

$S = 1.140$
 1029 reflections
 129 parameters
 H atom refined with a riding model
 $w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.4771P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	x	y	z	U_{eq}
Br	−0.21052 (10)	0.19080 (9)	−0.00055 (8)	0.0712 (3)
O1	−0.0925 (5)	−0.0922 (5)	0.0758 (5)	0.0479 (10)
O2	−0.4777 (7)	−0.3416 (6)	0.0274 (6)	0.0642 (15)
O3	−0.3892 (5)	−0.4940 (5)	0.1089 (5)	0.0474 (10)
N	−0.2783 (5)	−0.1059 (5)	0.2138 (5)	0.0361 (10)
C1	0.0882 (9)	0.2359 (9)	0.0767 (10)	0.066 (2)
C2	−0.0779 (7)	0.1528 (7)	0.1240 (6)	0.0438 (13)
C3	−0.1501 (7)	−0.0258 (7)	0.1358 (6)	0.0359 (12)
C4	−0.3553 (7)	−0.0435 (8)	0.2990 (7)	0.0435 (14)
C5	−0.4918 (11)	−0.1912 (11)	0.3543 (10)	0.081 (3)
C6	−0.4526 (10)	−0.3149 (9)	0.3501 (8)	0.065 (2)
C7	−0.3353 (7)	−0.2725 (7)	0.2363 (6)	0.0379 (13)
C8	−0.4105 (6)	−0.3697 (6)	0.1108 (6)	0.0386 (13)
C9	−0.4633 (9)	−0.6029 (8)	0.0014 (8)	0.061 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br—C2	1.963 (6)	N—C3	1.346 (7)
O1—C3	1.211 (7)	N—C7	1.453 (7)
O2—C8	1.175 (8)	N—C4	1.458 (8)
O3—C8	1.334 (7)	C2—C3	1.529 (8)
O3—C9	1.428 (8)		
C3—N—C7	117.8 (5)	C7—N—C4	113.1 (5)
C3—N—C4	128.3 (5)		
C7—N—C3—C2	−173.3 (5)	C3—N—C7—C8	−71.2 (6)

Since (I) crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988) and the absolute structure of the crystal used for the investigation was established as described by Flack (1983).

Data collection: *MSC CTR* (Molecular Structure Corporation, 1991). Cell refinement: *MSC CTR*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

We would like to acknowledge Dr P. R. Raithby for kindly allowing the use of a diffractometer for data collection.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Thiourea–1,5-Cyclooctadiene Clathrate at 173 K

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(Received 18 November 1993; accepted 4 July 1994)

Abstract

The structure of the host–guest-type clathrate, thiourea–1,5-cyclooctadiene (3/1) 3CH₄N₂S.C₈H₁₂, at 173 K, is reported. The thiourea molecules (host) form nearly hexagonal channels while the ordered 1,5-cyclooctadiene guest molecules occupy the channels. The channels result from hydrogen bonding between thiourea molecules. The channel axis is parallel to the *ac* bisector. Although the guest molecules are well defined, there seems to be slight orientational disorder about their centre of mass.

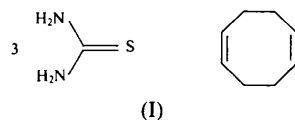
Comment

A great many studies (Schlessler & Flitter, 1952; Hagan, 1962; Fetterly, 1964) on inclusion compounds formed between urea or thiourea and guest molecules have been undertaken since the accidental discovery of such adducts by Bengen (1940). Urea and thiourea form, through an extensive network of hydrogen bonds, hexagonal channels much like a honeycomb. The guest molecules find their place in these channels. The urea channels are small and can only accommodate linear aliphatic molecules or polymers such as polyethers (Chenite & Brisse, 1991, 1992) or

aliphatic polyesters (Chenite & Brisse, 1993). Thiourea channels are larger so that benzene derivatives and cyclic molecules may form inclusion compounds. Some recently reported adducts with thiourea include bicyclo[2.2.2]octane, 1,2,4-trichlorobenzene (Fait, 1987), adamantane (Gopal, Robertson & Rutherford, 1989) and even organometallic compounds such as benzene-tricarbonylchromium(0) (Anderson, Calabrese, Tam & Williams, 1987).

