1,4,7,10-Tetraoxacyclododecane– triphenylmethanethiol (1/2)

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In the centrosymmetric formula unit of the title complex, $C_8H_{16}O_4 \cdot 2C_{18}H_{16}S$, the 1,4,7,10-tetraoxacyclododecane molecule adopts the biangular [66] conformation, and the triphenylmethanethiol molecules are linked to the macrocycle via a long S—H···O hydrogen bond [S···O = 3.460 (2) Å and S—H···O = 161 (2)°]. Attractive interactions of phenyl groups in edge-to-face conformations combine inversion-related formula units into chains running along the [111] direction in the crystal structure. Association of the chains into sheets is achieved via C—H···π interactions.

Comment

Thiols fulfill numerous functions in biological systems, including a central role in coordinating antioxidant defences (Sen & Packer, 2000). A search of the Cambridge Structural Database (CSD; Version 5.26, plus one 2005 update; Allen, 2002) revealed only a few examples of thiol-containing adducts with neutral organic molecules, predominantly with organic solvents or water. In 2-mercapto-6-methylpurine monohydrate (Srinivasan & Chandrasekaran, 1968) and D-N-γ-L-glutamyl-L-cysteine ethyl ester monohydrate (Takimoto-Kamimura et al., 1990), the thiol functional group is involved in an S—H···O(water) hydrogen bond, while in the case of adducts with organic solvents, the thiol molecules exhibit a tendency to be self-assembling and the thiol functional group contributes to the overall system of hydrogen bonding via S—H···O(=C), C—H···S(SH) (Evans et al., 1993; Pyrka et al., 1992), S—H···S (Ung et al., 1994; Hardy et al., 1979) or S—H···π interactions (Walsdorff et al., 1997). Only one compound, namely bis(4-aminophenyl) disulfide 4-amino-thiophenol (Vangala et al., 2002), exhibits assembly of different molecules via C—H···S hydrogen bonds.

For more than two decades, crown ethers have been a very useful tool for following interaction pathways between neutral molecules, including biologically important pathways. As a continuation of our contribution to this topic (Simonov et al.,

2003), we report here the crystal structure of the title binary adduct, (I), of triphenylmethanethiol with 1,4,7,10-tetraoxacyclododecane (12-crown-4, 12C4). Compound (I) is the first example of an adduct between a thiol and a crown ether to be structurally described. The main points of this report concern the mode of mutual interaction in this binary system, and the similarities and differences in the crystal packing of triphenylmethanethiol itself and its binary adduct.

(I)
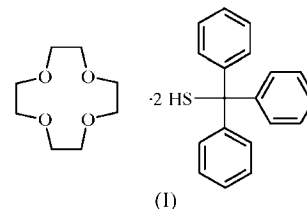
The published metal-free crystal structures of 12C4 with neutral molecules include a ternary clathrate with γ-cyclodextrin and water (Kamitori et al., 1986), binary adducts of the general formula 12C4·2D, where D is the zwitterion $^+H_3NSO_3^-$ (Simonov et al., 1993), Ph$_3$SiOH (Babaian et al., 1990), (PhSO$_2$)$_2$NH (Wijaya et al., 1998), (EtSO$_2$)$_2$CH$_2$ (Michalides et al., 1995) or Me$_2$CNNHC(=S)NH$_2$ (Moers et al., 1999), and the binary adduct with dithiobisurea, (NH$_2$CSNH)$_2$, in a 1:1 ratio (Simonov et al., 2003). The structures of these adducts are held together by O—H···O, N—H···O or C—H···O hydrogen bonds between the respective substrate and 12C4. No examples of crown ether complexes held together by S—H···O hydrogen bonds are known to date.

