

# The Structure of a 1 : 4 Adduct Between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Thiourea

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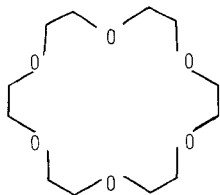
**Abstract.** The structure of 18-crown-6 · 4 thiourea has been determined by single crystal X-ray methods. The unit cell is monoclinic and the space group is  $P2_1$ , with  $a = 9.251(3)$ ,  $b = 19.285(8)$ ,  $c = 16.556(7)$  Å and  $\beta = 90.85(6)^\circ$ . There are two formula units,  $C_{12}H_{24}O_6 \cdot 4CH_4N_2S$ , in the asymmetric unit; final  $R = 0.086$ . One thiourea is attached at either side of the macrocycle ('biangular' conformation) via  $N-H \cdots O$  bonds and the patterns in the two crystallographically-independent adducts *A* and *B* differ slightly, involving two bifurcated hydrogen bonds in *A*. Core adducts are linked by additional thiourea molecules via  $N-H \cdots S$  bonds. As compared to the analogous 18-crown-6 · 5 urea, the present 1 : 4 stoichiometry might be attributed to the longer  $S \cdots N$  hydrogen bonding distance, i.e., to the bigger van der Waals radius of sulphur.

**Key words:** X-ray analysis, hydrogen bonds, molecular complexes, crown ethers.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82004 (31 pages). To obtain copies, see p. ii of this issue.

## 1. Introduction

'Crown ethers' (e.g., 18-crown-6, **I**) are macrocyclic oligoethers usually containing  $(-CH_2-CH_2O-)_n$  units. They display high binding abilities, particularly towards alkali and alkaline earth metal ions [1,2], and also towards small neutral organic molecules [3,4]. They bear some model character for compounds involved in processes of biological relevance (viz. ionophore antibiotics; interactions at biological receptors and substrates) and have been studied intensely during the last decade (e.g., [3,5–7]).



18-crown-6

(I)

In 1971, Pedersen [8] was the first to report on 'Crystalline Complexes of Macrocyclic Polyethers with Thiourea...' and found a variety of molar ratios. Since then, a number of further adducts between (N-alkyl)urea or thiourea (tu) and open-chain [9] or annular oligoethers [3,10] have been prepared. X-ray analyses proved N—H...O(ether) hydrogen bonds to play an essential role in stabilising these compounds [11–13]. This also holds for 18-crown-6/urea, where one guest molecule is attached at either side of the macrocyclic host molecule (sandwich configuration) and three more ureas link these 1 : 2 core adducts, resulting in a 1 : 5 stoichiometry [10].

However, a 1 : 4 ratio is observed with thiourea [3]. An X-ray investigation of the title compound thus seemed interesting; possible analogies and differences between the structures of the urea and the thiourea adduct might help to understand the reasons for the differing stoichiometries in both compounds.

## 2. Experimental

Suitable monoclinic crystals were obtained when a warm solution of the title compound in acetone was allowed to cool slowly in a Dewar vessel. A colourless prism ca.  $0.3 \times 0.5 \times 0.6$  mm was chosen for all crystallographic measurements, performed on an automated four-circle diffractometer at room temperature. Least-squares refinement of the settings of 25 strong reflections provided cell parameters  $a = 9.251(3)$ ,  $b = 19.285(8)$ ,  $c = 16.556(7)$  Å and  $\beta = 90.85(6)$ ; hence follows a calculated density of  $1.279 \text{ g cm}^{-3}$  for four formula units  $\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 4\text{CH}_4\text{N}_2\text{S}$  ( $M = 568.80$ ) per unit cell.

A total of 5346 unique data up to  $2\theta = 50^\circ$  were collected with monochromated  $\text{MoK}\alpha$  radiation in a profile-fitting mode [14]; an absorption correction was not applied ( $\mu = 0.35 \text{ mm}^{-1}$ ).

