Host–guest interaction in a thiourea–dimethyl oxalate (2/1) complex at 300 and 100 K

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The title complex, $2CH_4N_2S \cdot C_4H_6O_4$, is a host–guest system. The asymmetric unit consists of one complete thiourea molecule and one-half of a dimethyl oxalate molecule lying on an inversion centre. The host thiourea molecules are connected to form zigzag chains by N—H···S hydrogen bonds. The guest dimethyl oxalate molecules provide O-atom acceptors for N—H···O hydrogen bonds, thus interconnecting the chains of thiourea molecules to form completely connected sheets. The reduction in temperature from 300 to 100 K leaves the structure unchanged and still isostructural with that previously determined for the analogous thiourea–diethyl oxalate (2/1) complex. It does, however, induce closer packing of the molecules, general shrinkage of the unit cell and shortening of the hydrogen bonds, these last two to the extent of 1–2%.

Comment

Intermolecular interactions play a definitive role in crystal engineering. Indeed, the varied strength of hydrogen bonds plays a key role in designing new crystals. In this field, the crystal structures of complexes show a delicate interplay of strong and weak hydrogen bonds. Apart from the varied strength, their directional nature and flexibility can also be utilized to create new materials with specific physical properties. It is known that the melting point of dimethyl oxalate is 327 K and is higher than that of related carboxylic acid esters. This has been explained as being due to the stabilization of the crystal by weak intermolecular hydrogen bonds, *i.e.* C—H···O hydrogen bonds between the methyl groups and the carbonyl groups in this compound. Dimethyl oxalate (dmox) is the simplest molecule in the series of symmetric diesters and its structure is already known (Dougill & Jeffery, 1953; Jones *et al.*, 1989). X-ray analysis of the compound at room temperature showed that the molecule has a planar *trans–trans* configuration. It crystallizes in the space group $P2_1/n$ with

unit-cell parameters a = 3.891 (1) Å, b = 11.879 (2) Å, c = 6.213 (2) Å and β = 103.32 (2)°. To our knowledge, no complex of dmox has been reported to date.

Thiourea (tu) is known to form crystalline inclusion compounds with a range of guest molecules of appropriate size and shape (Takemoto & Sonoda, 1984; Hollingsworth & Harris, 1996). These compounds exhibit a wide range of interesting and important fundamental physicochemical properties (Harris, 1996). A complex of diethyl oxalate (detox) with tu has been reported (Chitra *et al.*, 2005) and is isostructural with the complex reported here. It is interesting to compare the geometric parameters and hydrogen bonding of the present complex, (I), with those of pure dmox, (II), and the tu–detox (2/1) complex, (III).
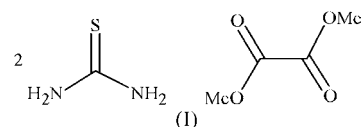
Data for (I) were obtained at 300 K, (I-300), and 100 K, (I-100), but on the basis of reduced unit cells differing in the choice of the unit-cell edge *b*. For ease of comparison of the structures, the 100 K unit cell and Miller indices were transformed for conformity with the 300 K case (see below). The asymmetric unit of (I) consists of one-half of a dmox molecule, which is completed by the operation of a crystallographic centre of symmetry, and a complete tu molecule (Fig. 1). The bond lengths and angles of the molecules in (I) are in the usual ranges and, as exemplified in Table 3 for dmox, are insensitive to inclusion in the complex or temperature. The tu and dmox molecules in (I) are, in themselves, planar and, for the asymmetric unit used in both refinements, coplanar within 1°.