In the first crystallographic study of a thiourea-cyclohexane adduct, Lenné (1954) discovered the shape and the general dimensions of the thiourea channels, but he could not observe the guest molecule which was in a very disordered state. This situation, the disordered guest, was also reported by Smith (1952) in his analysis of urea-hydrocarbon adducts.

The present paper reports the crystal structure determination and refinement of the thiourea-1,5-cyclooctadiene clathrate, (I), where the guest molecule is well resolved.



The atomic numbering scheme adopted for the thiourea and 1,5-cyclooctadiene molecules is given in Fig. 1. The geometrical features of the three independent thiourea molecules compare very well with those in pure thiourea (Truter, 1966; Elcombe & Taylor, 1968). The N—H and C—H distances all fall within the ranges 0.76–1.00 and 0.85–1.13 Å, respectively. In this clathrate, the thiourea molecules form a distorted hexagonal network through a series of hydrogen bonds, the characteristics of which are compared to those of pure thiourea in Table 3. This arrangement results in channels similar to those described by Smith (1952) for the urea-hydrocarbon clathrates and by Lenné (1954) for the thiourea-cyclohexane adduct. However, contrary to previous reports (Lenné, 1954; Gopal, Robertson & Rutherford, 1989; Harris & Thomas, 1990; Fait, 1987), the guest molecules (1,5-cyclooctadiene) are not disordered but very well resolved. At this stage the agreement index *R* reached 0.043. The bond distances, bond angles and torsion angles of the guest molecule are in good agreement with the corresponding values in the 1,5-cyclooctadiene (COD) ligand in Pt₂Co₂(CO)₈(COD) (Adams, Chen, Wu & Jin, 1990). Some of the distances in our molecule seem to be systematically shorter than in the above complex. A detailed inspection reveals some systematic discrepancies which may, however, be explained if one supposes that the guest molecule has two orientations. Thus, most molecules would have their double bonds at C(13)—C(14) and C(17)—C(18) while the others would have their double bonds at C(12)—C(13) and C(16)—C(17). This interpretation is further

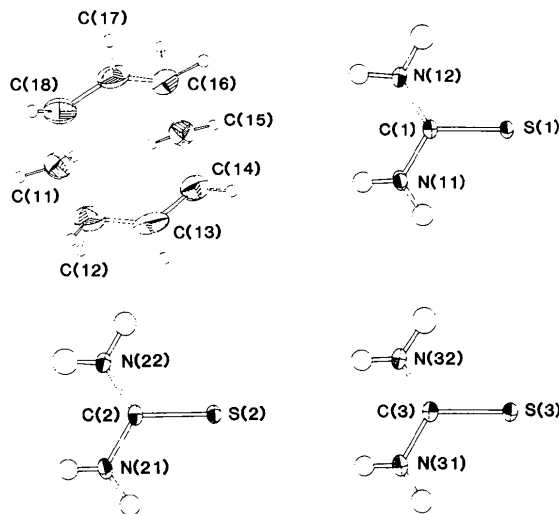


Fig. 1. Numbering scheme adopted for the thiourea and 1,5-cyclooctadiene molecules. Ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

supported by the fact that the displacement parameters of these atoms are significantly larger than those of the other ring atoms. However, attempts to refine the coordinates of two molecules with reduced occupation factors proved unsuccessful.

