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Acta Cryst. (1989). C45, 257–259

Adamantane* Inclusion Complexes with Thiourea and Selenourea

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(Received 6 July 1988; accepted 21 September 1988)

Abstract. Trigonal, $R\bar{3}c$, $Z = 6$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $T = 300 \text{ K}$. (I) $\text{C}_{10}\text{H}_{16}\cdot 3\text{SC}(\text{NH}_2)_2$, $M_r = 364.6$, $a = 16.187 (7)$, $c = 12.578 (7) \text{ \AA}$, $V = 2854 (4) \text{ \AA}^3$, $D_x = 1.273 \text{ g cm}^{-3}$, $\mu = 3.85 \text{ cm}^{-1}$, $F(000) = 1176$, $R = 0.094$ for 621 independent reflections. (II) $\text{C}_{10}\text{H}_{16}\cdot 3\text{SeC}(\text{NH}_2)_2$, $M_r = 505.3$, $a = 16.548 (11)$, $c = 12.830 (5) \text{ \AA}$, $V = 3043 (5) \text{ \AA}^3$, $D_x = 1.654 \text{ g cm}^{-3}$, $\mu = 58.6 \text{ cm}^{-1}$, $F(000) = 1500$, $R = 0.080$ for 511 independent reflections. Twofold disordered adamantane molecules are included in channels formed in the structure by molecules of the host linked through N—H...S or N—H...Se hydrogen bonds.

Introduction. The crystal structure of selenourea (Rutherford & Calvo, 1969) contains nine independent $\text{SeC}(\text{NH}_2)_2$ molecules, linked in three-molecule spiral chains by what appear to be hydrogen bonds. Hydrogen bonds involving Se seem to have a severely limited crystal chemistry, since only bonds in the closely related molecules *N*-phenyl-*N'*-benzylselenourea (Hope, 1965) and 2,4-diselenouracil (Shefter, James & Mautner, 1966) have been reported.

The three-molecule spiral chain also occurs in thiourea inclusion complexes, such as the cyclohexane adduct (Lenné, 1954). Van Bekkum, Remijnse & Wepster (1969) have reported a number of selenourea adducts which appeared to be isostructural with the thiourea complexes. Therefore it was felt that this would provide an opportunity to confirm the hydrogen-

bonding capability of selenourea, and, at the same time, obtain improved molecular dimensions.

Adamantane was chosen as guest since, being rigid and highly symmetric, it was unlikely to be highly disordered. Also the crystal structure and molecular dimensions of adamantane were already available (Nordman & Schmitkons, 1965; Donohue & Goodman, 1967).

Experimental. The preparation of van Bekkum *et al.* (1969) was followed. Colorless trigonal prismatic crystals were used for diffraction measurements using a Picker FACS-I diffractometer with graphite monochromator in the $\theta/2\theta$ scan mode. (I) Crystal dimensions $0.20 \times 0.25 \times 0.10 \text{ mm}$. Lattice parameters were determined using 21 reflections ($40 \leq 2\theta \leq 45^\circ$). Three standard reflections were measured every 100 reflections; during the data collection their intensity decreased by 2%. A total of 736 independent reflections was measured with $2\theta \leq 55^\circ$, $0 \leq h \leq 18$, $0 \leq k \leq 17$, $0 \leq l \leq 16$ at 300 (2) K; of these 621 were used in the refinement [$I/\sigma(I) > 0.9$]. Absorption corrections were not applied. $R = 0.094$, $wR = 0.117$, $S = 2.43$ based on F , 33 variables, $w = (2.6 - 0.0032|F| + 0.00028|F|^2)^{-2}$, maximum $\Delta/\sigma = 0.17$ in the final least-squares cycle, $(\Delta\rho)_{\text{max}} = 0.76 \text{ e \AA}^{-3}$ in the final difference map. (II) Crystal dimensions $0.10 \times 0.12 \times 0.20 \text{ mm}$. Lattice parameters were determined using 21 reflections ($32 \leq 2\theta \leq 43^\circ$). Three standard reflections were measured every 40 reflections; during the data collection their intensity decreased by 15% and the

* IUPAC name: tricyclo[3.3.1.1^{3,7}]decane.

