was obtained with the scheme $5{\cdot}2660/[\sigma^2(F) + 0{\cdot}001052 \times F^2]$ where $\sigma^2(F)$ values were derived from counting statistics. The programs *SHELX* (Sheldrick, 1976), *ORTEP* (Johnson, 1965) and the CAD-4 processor program, Queen Mary College, 1976, were run on the ICL System 4 in the Computer Department, Rothamsted Experimental Station. For calculation of molecular geometry the suite *X-RAY ARC* (1973) was used on the IBM 1130 computer. Atomic coordinates are given in Table 1 and a view of the molecule with the numbering scheme is shown in Fig. 1. H atoms of CH$_2$ groups on the 18-crown-6 molecule are referred to as C(n)A and C(n)B, n being the designation of the C atom.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* U_{eq} ($\times 10^3$) *with e.s.d.'s in the least significant figures in parentheses*

$U_{\rm eq}$ is defined as $\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*$ $(\mathbf{a}_i.\mathbf{a}_j)$. For H atoms the common $U_{\rm iso}$ value is shown.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$ (Å^2)
O(1)	3415 (2)	4562 (1)	−3299 (2)	64 (1)
C(2)	2423 (3)	3872 (2)	−3382 (4)	71 (1)
C(3)	3306 (3)	3237 (2)	−2232 (4)	70 (1)
O(4)	3517 (2)	3472 (1)	−549 (3)	67 (1)
C(5)	4314 (4)	2863 (2)	586 (5)	75 (1)
C(6)	4668 (4)	3174 (2)	2344 (4)	75 (1)
O(7)	5871 (2)	3759 (1)	2640 (2)	62 (1)
C(8)	6210 (4)	4124 (2)	4255 (3)	71 (1)
C(9)	7336 (4)	4809 (2)	4400 (3)	72 (1)
S(10)	8343 (1)	3886·7 (4)	−655 (1)	54·6 (2)
O(11)	7541 (3)	3125 (1)	−1153 (3)	85 (1)
O(12)	9201 (3)	4214 (2)	−1721 (3)	82 (1)
C(13)	6991 (3)	4613 (2)	−412 (4)	62 (1)
H(13)*A*	7524 (45)	5107 (24)	−87 (45)	92 (5)
H(13)*B*	6244 (45)	4657 (22)	−1630 (47)	92 (5)
H(13)*C*	6531 (44)	4365 (25)	237 (49)	92 (5)
C(14)	9674 (4)	3765 (2)	1342 (5)	78 (1)
H(14)*A*	10160 (46)	4263 (25)	1832 (48)	92 (5)
H(14)*B*	9139 (44)	3586 (23)	2206 (46)	92 (5)
H(14)*C*	10320 (46)	3351 (26)	1224 (47)	92 (5)

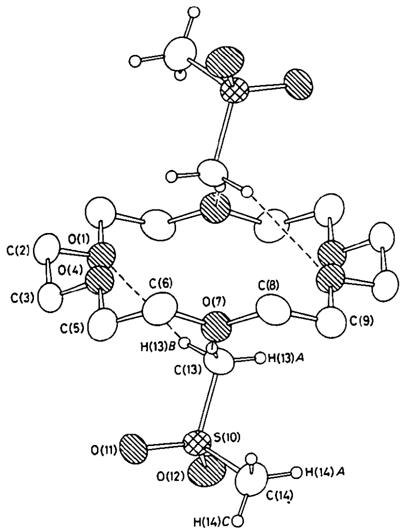

Fig. 1. One molecular complex showing the numbering of the atoms in the asymmetric unit; those related by the centre of symmetry are denoted by the superscript i in the text and Fig. 2. The broken lines indicate possible CH···O hydrogen bonds <2·50 Å.

Discussion

The dimensions (Table 2) of the 18-crown-6 molecule do not differ significantly from those of the uncomplexed molecule at room temperature (Dunitz & Seiler, 1974), including the apparent shortening of the bond lengths as a result of thermal motion as discussed

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35961 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in a recent paper describing the structure of the uncomplexed molecule at 100 K (Maverick, Seiler, Schweizer & Dunitz, 1980). The torsion angles differ from those of the uncomplexed molecule and correspond to approximate D_{3d} symmetry.

For dimethyl sulphone the structure determination at room temperature gave the dimensions (Langs, Silverton & Bright, 1970) S–O 1·446 (3), S–C 1·765 (5) Å, and O–S–O 117·6 (1), O–S–C 108·3 (2) and C–S–C 105·1 (2)° with C–H in the range 0·82–1·04 Å. The only significant difference in the complex with 18-crown-6 is in the shortening of the S–C bond (Δ/δ = 3·5). As similar thermal vibration parameters were found in both structures the difference in bond length may be real and an example of the general phenomenon, namely the shortening of a bond to a hydrogen-bond donor atom (Beagley, 1975).