The conformation adopted by 1,5-cyclooctadiene in the thiourea clathrate and that of the platinum coordination compound (Adams *et al.*, 1990) are compared in the polar map shown in Fig. 2 (Ounsworth & Weiler, 1987). The eight consecutive ring bonds are shown at regular intervals around the outer circle while the values of the torsion angles are plotted radially. It is clear that there are no major conformational differences be-

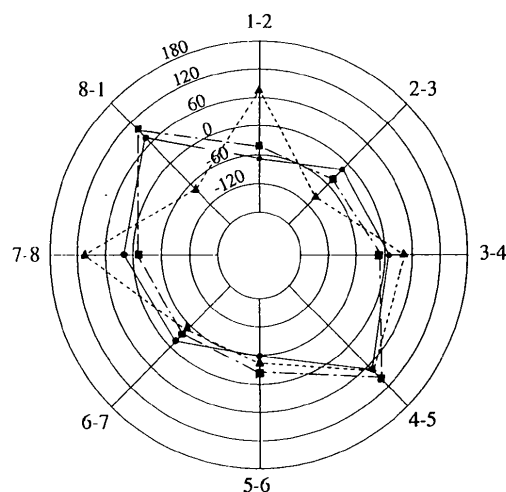


Fig. 2. Polar map in which the two 1,5-cyclooctadiene conformations (circles, this work; squares, COD in the platinum complex) are compared with that of cyclooctane in a thiourea-cyclooctane clathrate (triangles, Raymond & Brisse, 1995).

tween the two molecules, although the actual torsion angles may vary by up to 25°. The conformation of cyclooctane in the (thiourea)₃-cyclooctane clathrate is also shown in Fig. 2, which thus quickly reveals where the major conformational differences occur.

The disposition of the guest 1,5-cyclooctadiene molecule within the thiourea channel is shown in Fig. 3. The axes of the slightly distorted hexagonal channels run parallel to the bisector of the *ac* face of the unit cell. It should be pointed out that the planar thiourea molecules are tilted by about 10° from the channel axis; thus the walls of the channels are not flat but have a corrugated appearance.

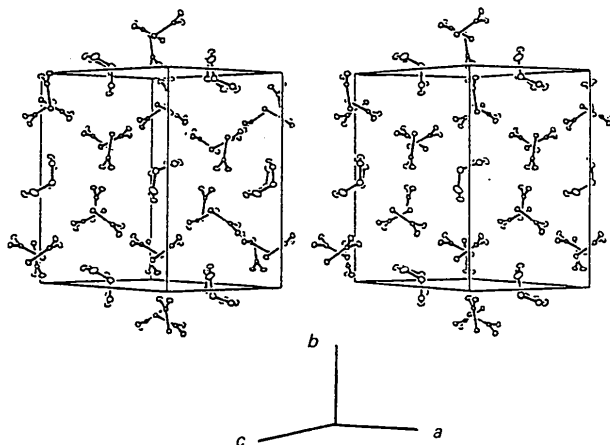


Fig. 3. Stereoview showing the channel formed by the thiourea molecules and the 1,5-cyclooctadiene guest molecule within the channel.

Experimental

Crystals of thiourea-1,5-cyclooctadiene were obtained upon cooling a warm saturated solution of thiourea in methanol to which a few ml of 1,5-cyclooctadiene were added. At room temperature, the crystals decompose in about a day when removed from their solution. The crystals were mounted quickly in a capillary, placed on the diffractometer and cooled to 173 K. The density was measured at room temperature by the flotation method using a mixture of benzene and bromobenzene. The stoichiometry of the host-guest adduct is three thiourea molecules per 1,5-cyclooctadiene.

Crystal data

3CH₄N₂S.C₈H₁₂

M_r = 336.53

Monoclinic

*P*2₁/*c*

a = 12.241 (5) Å

b = 16.05 (5) Å

c = 9.630 (4) Å

β = 110.73 (3)°

V = 1769.5 (12) Å³

Z = 4

D_x = 1.263 Mg m⁻³

D_m = 1.196 Mg m⁻³

Cu *K*α radiation

λ = 1.54178 Å

Cell parameters from 25 reflections

θ = 22–25°

μ = 3.78 mm⁻¹

T = 173 K

Hexagonal prism

0.53 × 0.30 × 0.28 mm

Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer

ω scans

Absorption correction: none

7758 measured reflections

3265 independent reflections

2513 observed reflections

[*I* ≥ 2.5σ(*I*)]