Table 1. Atomic parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Compound (I)				Compound (II)			
	x	y	z	U/U _{eq}	x	y	z	U/U _{eq}
SorSe(1)	0.3046 (1)	0	$\frac{1}{4}$	0.035 (1)	0.2993 (1)	0	$\frac{1}{4}$	0.038 (1)
C(1)	0.4110 (6)	0	$\frac{1}{4}$	0.033 (3)	0.4149 (9)	0	$\frac{1}{4}$	0.043 (9)
N(1)	0.4419 (5)	-0.0182 (4)	0.1605 (4)	0.045 (3)	0.4430 (8)	-0.0176 (8)	0.1627 (9)	0.055 (6)
H(1)	0.486 (6)	-0.017 (6)	0.153 (6)	0.045	0.489 (10)	-0.033 (9)	0.154 (10)	0.055
H(2)	0.415 (6)	-0.024 (6)	0.090 (7)	0.045	0.414 (11)	-0.031 (11)	0.108 (10)	0.055
C(A1)	0	0	0.145	0.117 (12)	0	0	0.153	0.24 (5)
C(A2)	0.101	0.032	0.185	0.183 (13)	0.101	0.054	0.193	0.11 (1)
C(A3)	0.101	0.032	0.308	0.107 (7)	0.101	0.054	0.313	0.11 (1)
C(A4)	0.069	0.101	0.349	0.125 (8)	0.047	0.101	0.353	0.30 (5)
H(A1)	0	0	0.065	0.117	0	0	0.075	0.24
H(A2)	0.146	0.098	0.159	0.183	0.132	0.119	0.167	0.11
H(A3)	0.122	-0.013	0.159	0.183	0.136	0.023	0.167	0.11
H(A4)	0.167	0.053	0.334	0.107	0.167	0.089	0.339	0.11
H(A5)	0.114	0.167	0.322	0.125	0.078	0.167	0.328	0.30
H(A6)	0.069	0.101	0.428	0.125	0.048	0.102	0.431	0.30

crystals discolored. A total of 784 independent reflections was measured with $2\theta \leq 55^\circ$, $0 \leq h \leq 10$, $0 \leq k \leq 18$, $-16 \leq l \leq 16$ at 300 (2) K; 511 were used in the refinement [$I/\sigma(I) > 0.9$]. Absorption corrections were not applied. $R = 0.080$, $wR = 0.082$, $S = 3.69$ based on F , 33 variables, $w = (11.61 - 0.136|F| + 0.00053|F|^2)^{-2}$, maximum $\Delta/\sigma = 0.08$ in the final least-squares cycle, $(\Delta\rho)_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$ in the final difference map.

The coordinates of the non-H atoms of the host of (I) were based on Lenné's (1954) coordinates. After refinement, first the guest C atoms, then the H atoms of the host were found in difference maps. The refined coordinates for (I) were used as the starting point for (II).

In both structures the adamantane molecule was refined as a rigid group, symmetry $\bar{4}3m$, C—C = 1.54 Å, C—H = 1.00 Å, all angles tetrahedral. Anisotropic temperature factors were used only for the non-H atoms of the host, and the adamantane H atoms were assigned the temperature factors of the C atoms to which they were attached. Atomic scattering factors were from Cromer & Mann (1968). Computations were carried out using the *GROUPLS* program (Stephens, 1976) for least squares and the *XRAY76* package (Stewart, 1976) for all other calculations.

Discussion. The relatively large values of R and wR obtained for both structures are probably a consequence of both the disorder, and the fact that it was necessary to treat part of the structure as a rigid body. The atomic parameters are given in Table 1 and the bond distances and angles within the host molecules in Table 2.* A general view of one channel in the thiourea

* Lists of structure amplitudes and anisotropic thermal parameters for the non-H host atoms for both complexes have been deposited with the British Document Supply Centre as Supplementary Publication No. SUP 51394 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) in the host

	Compound (I)	Compound (II)
S(e)(1)—C(1)	1.722 (7)	1.914 (15)
C(1)—N(1)	1.324 (7)	1.300 (14)
N(1)—H(1)	0.71 (12)	0.92 (20)
N(1)—H(2)	0.97 (9)	0.81 (16)
S(e)(1)—C(1)—N(1)	119.3 (5)	118 (1)
N(1)—C(1)—N(1)	121.4 (9)	124 (2)
C(1)—N(1)—H(1)	126 (6)	127 (9)
C(1)—N(1)—H(2)	126 (6)	125 (13)