The structure was solved by multiresolution direct methods and subsequent Fourier syntheses [15] in space group  $P2_1$ . Isotropic H atoms were included in calculated positions (C—H = 0.96 Å, N—H = 0.90 Å). Anisotropic refinement of non-H atoms converged at  $R = 0.086$  using 4252 reflections with  $I > 3\sigma(I)$ .

Final atomic coordinates are given in Table I; lists of thermal parameters, bond lengths and angles, torsion angles, and structure factors have been deposited with the British Library Lending Division under SUP 82004.

## 3. Results and Discussion

This study deals mainly with hydrogen bonds. It should therefore be mentioned at the outset that H-atom parameters are normally of low accuracy when determined by X-ray methods. Since electron densities, but not the positions of nuclei, are located in an X-ray analysis, Z—H distances derived from X-ray data (Z = C, N, O etc.) are necessarily shorter (and Z—H...Z hydrogen bonds are longer) than the 'genuine' bond lengths.

In the current structure H-atoms were included in calculated positions. An N—H distance of 0.90 Å was chosen to optimise agreement with the experimental data and to minimise the systematic errors for non-H atoms; but it should always be kept in mind that neutron scattering investigations of thiourea [16] prove the N—H bond length to be about 1.01 Å.

There are two crystallographically-independent 1 : 4 adducts, *A* and *B*, in the present compound; they are depicted in Figure 1. In each of them, one thiourea (tu) molecule is attached 'above' and one 'below' the plane of the six crown O-atoms (co-planar to within  $\pm 0.11$  Å in *A* and  $\pm 0.10$  Å in *B*, respectively), and further linked to a chelating second tu

Table I. Atomic coordinates ( $\times 10^4$ )