The centrosymmetric formula unit of (I) is shown in Fig. 1 and selected intramolecular geometric data are listed in Table 1. The geometries of both molecules are in reasonable agreement with the precise data obtained for crown ethers and triphenylmethanethiol itself (Bernardinelli et al., 1991). The macrocycle in (I) adopts the C_i symmetric and biangular [66] conformation, which also occurs in pure 12C4 (Groth, 1978) in the aforementioned 1:2 complexes and in several structures containing metal cations. The torsion angles of the 12C4 ring are given in Table 1.
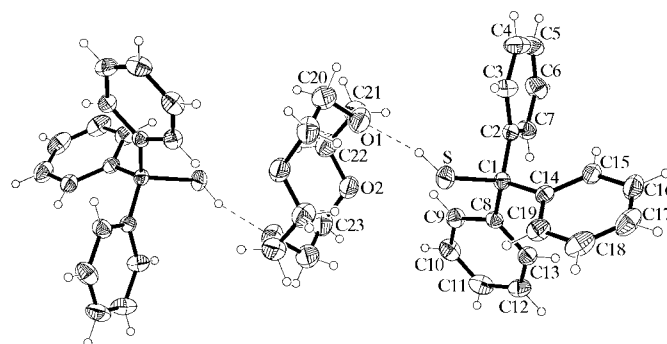

Figure 1
The structure of (I) in the crystal, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the asymmetric unit is numbered; unlabelled atoms are related by the symmetry code $(1 - x, -y, 1 - z)$. Hydrogen bonds are shown as dashed lines.

organic compounds

Within the centrosymmetric formula unit, a long S—H···O hydrogen bond (and its symmetry equivalent) links the thiol molecules to the crown ether. Inversion-related formula units are then associated into chains (Fig. 2) *via* attractive interactions of the phenyl groups in an edge-to-face (ef) conformation. This concerted intermolecular attraction uses six phenyl ef interactions from two inversion-related triphenylmethanethiol moieties. As shown in Fig. 2, the two Ph$_3$C groups approach each other such that each phenyl ring is interleaved between two rings on the other molecule, with two H atoms on each ring directed towards C atoms of a phenyl ring on the other molecule. This concerted motif, known as a sextuple phenyl embrace (SPE; Dance & Scudder, 1995), was primarily explored for structures containing PPh$_4^+$ cations or terminating XPh$_3$ ligands and covering P···P separations in the range 5.5–8.0 Å (Scudder & Dance, 2002). The SPE in (I) is characterized by a C1···C1($-x$, $1-y$, $-z$) distance of 6.393 (3) Å. Finally, interchain crosslinking is achieved *via* C—H···π interactions [C5—H5···Cg2: C···Cg = 3.679 (3) Å, H···Cg = 2.99 Å and C—H···Cg = 132°, where Cg2 is the centroid of phenyl ring C8–C13 at ($x-1$, y, z)], resulting in the association of the chains into sheets.

Some similarities between the supramolecular architecture of (I) and the triphenylmethanethiol molecules in the pure form (CSD refcode SIZBAE, space group $P\bar{1}$; Bernardinelli *et al.*, 1991) are noteworthy. There are two independent molecules in the SIZBAE structure. For the molecule containing atom S1, there is one significant S—H···π interaction [S1—H1···Cg: H···Cg = 2.62 Å, S···Cg = 3.73 Å and S—H···Cg = 141°, where Cg is the centroid of ring C14–C19 at ($1-x$, $2-y$, $1-z$)], which combines these molecules into centrosymmetric dimers. These dimers are further combined into chains *via* the SPE; the distance between the tetrahedral C atoms [C1···C1($1-x$, $1-y$, $1-z$)] is 6.058 Å. For the molecule containing atom S2, the SPE is characterized by the distance between the tetrahedral C atoms [C20···C20($1-x$, $-y$, $2-z$)] of 6.312 Å. Only the SPE interaction remains in

(I), while the S—H···π contact is replaced by the S—H···O(crown) hydrogen bonds.

Comparison of (I) with the complex 12C4·2Ph$_3$SiOH (CSD refcode SELFIY; Babaian *et al.*, 1990) reveals that these two structures are isomorphous. Similar to (I), the structure of SELFIY is sustained by two inversion-related O—H···O hydrogen bonds (H···O = 1.91 Å and O···O = 2.756 Å) and the SPE; there is an Si1···Si1($-x$, $1-y$, $-z$) separation of 6.538 Å.