The two molecules of 'guest' interact with the 'host' *via* two, or possibly three, C(13)–H···O contacts as shown in Table 3. Alternate O atoms O(1), O(7) and O(4^{i}) deviate from the best plane through all six O atoms by 0·115 (2), 0·098 (2) and 0·187 (2) Å respectively and C(13) is 1·632 (3) Å from this plane with the S–C bond making an angle of 18·9 (3)° with the normal to the plane. The angles subtended at the H atoms are 131 (3), 142 (3) and 165 (4)° for H(13)*A*, H(13)*B* and H(13)*C* respectively. All the O atoms of the crown molecule appear to be recipients of hydrogen bonds which are nearly coplanar with the CH_2–O–CH_2 groups consistent with a trigonal, rather than a tetrahedral, distribution of neighbours around the O atoms. The interaction with all three methyl H atoms found in this complex contrasts with the bonding between 18-crown-6 and the methyl groups of the acetylenedicarboxylic acid ester (Goldberg, 1975). While the approximate D_{3d} symmetry and the centrosymmetrical relation between the two ligand methyl groups are common features, in the methyl ester only two of the H atoms are bonded to the crown ether, one at 2·32 Å and the other at 2·45 Å, to a pair of centrosymmetrically related O atoms (each of these O atoms thus receives two hydrogen bonds and should have tetrahedral hybridization). For these hydrogen contacts the C–H···O angles are 162 and 169°. The shorter C–O distance is 3·38 Å. The third H atom points away from the crown ether. The methyl C atom is 1·89 Å from the mean plane through the six O atoms. A secondary feature noted by Goldberg was another O atom contact to the methyl C at 3·079 Å. The bonding by the methyl ester is very similar to that shown by malononitrile in the 2:1 complex (Kaufman *et al.*, 1977). The guest has two available H atoms which are at 2·24 (3) and 2·69 (4) Å from a pair of centrosymmetrically related O atoms, the shorter C···O distance being 3·257 (3) Å.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

In 18-crown-6

W–*X*–*Y*–*Z*	Distance *X*–*Y*	Angle *W*–*X*–*Y*	Torsion angle
C(9^{i})–O(1)–C(2)–C(3)	1·423 (4)	112·8 (2)	178·5 (2)
O(1)–C(2)–C(3)–O(4)	1·477 (4)	109·5 (2)	71·9 (3)
C(2)–C(3)–O(4)–C(5)	1·421 (4)	110·1 (2)	178·0 (2)
C(3)–O(4)–C(5)–C(6)	1·417 (3)	111·5 (2)	173·8 (2)
O(4)–C(5)–C(6)–O(7)	1·503 (5)	109·5 (3)	−71·8 (3)
C(5)–C(6)–O(7)–C(8)	1·401 (3)	109·4 (2)	176·2 (2)
C(6)–O(7)–C(8)–C(9)	1·429 (3)	113·0 (2)	−172·6 (2)
O(7)–C(8)–C(9)–O(1^{i})	1·484 (5)	110·0 (2)	66·9 (3)
C(8)–C(9)–O(1^{i})–C(2^{i})	1·413 (3)	109·1 (2)	178·9 (2)

In dimethyl sulphone

S(10)–O(11)	1·439 (2)	O(11)–S(10)–O(12)	116·8 (2)
S(10)–O(12)	1·440 (2)	O(11)–S(10)–C(13)	109·5 (1)
S(10)–C(13)	1·745 (3)	O(11)–S(10)–C(14)	108·1 (2)
S(10)–C(14)	1·748 (3)	O(12)–S(10)–C(13)	108·9 (2)
		O(12)–S(10)–C(14)	108·0 (2)
		C(13)–S(10)–C(14)	104·8 (2)
C(13)–H(13)*A*	0·938 (39)	H(13)*A*–C(13)–H(13)*B*	110·0 (3·0)
C(13)–H(13)*B*	1·040 (37)	H(13)*A*–C(13)–H(13)*C*	120·8 (3·4)
C(13)–H(13)*C*	0·872 (40)	H(13)*B*–C(13)–H(13)*C*	111·5 (3·3)
C(14)–H(14)*A*	0·958 (40)	H(14)*A*–C(14)–H(14)*B*	100·7 (3·0)
C(14)–H(14)*B*	1·020 (38)	H(14)*A*–C(14)–H(14)*C*	117·9 (3·3)
C(14)–H(14)*C*	0·914 (40)	H(14)*B*–C(14)–H(14)*C*	107·5 (3·2)
		S(10)–C(13)–H(13)*A*	108·9 (2·3)
		S(10)–C(13)–H(13)*B*	100·9 (2·0)
		S(10)–C(13)–H(13)*C*	102·5 (2·6)
		S(10)–C(14)–H(14)*A*	113·6 (2·3)
		S(10)–C(14)–H(14)*B*	113·0 (2·1)
		S(10)–C(14)–H(14)*C*	104·2 (2·4)

A 2:1 stoichiometry does not necessarily induce D_{3d} symmetry, as shown in the benzenesulphonamide (Knöchel, Kopf, Oehler & Rudolph, 1978) and guanidinium nitrate (Bandy, Truter & Wingfield, 1981) complexes.