		x	y	z			x	y	z
tu(1)	S(1)	15105(3)	2257	1571(2)	tu(8)	N(71)	2321(7)	7914(4)	6626(4)
	C(10)	13324(8)	2559(4)	1557(5)		N(72)	2322(7)	7895(3)	5252(4)
	N(11)	12708(8)	2699(4)	2245(4)		H(71e)	3229	7748	6612
	N(12)	12616(7)	2635(3)	878(4)		H(71f)	1902	7997	7103
	H(11e)	11787	2849	2252		H(72e)	3232	7730	5283
	H(11f)	13207	2645	2712		H(72f)	1898	7965	4766
	H(12e)	11695	2785	879		S(8)	-191(3)	8420(2)	921(2)
tu(2)	H(12f)	13046	2537	407	C(80)	1482(8)	8123(4)	935(4)	
	S(2)	5678(2)	7448(1)	5937(1)	N(81)	2228(7)	8034(4)	1642(4)	
	C(20)	5133(9)	6590(4)	6005(5)	N(82)	2213(7)	7955(3)	277(4)	
	N(21)	4983(8)	6241(3)	5279(4)	H(81e)	3141	7873	1638	
	N(22)	4910(7)	6298(3)	6667(4)	H(81f)	1808	8136	2114	
	H(21e)	4719	5792	5275	H(82e)	3126	7797	324	
	H(21f)	5150	6463	4812	H(82f)	1795	7999	-215	
tu(3)	H(22e)	4645	5850	6678	crown A	O(1)	-400(7)	5818(2)	6037(4)
	H(22f)	5014	6537	7131		C(2)	288(20)	6339(5)	5573(7)
	S(3)	9330(3)	3077(1)	1573(1)		C(3)	849(13)	6020(4)	4823(6)
	C(30)	9629(8)	3931(5)	1639(5)		O(4)	1778(7)	5443(3)	4949(3)
	N(31)	9636(8)	4363(4)	1003(5)		C(5)	2273(11)	5146(5)	4222(4)
	N(32)	9927(8)	4234(4)	2335(4)		C(6)	3200(8)	4544(5)	4461(6)
	H(31e)	9835	4815	1075		O(7)	4451(6)	4777(4)	4878(4)
tu(4)	H(31f)	9442	4198	504	C(8)	5259(17)	4193(5)	5145(9)	
	H(32e)	10114	4692	2352	C(9)	6167(9)	4511(6)	5794(5)	
	H(32f)	9946	3983	2793	O(10)	5386(8)	4759(4)	6465(5)	
	S(4)	-620(3)	3110(1)	6576(1)	C(11)	4563(13)	4270(4)	6906(4)	
	C(40)	-88(8)	3934(5)	6581(5)	C(12)	4190(12)	4585(5)	7698(3)	
	N(41)	198(8)	4268(4)	5856(5)	O(13)	3249(7)	5154(3)	7554(3)	
	N(42)	145(8)	4299(4)	7218(4)	C(14)	2766(11)	5441(4)	8291(3)	
tu(5)	H(41e)	523	4708	5858	C(15)	1888(9)	6059(3)	8047(6)	
	H(41f)	58	4044	5385	O(16)	635(7)	5778(3)	7673(4)	
	H(42e)	471	4737	7174	C(17)	-164(12)	6328(3)	7308(7)	
	H(42f)	-16	4117	7709	C(18)	-1217(6)	6111(7)	6669(5)	
	S(5)	5583(2)	7569(1)	947(1)	crown B	O(1')	10171(4)	5712(2)	2498(4)
	C(50)	5283(9)	6673(4)	941(6)		C(2')	9031(7)	6163(4)	2694(7)
	N(51)	5083(8)	6378(4)	191(4)		C(3')	7936(8)	5744(4)	3127(4)
N(52)	5274(7)	6332(3)	1602(4)	O(4')		7202(6)	5292(3)	2576(3)	
H(51e)	4935	5919	146	C(5')		6153(9)	4871(5)	2952(5)	
H(51f)	5102	6645	-255	C(6')		5466(12)	4416(5)	2332(5)	
H(52e)	5130	5871	1593	O(7')		4640(6)	4785(2)	1744(3)	
tu(6)	H(52f)	5410	6553	2076	C(8')	3945(9)	4307(4)	1220(2)	
	S(6)	5130(3)	2185(1)	6545(2)	C(9')	3637(9)	4617(7)	422(4)	
	C(60)	3375(9)	2530(4)	6528(5)	O(10')	4912(7)	4905(3)	90(3)	
	N(61)	2641(7)	2575(4)	5860(4)	C(11')	6067(8)	4495(4)	-191(5)	
	N(62)	2816(7)	2716(4)	7231(4)	C(12')	7138(8)	4941(4)	-610(3)	
	H(61e)	1727	2735	5864	O(13')	7831(6)	5380(3)	-34(3)	
	H(61f)	3042	2447	5391	C(14')	8860(11)	5812(5)	-405(4)	
tu(7)	H(62e)	1904	2878	7251	C(15')	9488(10)	6284(3)	218(4)	
	H(62f)	3350	2680	7688	O(16')	10328(7)	5889(3)	781(3)	
	S(7)	-115(2)	8295(1)	5930(1)	C(17')	11001(14)	6387(4)	1294(4)	
	C(70)	1594(8)	8037(3)	5940(4)	C(18')	11300(5)	6061(4)	2090(4)	

