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Structure of a 1:2 Adduct between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Thiourea, C₁₂H₂₄O₆·2CH₄N₂S

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Abstract. $M_r = 416.4$, triclinic, $P\bar{1}$, $a = 8.368$ (7), $b = 8.691$ (9), $c = 8.680$ (9) Å, $\alpha = 114.9$ (1), $\beta = 106.8$ (1), $\gamma = 71.5$ (1)°, $V = 534.0$ Å³, $Z = 1$, $D_x = 1.29$, $D_m = 1.26$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 2.81$ cm⁻¹, $F(000) = 224$, room temperature, final $R = 0.061$ for 1829 independent observed reflections. The 18-crown-6 molecule contains a crystallographic centre of symmetry. Two thioureas are hydrogen-bonded on either side of the 18-crown-6 molecule *via* three N–H···O interactions. These crown.2thiourea adducts are connected *via* N–H···S hydrogen bonds to form a polymeric chain along the y axis.

Introduction. There has been an enormous amount of interest in adducts of the crown ethers particularly 18-crown-6 and over 300 structures containing this molecule have been reported so far. Of particular relevance to the present study are the 1:5 adduct with urea (Harkema, Van Hummel, Daasvatn & Reinhoudt, 1981), the 1:4 adduct with thiourea (Weber, 1984) and

the 1:2 adduct with N,N' -dimethylthiourea (Weber, 1983). We are also studying adducts between crown ethers and thiourea. We found that methanol solutions containing ratios of 18-crown-6 to thiourea of 1:1.25 and greater gave 1:4 adducts isomorphous with those of Weber. However, with a ratio of 1:1 we produced triclinic crystals with a 1:2 ratio of 18-crown-6 to thiourea. Accordingly we report here the crystal structure of this adduct (1).

Experimental. The 1:2 adduct was prepared by dissolving thiourea (0.76 g) in hot methanol (10 ml) and adding a hot solution of 18-crown-6 (2.64 g) in methanol (10 ml). The complex crystallized out after several hours and crystals suitable for diffraction work were washed in 2-propanol in order to remove the excess crown ether which adhered to them. The 1:4 adduct was prepared similarly, but with 3.20 g of 18-crown-6 and a total of 10 ml methanol. Crystals suitable for X-ray diffraction were formed overnight.

This complex was shown by single-crystal X-ray methods to be isomorphous with that obtained by Weber (1984) from acetone solutions.

Density measured by flotation in CCl_4 /ligroin. Precession photographs established preliminary cell constants. A suitable crystal of approximate size $0.2 \times 0.3 \times 0.3$ mm obtained as described above was mounted on a Stoe STADI-2 diffractometer to rotate about the a axis. Cell dimensions obtained by measurement of ca 20 high-angle ($35 < 2\theta < 50^\circ$) axial reflections. Intensity data collected *via* variable-width ω -scan, background counts 20 s, step-scan rate of $0.033^\circ \text{ s}^{-1}$ applied to a width of $(1.5 + \sin\mu/\tan\theta)^\circ$. Absorption and extinction corrections not applied. Standard reflections $h22$ measured every 20 measurements for each layer: no significant change in intensity. 2519 ($-10 \leq h \leq 11$, $-11 \leq k \leq 10$, $-12 \leq l \leq 11$) data measured with $2\theta_{\text{max}} = 50^\circ$. 1829 independent data with $I > 3\sigma(I)$ refined (on F) to R 0.061 (wR 0.065, S 1.75). Weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$ [$\sigma(F)$ from counting statistics] chosen to give similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F_o .

Structure determined using *MITHRIL* (Gilmore, 1984). Hydrogen atoms bonded to carbon included in calculated positions and their thermal parameters refined. Hydrogen atoms bonded to nitrogen allowed to refine independently. Hydrogen atoms on the same atom given an equivalent thermal parameter. Non-hydrogen atoms refined anisotropically *via* full-matrix least squares. Scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Final difference Fourier maps showed no important features (max. 0.29 , min. $-0.35 \text{ e } \text{\AA}^{-3}$) and in final cycles of refinement no shift $> 0.1\sigma$. Calculations performed using *SHELX76* (Sheldrick, 1976) and our own programs on the Amdahl V7A at the University of Reading.