The molecules in (I) are interconnected by N—H···S and N—H···O hydrogen bonds (Tables 1 and 2) to form sheets parallel to $(1\bar{1}1)$ (Fig. 2). The N—H···S hydrogen bonds connect the tu molecules to form zigzag chains. The N—H···O hydrogen bonds employ the O atoms of dmox as acceptors to
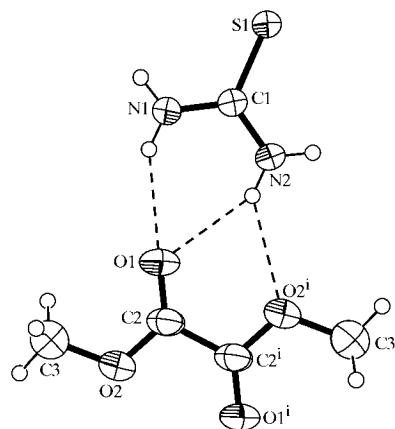

Figure 1
The molecules in (I); the example shown is (I-300). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]
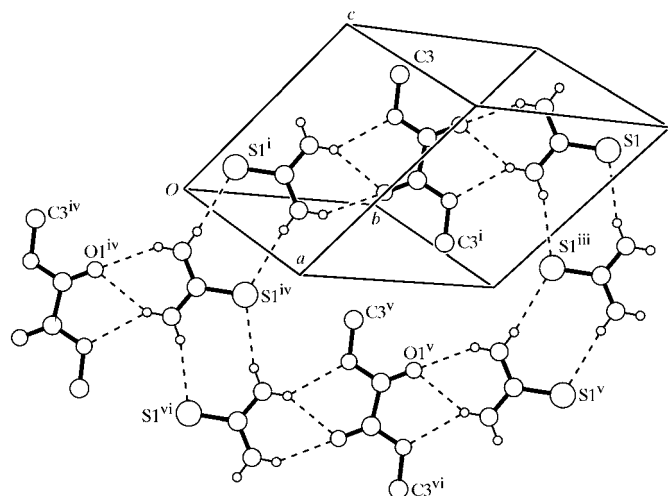
organic compounds

Figure 2
A layer of molecules of (I); the example shown is (I-300). Selected atoms are labelled. [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (iii) $-x + 2$, $-y + 2$, $-z + 1$; (iv) x, $y - 1$, $z - 1$; (v) $x + 1$, y, $z - 1$; (vi) $-x + 2$, $-y + 1$, $-z$.]

interconnect adjacent chains of tu molecules and complete the connectivity within the layer. Precisely the same arrangement is found in the structure of (III) (Chitra *et al.*, 2005). Complex (III) differs from (I) in having a larger cell edge *a* and longer N···S distances in the chains of tu molecules [somewhat more linear than they are in (I)] in order to accommodate the larger detox molecule. The smaller size of the unit cell of (I) at 100 K compared with its size at 300 K is evident from values given in the crystal data tables below. The effect of cooling, bringing about closer packing of the molecules, is also evident in the change in the hydrogen-bond geometries, especially the $D \cdots A$ distances (Tables 1 and 2). Assessment of the shrinkage of the unit cell upon cooling based upon the reduced cells used in data collection but not, as indicated above, for the refinement of the structure at 100 K exaggerates the effect. This is misleading because it fails to recognize that *b* is chosen differently in the two reduced cells. The disparity in the choice of *b* in the reduced cells creates an interesting situation for cell search algorithms that employ cell reduction as part of their search strategy.

Experimental

Colourless single crystals of (I) were grown from a methanol solution containing stoichiometric amounts of thiourea and oxalic acid.

Compound (I-300)

Crystal data

2CH$_4$N$_2$S·C$_4$H$_6$O$_4$
$M_r = 270.33$
Triclinic, $P\bar{1}$
$a = 6.1010 (3)$ Å
$b = 7.6447 (4)$ Å
$c = 8.4463 (5)$ Å
$\alpha = 66.239 (3)°$
$\beta = 70.516 (3)°$
$\gamma = 67.479 (3)°$

$V = 325.48 (3)$ Å^3
$Z = 1$
$D_x = 1.379$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.42$ mm^{-1}
$T = 300 (2)$ K
Irregular shape, colourless
$0.30 \times 0.20 \times 0.15$ mm

Data collection

Bruker–Nonius X8 APEX-II 4K
  CCD diffractometer
φ and ω scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 2003)
  $T_{min} = 0.797$, $T_{max} = 1.000$
  (expected range = 0.749–0.940)

4488 measured reflections
2151 independent reflections
1463 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 34.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.113$
$S = 1.02$
2151 reflections
81 parameters
Only H-atom displacement
  parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2$
  $+ 0.0265P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I-300).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.26	3.0413 (17)	150
N2—H3···O1	0.86	2.30	3.0683 (19)	149
N2—H3···O2^i	0.86	2.45	3.1498 (16)	139
N1—H2···S1^{ii}	0.86	2.57	3.4292 (15)	172
N2—H4···S1^{iii}	0.86	2.53	3.3791 (14)	167

Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x + 1$, $-y + 2$, $-z + 2$; (iii) $-x + 2$, $-y + 2$, $-z + 1$.