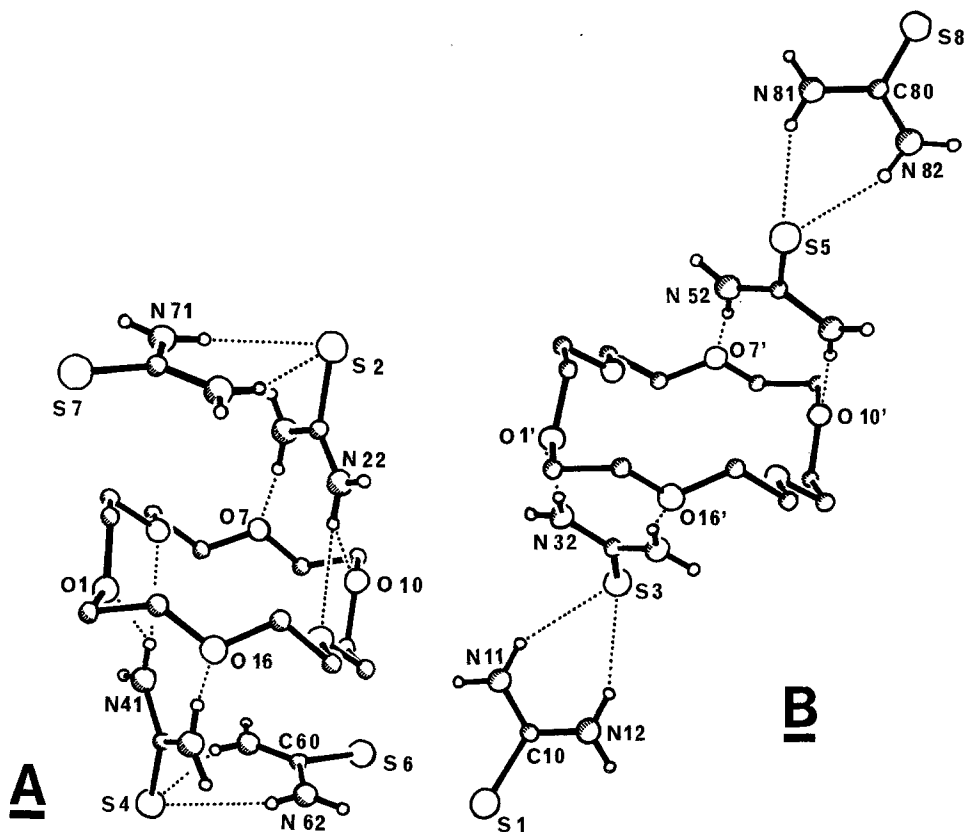


Fig. 1. Perspective views of the 18-crown-6·4tu adducts *A* (top) and *B* (bottom), also showing the numbering scheme adopted. Radii are arbitrary, ligand H-atoms omitted for clarity. Hydrogen bonds are indicated by dotted lines (for distances and angles see Table II).

molecule. Nevertheless, the grouping of molecules in *A* and *B* differs slightly, as is particularly reflected in the dihedral angles between planes: O-atoms in *A*/tu(4) and tu(2), respectively, ca.  $84^\circ$ , O-atoms in *B*/tu(3) and tu(5) ca.  $60^\circ$ ; tu(4)/tu(6), tu(2)/tu(7) ca.  $87^\circ$  in *A*, but tu(3)/tu(1) and tu(5)/tu(8) ca.  $79^\circ$  in *B*; O-atoms in *A*/tu(6) and tu(7) ca.  $5^\circ$ , but O-atoms in *B*/tu(1) and tu(8) ca.  $40^\circ$ .

These differences are associated with differing hydrogen bond patterns in *A* and *B* (Figures 1 and 2, Table II). In *A* all the six crown O-atoms serve as  $e^-$  donors. This requires two-fold interactions of two H-atoms, namely H(22e) and H(41e) (cf. Table I); O—H distances of 2.2 to 2.4 Å and  $O\cdots H-N$  angles of  $135$  to  $145^\circ$  correspond to values given by Donohue [17] for 'clearly bifurcated hydrogen bonds'.

In complex *B*, each of the two 'inner' tu molecules is linked to two adjacent O-atoms in the crown ether; thus only four oxygen atoms are involved in interactions, which appear slightly stronger (mean  $O\cdots H$  ca. 2.07 Å, mean  $O\cdots H-N$  ca.  $168^\circ$ ) than in *A*.

Despite these different hydrogen bond patterns, the macrocycle adopts a 'biangular[99]' conformation [6] in *A* and in *B*, with endocyclic torsion angles  $ag^- - ag^- - ag^+ - g^+ - ag^+ - ag^+ - ag^- - g^-$  [starting at C(18)—O(1)—C(2)—C(3)] (Figure 2). This conformation is less common than the typical 'round'  $D_{3d}$ -conformation [6] but possibly more favourable from an energetic point of view [7]. It is occasionally observed in host-guest complexes of 18-crown-6 and its