Discussion. Final coordinates are given in Table 1 and molecular dimensions in Table 2.* The torsion angles (see Table 3) show the 18-crown-6 to have a D_{3d} centrosymmetric conformation with all $\text{O}-\text{C}-\text{O}$ torsion angles close to $\pm 70^\circ$ and all $\text{C}-\text{C}-\text{O}-\text{C}$ torsion angles close to 180° . Molecular-mechanics calculations (Bovill, Chadwick, Sutherland & Watkin, 1980) show that in isolation this is a relatively high-energy conformation for 18-crown-6 but it is clearly stabilized in some adducts. This conformation is observed in the 1:2 adduct of 18-crown-6 with dimethylthiourea (Weber, 1983) and it is noted that it occurs in a number of other 1:2 adducts, although a

different conformation (the so-called 'biangular' type) is found in the 1:5 adduct with urea (Harkema *et al.*, 1981) and the 1:4 adduct with thiourea (Weber, 1984).

Of particular interest are the intermolecular hydrogen bonds in the crystal. These are listed in Table 4 and illustrated in Figs. 1 and 2. All four hydrogen atoms in the thiourea molecule form hydrogen bonds; H(131) to O(7), H(132) a bifurcated bond to O(1) and O(4), H(121) to O(1) and H(122) to S(10). So three of these hydrogen atoms associate the two thiourea molecules with one crown. The attachment of two thioureas (or indeed ureas) on either side of the macrocycle (see Fig. 1) constitutes what may be termed a 1:2 core which is also found in the 1:4 thiourea adduct and also the 1:5 adduct with urea. In these latter examples these 1:2 core adducts are themselves linked by additional thiourea (or urea) molecules. However, in (1), they link themselves along the y axis *via* $\text{S}(10)\cdots\text{H}(122)-\text{N}(12)$

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

$$\bar{U} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	\bar{U}
S(10)	919 (1)	7391 (1)	2137 (1)	88 (1)
C(11)	2473 (3)	5610 (3)	2190 (3)	74 (3)
N(12)	2337 (4)	4026 (4)	1116 (4)	85 (3)
N(13)	3914 (3)	5726 (5)	3332 (4)	92 (4)
O(1)	5694 (3)	1598 (3)	2287 (3)	96 (3)
C(2)	7415 (4)	1291 (4)	2136 (5)	103 (4)
C(3)	7664 (4)	2742 (5)	1838 (5)	118 (5)
O(4)	7642 (3)	4228 (3)	3386 (3)	110 (3)
C(5)	7919 (4)	5665 (5)	3229 (5)	141 (5)
C(6)	8015 (4)	7102 (5)	4931 (5)	130 (5)
O(7)	6354 (3)	7860 (3)	5359 (3)	91 (3)
C(8)	6326 (5)	9244 (4)	6952 (5)	97 (5)
C(9)	4601 (6)	9749 (4)	7367 (4)	103 (4)

Table 2. Bond distances (\AA) and angles ($^\circ$)

S(10)-C(11)	1.685 (3)	O(4)-C(5)	1.407 (4)
C(11)-N(12)	1.317 (4)	C(5)-C(6)	1.479 (5)
C(11)-N(13)	1.323 (3)	C(6)-O(7)	1.419 (4)
O(1)-C(2)	1.414 (4)	O(7)-C(8)	1.400 (4)
C(2)-C(3)	1.474 (5)	C(8)-C(9)	1.474 (6)
C(3)-O(4)	1.418 (4)	C(9)-O(1 ¹)	1.430 (3)
S(10)-C(11)-N(12)	122.72 (20)	O(4)-C(5)-C(6)	109.63 (27)
S(10)-C(11)-N(13)	121.48 (24)	C(5)-C(6)-O(7)	109.61 (25)
N(12)-C(11)-N(13)	115.79 (28)	C(6)-O(7)-C(8)	113.38 (28)
O(1)-C(2)-C(3)	109.92 (27)	O(7)-C(8)-C(9)	108.25 (27)
C(2)-C(3)-O(4)	109.57 (27)	C(8)-C(9)-O(1 ¹)	110.11 (25)
C(3)-O(4)-C(5)	113.34 (26)	C(9)-O(1 ¹)-C(2)	112.09 (21)

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

Table 3. Torsion angles ($^\circ$) in the 18-crown-6

O(1)-C(2)-C(3)-O(4)	72.9 (1)	C(6)-O(7)-C(8)-C(9)	-171.8 (1)
C(2)-C(3)-O(4)-C(5)	178.3 (1)	O(7)-C(8)-C(9)-O(1 ¹)	68.3 (1)
C(3)-O(4)-C(5)-C(6)	-175.5 (1)	C(8)-C(9)-O(1 ¹)-C(2)	-171.2 (1)
O(4)-C(5)-C(6)-O(7)	-73.1 (1)	C(9)-O(1 ¹)-C(2)-C(3)	178.1 (1)
C(5)-C(6)-O(7)-C(8)	-179.6 (1)		

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

* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42256 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

intermolecular hydrogen bonds (see Fig. 2). A similar polymeric linkage is observed in the 1:2 adduct with dimethylthiourea (Weber, 1983) where the H...S distance is 2.54 (1) Å, rather similar to the present value.