*R*_{int} = 0.045

θ_{max} = 70°

h = 0 → 15

k = -19 → 19

l = -11 → 11

7 standard reflections

frequency: 60 min

intensity decay: 5.0%

Refinement

Refinement on *F*

R = 0.0432

wR = 0.0539

S = 1.872

2513 reflections

277 parameters

H atoms refined isotropically

w = 1/[σ²(*F*) + 0.0001*F*²]

(Δ/σ)_{max} = 0.011

Δρ_{max} = 0.31 e Å⁻³ [inside the eight-membered ring, 1.16 Å from C(18)]

Δρ_{min} = -0.40 e Å⁻³

Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	0.58105 (6)	0.35430 (4)	0.07068 (7)	0.0324
S(2)	0.22546 (6)	0.19680 (4)	0.28291 (8)	0.0326
S(3)	0.12311 (6)	0.86016 (4)	0.01734 (8)	0.0340
N(11)	0.5899 (2)	0.2973 (2)	0.3326 (3)	0.0374
N(12)	0.4213 (2)	0.2690 (2)	0.1374 (3)	0.0402
N(21)	0.1399 (2)	0.0475 (2)	0.1872 (3)	0.0401
N(22)	0.3359 (3)	0.0523 (2)	0.3222 (3)	0.0432
N(31)	-0.0290 (2)	0.7575 (2)	0.0660 (3)	0.0401
N(32)	0.1330 (3)	0.7879 (2)	0.2686 (3)	0.0406
C(1)	0.5269 (2)	0.3032 (2)	0.1886 (3)	0.0303
C(2)	0.2345 (2)	0.0912 (2)	0.2630 (3)	0.0329
C(3)	0.0717 (2)	0.7976 (2)	0.1251 (3)	0.0322
C(11)	0.4001 (3)	0.0251 (2)	0.8124 (4)	0.0534
C(12)	0.3363 (5)	0.0693 (3)	0.8935 (5)	0.0761
C(13)	0.2131 (4)	0.0777 (3)	0.8483 (4)	0.0668
C(14)	0.1277 (4)	0.0708 (2)	0.7052 (4)	0.0563
C(15)	0.1527 (3)	0.0358 (2)	0.5760 (4)	0.0526
C(16)	0.1764 (4)	-0.0545 (3)	0.5816 (6)	0.0777
C(17)	0.2680 (4)	-0.0968 (2)	0.6906 (5)	0.0610
C(18)	0.3749 (4)	-0.0660 (2)	0.7877 (5)	0.0593

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.713 (3)	C(11)—C(12)	1.468 (7)
S(2)—C(2)	1.714 (3)	C(12)—C(13)	1.420 (8)
S(3)—C(3)	1.716 (3)	C(13)—C(14)	1.409 (6)
C(1)—N(11)	1.330 (4)	C(14)—C(15)	1.492 (6)
C(2)—N(21)	1.329 (4)	C(15)—C(16)	1.475 (6)
C(3)—N(31)	1.327 (4)	C(16)—C(17)	1.410 (7)
C(1)—N(12)	1.328 (4)	C(17)—C(18)	1.402 (6)
C(2)—N(22)	1.325 (4)	C(11)—C(18)	1.496 (5)
C(3)—N(32)	1.328 (4)		
N(11)—C(1)—N(12)	119.1 (3)	C(18)—C(11)—C(12)	116.0 (4)
N(21)—C(2)—N(22)	119.3 (3)	C(11)—C(12)—C(13)	126.2 (4)
N(31)—C(3)—N(32)	119.1 (3)	C(12)—C(13)—C(14)	129.2 (4)
S(1)—C(1)—N(11)	120.5 (2)	C(13)—C(14)—C(15)	123.0 (4)
S(2)—C(2)—N(21)	120.3 (2)	C(14)—C(15)—C(16)	115.8 (4)
S(3)—C(3)—N(31)	120.6 (2)	C(15)—C(16)—C(17)	126.5 (4)
S(1)—C(1)—N(12)	120.4 (2)	C(16)—C(17)—C(18)	129.5 (4)
S(2)—C(2)—N(22)	120.4 (2)	C(17)—C(18)—C(11)	122.8 (4)
S(3)—C(3)—N(32)	120.3 (2)		