Table II. Distances (Å) and angles (°) in hydrogen bonds

Interactions between thiourea and crown molecules					
<i>Crown A</i>					
O(1)···N(41)	3.06(1)	O(1)···H(41e)	2.33(1)	O(1)···H(41e)-N(41)	138.2(7)
O(4)···N(41)	3.10(1)	O(4)···H(41e)	2.38(1)	O(4)···H(41e)-N(41)	136.4(7)
O(7)···N(21)	2.94(1)	O(7)···H(21e)	2.08(1)	O(7)···H(21e)-N(21)	160.1(8)
O(10)···N(22)	3.02(1)	O(10)···H(22e)	2.24(1)	O(10)···H(22e)-N(22)	144.6(7)
O(13)···N(22)	3.08(1)	O(13)···H(22e)	2.37(1)	O(13)···H(22e)-N(22)	135.0(6)
O(16)···N(42)	2.98(1)	O(16)···H(42e)	2.18(1)	O(16)···H(42e)-N(42)	149.0(6)
<i>Crown B</i>					
O(1')···N(32)	2.87(1)	O(1')···H(32e)	1.98(1)	O(1')···H(32e)-N(32)	169.1(6)
O(7')···N(52)	3.05(1)	O(7')···H(52e)	2.16(1)	O(7')···H(52e)-N(52)	171.5(7)
O(10')···N(51)	2.85(1)	O(10')···H(51e)	1.96(1)	O(10')···H(51e)-N(51)	171.6(7)
O(16')···N(31)	3.04(1)	O(16')···H(31e)	2.18(1)	O(16')···H(31e)-N(31)	159.5(6)
Interactions between thiourea molecules					
S(1)···N(22) <sup>i</sup>	3.45(1)	S(5)···N(12) <sup>viii</sup>	3.47(1)	S(4)···H(72f) <sup>vii</sup>	2.52(1)
S(1)···N(51) <sup>ii</sup>	3.38(1)	S(5)···N(62) <sup>iv</sup>	3.35(1)	S(4)···H(81f) <sup>vii</sup>	2.45(1)
S(2)···N(71)	3.44(1)	S(6)···N(21) <sup>v</sup>	3.53(1)	S(5)···H(81e)	2.61(1)
S(2)···N(72)	3.40(1)	S(6)···N(52) <sup>v</sup>	3.51(1)	S(5)···H(82e)	2.52(1)
S(2)···N(11) <sup>iii</sup>	3.37(1)	S(1)···H(22f) <sup>i</sup>	2.56(1)	S(5)···H(12f) <sup>viii</sup>	2.59(1)
S(2)···(61) <sup>iv</sup>	3.39(1)	S(1)···H(51f) <sup>ii</sup>	2.48(1)	S(5)···H(62f) <sup>iv</sup>	2.46(1)
S(3)···N(11)	3.38(1)	S(2)···H(71e)	2.61(1)	S(6)···H(21f) <sup>v</sup>	2.65(1)
S(3)···N(12)	3.38(1)	S(2)···H(72e)	2.55(1)	S(6)···H(52f) <sup>v</sup>	2.64(1)
S(3)···N(71) <sup>v</sup>	3.39(1)	S(2)···H(11f) <sup>iii</sup>	2.48(1)	S(7)···N(32) <sup>iv</sup>	3.40(1)
S(3)···N(82) <sup>vi</sup>	3.37(1)	S(2)···H(61f) <sup>iv</sup>	2.51(1)	S(7)···N(41) <sup>ix</sup>	3.50(1)
S(4)···N(61)	3.42(1)	S(3)···H(11e)	2.56(1)	S(8)···N(31) <sup>x</sup>	3.71(1)
S(4)···N(62)	3.43(1)	S(3)···H(12e)	2.55(1)	S(8)···N(42) <sup>ix</sup>	3.52(1)
S(4)···N(72) <sup>vii</sup>	3.42(1)	S(3)···H(71f) <sup>v</sup>	2.49(1)	S(7)···H(32f) <sup>iv</sup>	2.50(1)
S(4)···N(81) <sup>vii</sup>	3.33(1)	S(3)···H(82f) <sup>vi</sup>	2.47(1)	S(7)···H(41f) <sup>ix</sup>	2.61(1)
S(5)···N(81)	3.44(1)	S(4)···H(61e)	2.59(1)	S(8)···H(31f) <sup>x</sup>	2.89(1)
S(5)···N(82)	3.38(1)	S(4)···H(62e)	2.61(1)	S(8)···H(42f) <sup>ix</sup>	2.64(1)