Experimental

A solution of 12C4 (0.176 g, 1 mmol) and Ph$_3$CSH (276 mg, 1 mmol) in a benzene–ethyl ether mixture (1:2 v/v, 4.5 ml) was stored for 1 d at 293 K in an open flask. Colourless transparent crystals of (I) suitable for X-ray analysis separated in a yield of 83% (0.303 g; m.p. 341–343 K). The crystals were soluble in methanol, ethanol, acetone and chloroform. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.62 (s, 2H, SH), 3.71 (s, 16H, 12C4), 7.22–7.30 (m, 30H, aromatic H). Analysis calculated for C$_{46}$H$_{48}$O$_4$S$_2$: C 75.79, H 6.64, S 8.80%; found: C 75.81, H 6.69, S 8.77%.

Crystal data

C$_8$H$_{16}$O$_4$·2C$_{19}$H$_{16}$S	$Z = 1$
$M_r = 728.96$	$D_x = 1.218$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.596$ (1) Å	Cell parameters from 25
$b = 9.803$ (1) Å	reflections
$c = 12.353$ (1) Å	$\theta = 4.8$–$12.5°$
$\alpha = 84.35$ (1)°	$\mu = 0.18$ mm^{-1}
$\beta = 89.18$ (1)°	$T = 293$ (2) K
$\gamma = 73.61$ (1)°	Prism, yellow
$V = 993.7$ (2) Å^3	$0.40 \times 0.36 \times 0.21$ mm

Data collection

Siemens $P4$ diffractometer	2730 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: empirical	$\theta_{max} = 26.0°$
(using intensity measurements)	$h = 0 \rightarrow 10$
(*SHELXTL-Plus*; Sheldrick,	$k = -11 \rightarrow 12$
1995)	$l = -15 \rightarrow 15$
$T_{min} = 0.877$, $T_{max} = 0.964$	3 standard reflections
4190 measured reflections	every 97 reflections
3914 independent reflections	intensity decay: 13.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 0.0975P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
3914 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
239 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

S—C1	1.8632 (17)		
C2—C1—S	109.48 (12)	C8—C1—S	108.70 (12)
C14—C1—S	104.82 (11)		
C20—O1—C21—C22	−89.1 (3)	C22—O2—C23—C20^i	−106.5 (3)
O1—C21—C22—O2	−69.4 (3)	O2—C23—C20^i—O1^i	72.2 (3)
C21—C22—O2—C23	171.6 (2)	C23—C20^i—O1^i—C21^i	−141.6 (2)

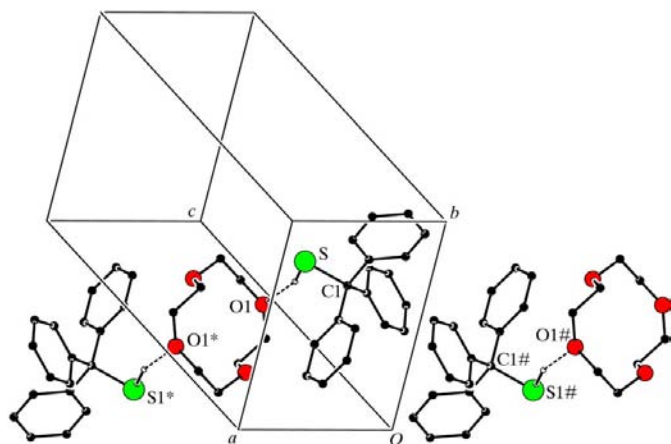Symmetry code: (i) $-x+1$, $-y$, $-z+1$.

Figure 2
The chain organization in (I) sustained by S—H···O hydrogen bonds and SPE interactions. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($1-x$, $-y$, $1-z$) and ($-x$, $1-y$, $-z$), respectively. Only S-bound H atoms are shown.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$S-H1\cdots O1$	1.33 (3)	2.17 (3)	3.460 (2)	161 (2)

The S-bound H atom was located in a difference Fourier map and refined isotropically. C-bound H atoms were placed in calculated positions, with C—H distances of 0.93 or 0.97 Å, and were treated using a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1238). Services for accessing these data are described at the back of the journal.

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