X-ray (Kunchur & Truter, 1958; Truter, 1967) and neutron (Elcombe & Taylor, 1968) diffraction studies on thiourea itself have shown the molecule to be planar to within 0.01 Å excluding those hydrogen atoms involved in hydrogen bonding. This is to be expected for a system with delocalized π molecular orbitals involving the nitrogen atoms. The molecules are linked by almost linear N—H...S hydrogen bonds (N—S 3.35 to 3.43 Å and N—H...S 169 and 171°), values similar to those observed in (1). In (1), the S,C,N,N atoms are coplanar to within 0.00 (1) Å. In tetramethylthiourea, electron

diffraction (Fernholt, Samdal & Seip, 1981) reveals a pyramidal configuration at the nitrogen atoms with pyramid heights of 0.11 Å. Similar observations (X-ray diffraction) are reported by Åse & Roti (1974) and Hough & Nicholson (1981) for tetramethylthiourea complexed *via* the sulphur atom. This is not found in (1) as both CNH₂ groups are coplanar with a maximum deviation of 0.01 (3) Å. The hydrogen bonding in thiourea itself and (1) does not significantly influence the C—S bond length which in (1) is identical to the 1.673 (3) Å found by Fernholt *et al.* (1981) in tetramethylthiourea.

The existence of the 1:2 and 1:4 adducts of 18-crown-6 with thiourea indicates the difficulty of making predictions on the basis of just one crystal structure. Thus Weber (1984) has suggested that the reason why the 1:4 adduct is favoured for thiourea over the 1:5 adduct found in urea can be attributed to the longer S...N hydrogen-bond distance. Clearly the structure of the 1:2 adduct presented here suggests that this explanation is too simple. The formation of the 1:2 core adduct is clearly favoured in all three structures, but there are several ways of forming intermolecular hydrogen bonds between two thiourea (or two urea) molecules that are of similar energy. This results in the two types of adduct (1:2 and 1:4) for 18-crown-6 with thiourea. Clearly the existence of a 1:2 adduct with urea cannot be ruled out.

Table 4. *Intermolecular hydrogen bonds in 18-crown-6.2thiourea*

	N...O	H...O	N—H...O
N(12)—H(121)...O(1)	3.126 (4) Å	2.38 (4) Å	155 (3)°
N(13)—H(131)...O(7)	2.878 (4)	2.14 (5)	161 (3)
N(13)—H(132)...O(1)	3.249 (4)	2.47 (4)	153 (4)
N(13)—H(132)...O(4)	2.971 (3)	2.40 (5)	125 (6)
N(12)—H(122)...S(10 ⁱ)	3.415 (3)	2.65 (4)	168 (4)

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

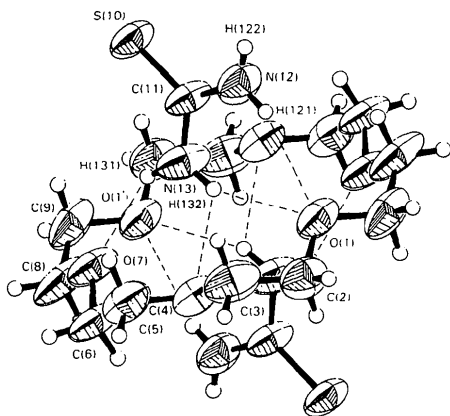


Fig. 1. The 18-crown-6-thiourea (1:2) adduct with thermal ellipsoids showing 50% probability. Hydrogen atoms are shown as small circles. The N—H...O intermolecular hydrogen bonds are shown as dashed lines.

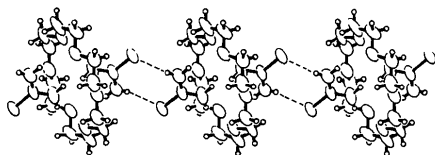


Fig. 2. The packing of the 18-crown-6-thiourea (1:2) adduct along the *y* axis. The N—H...S intermolecular hydrogen bonds are shown as dashed lines.

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