## Symmetry codes

i = 2 - x, -0.5 + y, 1 - z

iii = 2 - x, 0.5 + y, 1 - z

v = 1 - x, -0.5 + y, 1 - z

vii = -x, -0.5 + y, 1 - z

ix = -x, 0.5 + y, 1 - z

ii = 2 - x, -0.5 + y, -z

iv = 1 - x, 0.5 + y, 1 - z

vi = 1 - x, -0.5 + y, -z

viii = 2 - x, 0.5 + y, -z

x = 1 - x, 0.5 + y, -z

refer to coordinates as given in Table I.

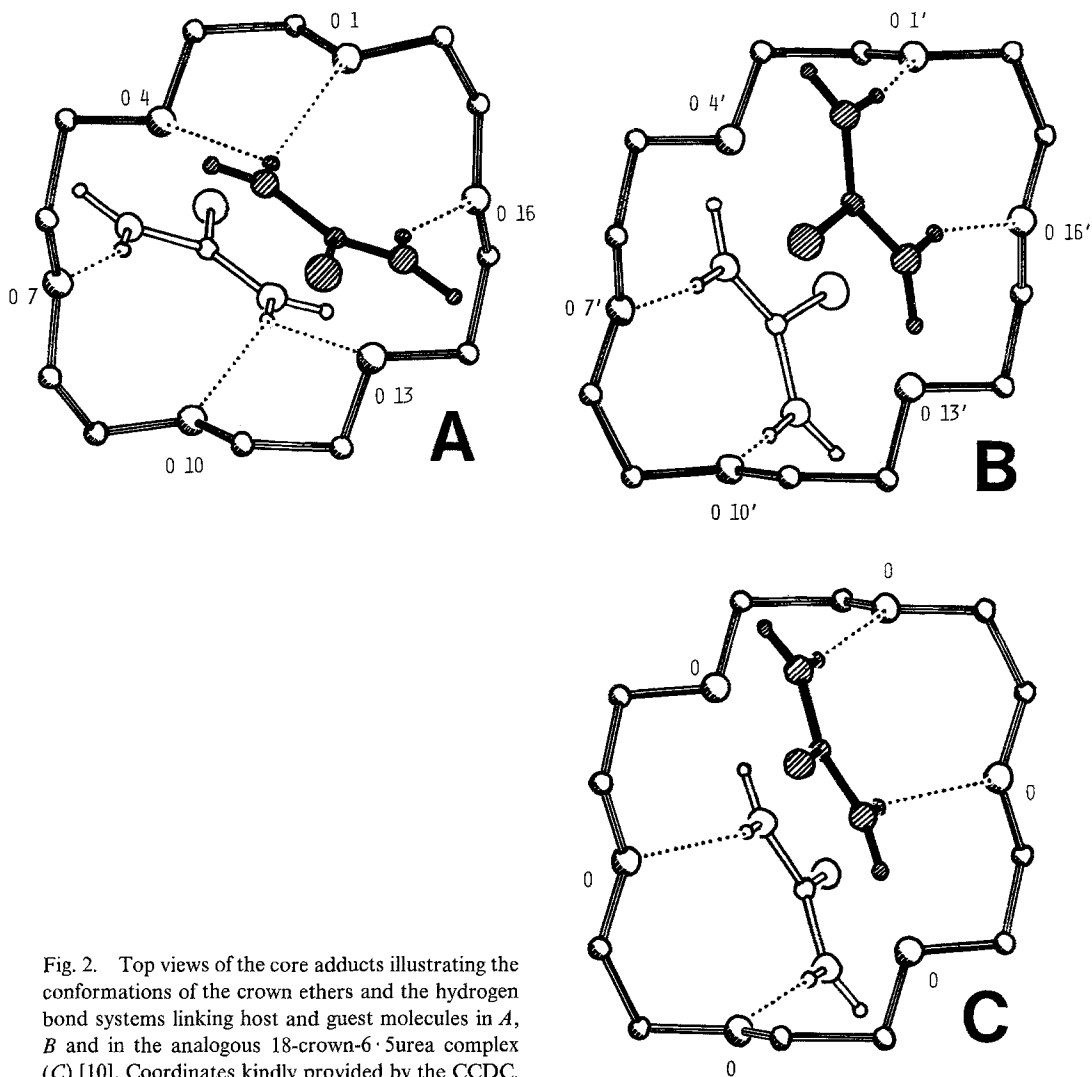


Fig. 2. Top views of the core adducts illustrating the conformations of the crown ethers and the hydrogen bond systems linking host and guest molecules in *A*, *B* and in the analogous 18-crown-6·5urea complex (*C*) [10]. Coordinates kindly provided by the CCDC.

analogues with small neutral molecules containing H-acidic  $\text{CH}_2$  [18] and  $\text{NH}_2$  groups [12,19], and it was found in the 18-crown-6·5 urea compound (*C*) [10]. In Figure 2 the conformational similarities of *A*, *B* and *C* are illustrated, as are the nearly identical H bond patterns present in the core adducts of *B* and *C*.

In the room temperature modification of thiourea [16], each amino group forms two hydrogen bonds of ca. 2.40 and 2.76 Å, respectively, and one more (doubtful) of ca. 3.06 Å, i.e., each S-atom is involved in four (or possibly six) secondary interactions. In the current structure each amino group also forms two hydrogen bonds [N(22) and N(41) three, including bifurcation], but the electron donor sulphur is partially substituted by crown O-atoms in the lattice. Accordingly, only four out of the eight S-atoms accept four hydrogen bonds and the remaining four accept only two (Table II).

The core adducts are thus linked three-dimensionally by additional tu's to give alternating layers of crown/tu complexes and of tu molecules (Figure 3), comparable to those in