Approximate D_{3d} symmetry is found in 18-crown-6 complexes of 1:1 stoichiometry having RNH_3^+ as the coordinating entity. Goldberg (1980) suggested that all six O atoms were involved, three as recipients of

Table 3. *Intramolecular distances* $\lesssim$3·5 Å *for non*-H *atoms*, <2·75 Å *for* O···H *contacts*, <2·6 Å *for* H···H *contacts*

(*a*) Between dimethyl sulphone and the 18-crown-6 molecule centred at $\frac{1}{2}$,$\frac{1}{2}$,0

C(13)···O(1)	3·363 (4)	H(13)*B*···O(1)	2·48 (4)
C(13)···O(4^{i})	3·314 (4)	H(13)*C*···O(7)	2·47 (4)
C(13)···O(7)	3·321 (4)	O(11)···H(3)*A*	2·71
H(13)*A*···O(4^{i})	2·62 (4)	O(11)···H(5)*B*	2·73

(*b*) Between (dimethyl sulphone)$_2$ 18-crown-6 entities

O(12^{ii})···C(9^{iii})	3·326 (4)	O(11^{ix})···C(6^{viii})	3·333 (4)
O(12^{ii})···H(9^{iii})*B*	2·64	H(3^{vi})*B*···H(5^{vii})*B*	2·47
O(12^{v})···H(2^{iv})*A*	2·61	H(3^{vi})*B*···H(14^{vii})*B*	2·56
O(12^{xi})···C(14^{xi})	3·456 (5)	H(5^{vi})*A*···H(8^{vii})*B*	2·46
O(12^{xi})···H(14^{xi})*A*	2·58 (4)	H(8^{x})*A*···H(8^{x})*A*	2·50

Symmetry code: (i) $1 - x, 1 - y, -z$; (ii) $x, y, z - 1$; (iii) $x, y, 1 + z$; (iv) $x - 1, y, z$; (v) $1 + x, y, z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (viii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (ix) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (x) $1 - x, 1 - y, 1 - z$; (xi) $2 - x, 1 - y, -z$.

hydrogen bonds, and the other three having lone pairs directed towards the N^+. The methyl group on one side of the 18-crown-6 in the dimethyl sulphone complex can be visualized as comparable with the RNH_3^+ entity. The difference is that the uncharged C atom does not attract lone pairs from the other three O atoms so they can act as recipients to hydrogen bonds from a second methyl group yielding a complex with stoichiometry 1:2.

Within the asymmetric unit the methyl C—H···O (ether) distances are shorter than the methylene C—H···O (dimethyl sulphone) distances. The shortest of the latter type of contacts are H(3)*A* and H(5)*B*···O(11) at 2·71 and 2·73 Å respectively, with the corresponding C···O distances greater than 3·5 Å. These are longer than the intermolecular contacts, of which the shortest is between dimethyl sulphone molecules related by the centre of symmetry at $1,\frac{1}{2},0$, $H(14^{xi})A\cdots O(12^{xi})$, see Fig. 2 and Table 3, the C(14)···O(12) distance being 3·456 (5) Å. The next shortest contacts are between the dimethyl sulphone and a crown molecule. Intermolecular contacts involving dimethyl sulphone are shorter than in the crystal of the uncomplexed molecule (Langs *et al.*, 1970) for which there are no non-H contacts <3·5 Å. The volume occupied per complex molecule is not significantly different from that occupied by the components as packed in their pure crystals.

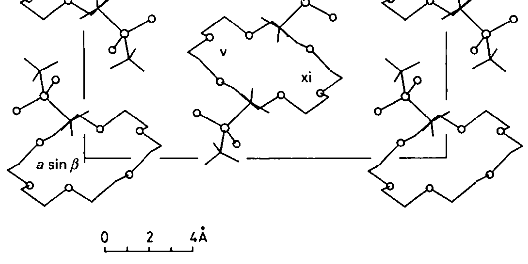

Fig. 2. The structure projected along the *c* axis. Roman numerals are defined in Table 3. ii and iii are respectively below and above the crystal chemical unit; viii is above vi; ix is below vii; x is above i.

18-Crown-6 bis(dimethyl sulphone) complex (by F. Vögtle)

264 mg (1·0 mmol) of 18-crown-6 and 188 mg (2·0 mmol) of dimethyl sulphone in 4 ml methyl acetate are refluxed for 30 min. After cooling to room temperature colourless crystals are obtained with m.p. 367–368 K in 312 mg (68·9%) yield. $C_{16}H_{36}O_{10}S_2$ (452·6): Calc. C, 42·46; H, 8·03%. Found: C, 42·45, H, 8·02%.

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