Compound (I-100)

Crystal data

2CH$_4$N$_2$S·C$_4$H$_6$O$_4$
$M_r = 270.33$
Triclinic, $P\bar{1}$
$a = 6.030 (1)$ Å
$b = 7.511 (2)$ Å
$c = 8.414 (2)$ Å
$\alpha = 65.613 (4)°$
$\beta = 70.475 (3)°$
$\gamma = 66.168 (3)°$

$V = 311.01 (12)$ Å^3
$Z = 1$
$D_x = 1.443$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.43$ mm^{-1}
$T = 100 (2)$ K
Irregular shape, colourless
$0.30 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 2003)
  $T_{min} = 0.754$, $T_{max} = 1.000$
  (expected range = 0.706–0.937)

2389 measured reflections
1288 independent reflections
1091 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.103$
$S = 1.11$
1288 reflections
81 parameters
Only H-atom displacement
  parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2$
  $+ 0.0376P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

For the refinement of the 100 K structure of (I), the reduced cell with $a = 6.030 (1)$ Å, $b = 7.495 (2)$ Å, $c = 8.414 (2)$ Å, $\alpha = 98.334 (4)°$, $\beta = 109.525 (3)°$ and $\gamma = 113.551 (3)°$ used in data collection was re-evaluated in the same setting as the cell of the 300 K structure and the indices of the intensity data transformed accordingly by means of the (row-wise) transformation matrix ($\bar{1}00$, $\bar{1}\bar{1}0$, 001). In both structures,

Table 2
Hydrogen-bond geometry (Å, °) for (I-100).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1⋯O1	0.88	2.20	2.989 (2)	150
N2—H3⋯O1	0.88	2.24	3.019 (2)	148
N2—H3⋯O2^i	0.88	2.40	3.123 (2)	139
N1—H2⋯S1^{ii}	0.88	2.53	3.405 (2)	172
N2—H4⋯S1^{iii}	0.88	2.49	3.3494 (19)	167

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+2$; (iii) $-x+2, -y+2, -z+1$.

Table 3
Bond lengths and angles (Å, °) in dmox in (I-300), (I-100) and (II).

	(I-300)	(I-100)	(II)^a
C2—C2^i	1.525 (3)	1.535 (5)	1.534 (4)
O1—C2	1.2029 (18)	1.202 (3)	1.186 (3)
O2—C2	1.318 (2)	1.316 (3)	1.324 (3)
O2—C3	1.452 (2)	1.458 (3)	1.451 (3)
O1—C2—O2	126.07 (17)	126.7 (2)	126.2 (2)
O1—C2—C2^i	123.5 (2)	123.4 (3)	124.1 (2)
O2—C2—C2^i	110.40 (16)	110.0 (2)	109.6 (2)
C2—O2—C3	116.52 (14)	115.50 (17)	115.5 (2)

Note: (a) data for equivalent bonds and angles from Jones *et al.* (1989). Symmetry code: (i) $-x+1, -y+1, -z+1$.

in the final stages of refinement, H atoms were introduced in calculated positions, with N—H and C—H distances set at 0.86 and 0.96 Å, respectively, for (I-300), and 0.88 and 0.98 Å for (I-100). H atoms attached to N atoms were restrained to be coplanar with the non-H atoms of the tu molecule. All H atoms were then refined with a riding model, while their isotropic displacement parameters were refined freely, as was the rotational orientation of the methyl group.

Data collection: *APEX2* (Bruker–Nonius, 2003) for (I-300) and *SMART* (Bruker, 2004) for (I-100); cell refinement: *SAINT* (Bruker, 2003) for (I-300) and *SMART* for (I-100). For both determinations, data reduction: *SAINT*; 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*.

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