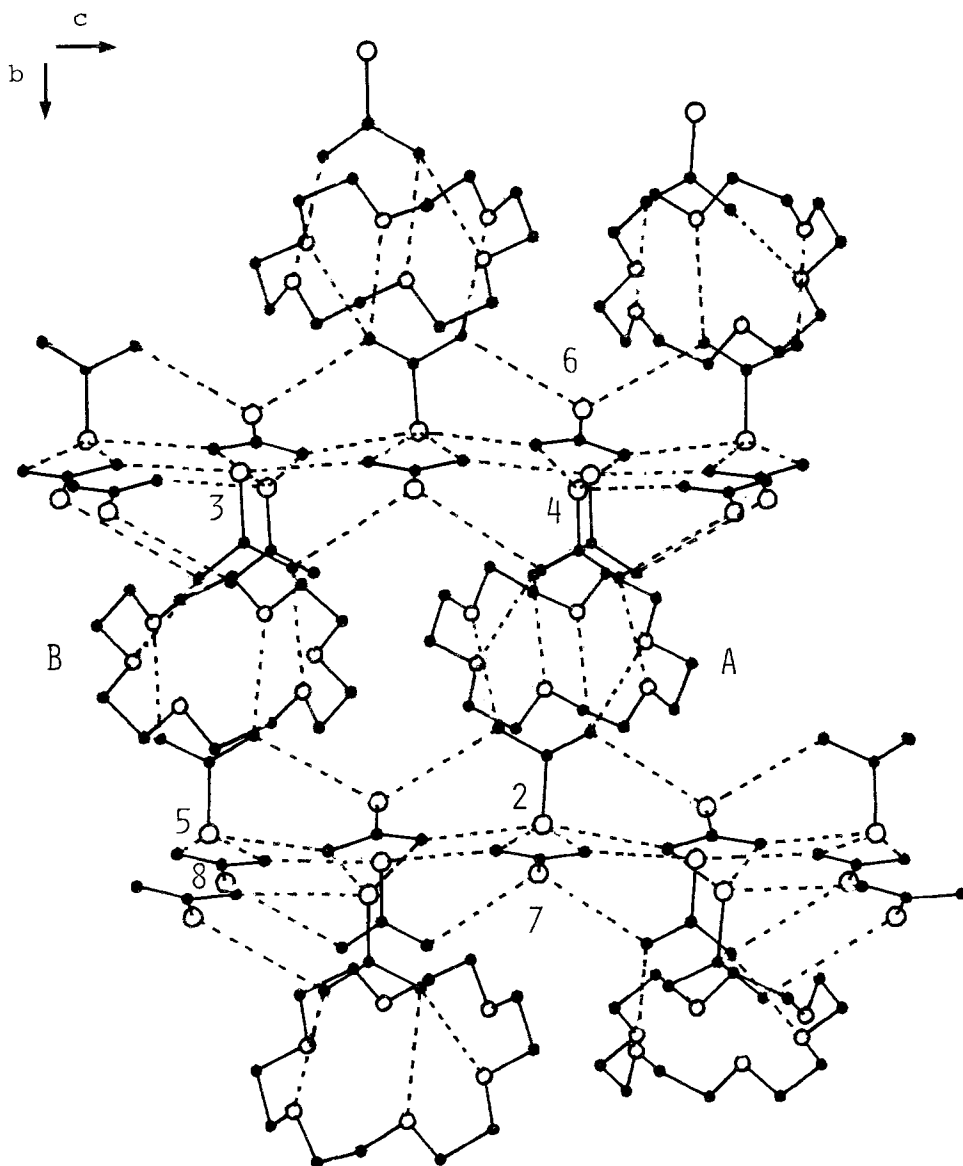


Fig. 3. A section of the three-dimensional network of hydrogen bonds in the lattice, viewed along *a*. Letters represent the crown, numbers the thiourea molecules.

18-crown-6·5 urea [10].  $S\cdots H$  distances range from 2.45 to 2.65 Å [neglecting  $S(8)\cdots H(31f) = 2.89(1)$  Å, accompanied by  $S\cdots H-N = 152.2(9)^\circ$ ] and thus indicate stronger interactions than in thiourea itself; this is confirmed by  $S\cdots H-N$  angles averaging  $170^\circ$  in bridging linkages (cf.  $169^\circ$ ,  $134^\circ$ ,  $122^\circ$  in thiourea). Mean  $S\cdots H-N$  angles of  $154^\circ$  in chelating linkages probably reflect some geometrical strain but are still more favourable than in thiourea [16].

The three-dimensional network of hydrogen bonds seems to be an essential stabilising factor in crown ether/(thio)urea compounds; it is found not only in the current structure and

in the 18-crown-6/urea adduct [10] but also in the analogous complex of tetraoxadiazacyclooctadecane (tdco) with thiourea [12]; in 18-crown-6/*N,N'*-dimethyl-thiourea the number of strong N—H···O(ether) bonds is reduced to two in favour of additional thiourea···thiourea linkages [13].

The requirement for these bridging hydrogen bonds in the thiourea layer might explain the differing stoichiometries in adducts between host molecules of comparable diameters and guests of differing sizes [8]. The packing in 18-crown-6/thiourea and in 18-crown-6/urea [10] consists of alternating layers of core adducts and (thio)urea guest molecules (see Figure 3). However, in the title structure, four tu molecules are required to bridge the neighbouring crown ethers *A* and *B* to the next pair along *c*, whilst in 18-crown-6/urea five are necessary. That means that the guest (urea, thiourea) layers incorporate differing numbers of molecules per given length, corresponding to one crown molecule, of the neighbouring host layer (see Figure 3). Thus the 1 : 5 ratio found for 18-crown-6/urea (though prepared from nearly equimolar ratios [10]) and the 1 : 4 ratios found for adducts of 18-crown-6 and of the similar-sized 'tdco' with thiourea [12] can probably be attributed to the different van der Waals radii of oxygen and sulphur:  $5 \times r_{\text{vdW}}(\text{O}) = 7.0 \text{ \AA}$  corresponds approximately to  $4 \times r_{\text{vdW}}(\text{S}) = 7.4 \text{ \AA}$  [20].

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