C(18)—C(11)—C(12)—C(13)	—61.0 (6)
C(11)—C(12)—C(13)=C(14)	—21.8 (8)
C(12)—C(13)=C(14)—C(15)	12.7 (7)
C(13)=C(14)—C(15)—C(16)	69.5 (6)
C(14)—C(15)—C(16)—C(17)	—60.7 (6)
C(15)—C(16)—C(17)=C(18)	—22.1 (8)
C(16)—C(17)=C(18)—C(11)	13.0 (7)
C(17)=C(18)—C(11)—C(12)	69.9 (6)

Table 3. Geometrical characteristics of hydrogen bonds (\AA , $^\circ$)

	N—H...S	H...S	N—H...S
(Thiourea) ₃ —1,5-cyclooctadiene* (173 K)	3.366(3)—3.457(3)	2.44(4)—2.66(3)	151(3)—172(3)
Pure thiourea† (110 K)	3.348(4)—3.417(6)	2.354(8)—2.415(10)	169.5(5)—170.5(7)
Pure thiourea† (298 K)	3.394(4)—3.526(8)	2.397(6)—3.055(12)	133.7(7)—168.9(5)

* This work.

† Elcombe & Taylor (1968).

The structure was solved by direct methods and difference Fourier synthesis using *SHELXS86* (Sheldrick, 1985). The parameters were refined with *SHELX76* (Sheldrick, 1976).

We wish to thank the Ministère de l'Éducation du Québec for its financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 541–543

1-Cyclohexyl-2-cyclohexylamino-5(4H)-imidazolone

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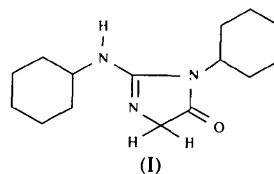
(Received 22 February 1994; accepted 6 June 1994)

Abstract

The structure of the title compound, $\text{C}_{15}\text{H}_{25}\text{N}_3\text{O}$, a product of the reaction of glycine ethyl ester with *N,N'*-dicyclohexylcarbodiimide, was elucidated by X-ray diffraction. The imidazolone ring is planar and the two cyclohexyl rings adopt chair conformations.

Comment

It has been reported (Muramatsu, 1961) that glycine ethyl ester reacts with *N,N'*-dicyclohexylcarbodiimide to form 1-cyclohexyl-2-cyclohexylamino-5(4H)-imidazolone, (I). The product was studied by IR spectroscopy and the structure proposed on the basis of analogy with guanidine formation observed for related reactions (DeTar, Silverstein & Rogers, 1966).



The title compound was synthesized by the method of Merrifield, Gisin & Bach (1977) and identified by comparison of its melting point with that given by Muramatsu (1961). A drawing of the molecule showing displacement ellipsoids is presented in Fig. 1.

Atom C4 is involved in three C—N bonds [C4—N1 1.405 (3), C4—N2 1.288 (2) and C4—N3 1.348 (6) \AA] which are different from the bond lengths observed for fully delocalized π bonds ($d_{\text{opt}} = 1.334 \text{ \AA}$; Krygowski, 1993). The distances are similar to the values expected for localized bonds (Allen *et al.*, 1987). This suggests low (if any) delocalization of π electrons in this region.

The title structure has an intramolecular hydrogen bond: $\text{N3} \cdots \text{N2}^i$ 3.058 (8), $\text{H3N} \cdots \text{N2}^i$ 2.23 (5) \AA , $\text{N3} \cdots \text{H3N} \cdots \text{N2}^i$ 159 (4) $^\circ$ [symmetry code: (i) $y - \frac{1}{2}$, $x - \frac{1}{2}$, $z - \frac{1}{2}$]. Its energy is estimated as 2.8 kJ using the empirical formula of Krygowski *et al.* (1991).