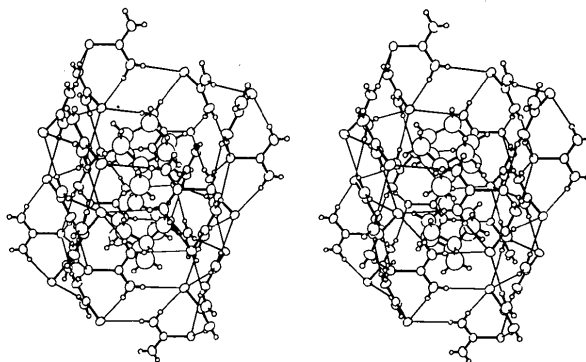


Fig. 1. ORTEP stereoscopic view (Johnson, 1976) of a channel in the thiourea complex. Only one orientation of the adamantane molecule is shown in each site.

complex is shown in Fig. 1. Only one orientation of the adamantane molecule is shown in each site; it is twofold disordered, as it is in adamantane itself. The centroid of the adamantane molecule is displaced 0.22 (2) Å from the 32 symmetry point in (I) and 0.30 (3) Å in (II). However, the most marked difference between the two structures is in the orientation of the guest about the threefold axis; the projection of the bond C(A1)—C(A2) onto the basal plane makes an angle of 18.1 (6)° in (I) and 32 (1)° in (II) with the x axis, which is the twofold axis along which the chalcogen projects into the cavity. Both of these differences permit more efficient packing

as the cavity changes shape with changes in the chalcogen van der Waals radius.

The host molecules are planar, with dimensions similar to those determined for the pure compounds (Truter, 1967; Rutherford & Calvo, 1969). However, the bond lengths found here for selenourea [C–Se = 1.914 (15), C–N = 1.300 (15) Å compared with 1.86 (3) and 1.37 (2) Å found previously] suggest that the ionic contributions to the electronic structure must be considerable.

The structures confirm the general features of the inclusion complexes as described by Lenné (1954). The guest molecules in the 1:3 rational adducts lie in the vicinity of the 32 symmetry point in the structure, and the channel is constricted around the $\bar{3}$ point by $-\text{NH}_2$ groups. The host molecules are hydrogen-bonded to one another, the $\text{N}\cdots\text{X}$ distances being 3.462 (7) and 3.496 (5) Å for (I), and 3.51 (2) and 3.65 (2) Å for (II), for the hydrogen bonds between chains and within chains respectively. The distances for the thiourea host fall between those found by Truter (1967) for thiourea itself (3.42, 3.54 Å), while those for (II) almost precisely reverse those for selenourea, where the average distances are 3.64 (2) between chains and 3.51 (2) Å within chains. The greater variability in the length of the weaker $\text{N}-\text{H}\cdots\text{Se}$ bonds, together with an ability to adjust the position of the selenourea molecule within the chain to promote efficient packing, would appear to explain van Bekkum *et al.*'s (1969) observation of a larger variation in cell dimensions for the selenourea complexes. With regard to the packing of

the selenourea molecules, in selenourea itself, on average, the Se atom projects 0.81 (7) Å beyond the chain axis, while in the adamantane complex the Se atom is pushed back out of the cavity to project only 0.56 (1) Å.

The authors acknowledge the support of the Natural Sciences and Engineering Research Council of Canada for an Operating Grant to BR and the University of Regina for computing time. The authors thank Darren Thompson for assistance with the preparation of the manuscript.

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Acta Cryst. (1989). **C45**, 259–263

A *cis* and a *trans* 4'-Methyl Cyclopentamethylenemercaptopropionic Acid (Pmp)

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(Received 3 May 1988; accepted 19 September 1988)

Abstract. (I): *trans*-4-Methyl-1-[(4-methylphenyl)-methyl]thio]cyclohexaneacetic acid, $\text{C}_{17}\text{H}_{24}\text{O}_2\text{S}$, $M_r = 292.44$, monoclinic, $P2_1/n$, $a = 8.588$ (3), $b = 9.812$ (3), $c = 19.696$ (9) Å, $\beta = 91.90$ (3)°, $V = 1658.8$ (19) Å³, $Z = 4$, $D_x = 1.171$ Mg m⁻³, $\lambda(\text{Mo } K\alpha)$

$= 0.71073$ Å, $\mu = 0.1856$ cm⁻¹, $F(000) = 632$, $T = 295$ K, $R = 0.046$, $wR = 0.060$ for 2015 observations. (II): *cis*-4-Methyl-1-[(phenylmethyl)thio]cyclohexaneacetic acid, $\text{C}_{16}\text{H}_{22}\text{O}_2\text{S}$, $M_r = 278.42$, monoclinic, $P2_1/n$, $a = 15.884$ (3), $b = 9.391$ (4), $c = 22.429$ (4) Å, $\beta = 109.95$ (2)°, $V = 3145.0$ (29) Å³, $Z = 8$, $D_x = 1.176$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu =$

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