

4,6-Dimethyl-2-thioxo-1,2-dihydropyrimidin-3-ium chloride–thiourea (1/1)

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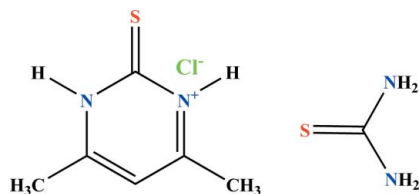
Received 2 April 2009; accepted 5 May 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.055; wR factor = 0.175; data-to-parameter ratio = 13.0.

In the title compound, $\text{C}_6\text{H}_9\text{N}_2\text{S}^+\cdot\text{Cl}^-\cdot\text{CH}_4\text{N}_2\text{S}$, the 4,6-dimethyl-2-thioxo-1,2-dihydropyrimidin-3-ium cation is protonated at one of the pyrimidine N atoms. The cations are bridged by the chloride anions through a pair of $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The amino groups of each thiourea adduct interact with the chloride anions through a pair of $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds and the S atom of another thiourea adduct through a pair of $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds. These interactions result in a layered hydrogen-bonded network propagating parallel to the bc plane. Except for two H atoms, all atoms are on special positions.

Related literature

For related structures, see: Seth & Sur (1995); Jianqiang *et al.* (2006). For bond-length data, see: Arslan *et al.* (2004); Hemamalini *et al.* (2005).



Experimental

Crystal data

$\text{C}_6\text{H}_9\text{N}_2\text{S}^+\cdot\text{Cl}^-\cdot\text{CH}_4\text{N}_2\text{S}$
 $M_r = 252.78$
 Orthorhombic, $Cmcm$
 $a = 6.6459$ (4) Å
 $b = 21.6144$ (14) Å
 $c = 8.3878$ (5) Å

$V = 1204.88$ (12) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.63$ mm⁻¹
 $T = 293$ K
 $0.10 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: none
 1080 measured reflections

636 independent reflections
 447 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.175$
 $S = 1.05$
 636 reflections

49 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl1}^{\text{i}}$	0.86	2.46	3.310 (4)	171
$\text{N2}-\text{H2A}\cdots\text{Cl1}$	0.86	2.50	3.297 (5)	154
$\text{N2}-\text{H2B}\cdots\text{S2}^{\text{ii}}$	0.86	2.49	3.347 (5)	173

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x, -y, -z + 1$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON/PLUTON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors thank the Agence Universitaire de la Francophonie for financial support (AUF-PSCI No. 6314PS804).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2066).

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supplementary materials

Acta Cryst. (2009). E65, o1252 [doi:10.1107/S1600536809016857]

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Comment

The title compound, $C_6H_9N_2S \cdot CH_4N_2S \cdot Cl$, was characterized by 1H and ^{13}C NMR, solid-state IR and X-ray crystallographic techniques. The X-ray structure determination reveals that the compound crystallizes in the orthorhombic space group *Cmcm* with a protonated molecular moiety, a chloride anion and one thiourea adduct in the asymmetric unit. The molecular geometry is illustrated in Fig. 1. The C—S bond length of 1.649 (7) Å in the molecular adduct and 1.698 (8) Å in the thiourea are double bonds character and are comparable to those observed for 1-(biphenyl-4-carbonyl)-3-p-tolyl-thiourea [1.647 (3) Å for C—S (Arslan et al., 2004)]. The C—N bond lengths are in the range [1.322 (6)-1.371 (6) Å] and are shorter than the double C—N bond length (Hemamalini et al. <i>et al.</i>, 2005). All atoms, except H5B and H5C, lie on a mirror plane, similar to the observed structure of 4,6-dimethylpyrimidine-2(1H</>)-thione (Seth & Sur, 1995). The molecular adduct forms hydrogen bonds with two chloride anions by $N1—H1 \cdots Cl1(-x + 1/2, -y + 1/2, -z + 1)$ (Fig. 2). Each thiourea molecule is linked to two other thiourea molecule by hydrogen bonds and one chloride anion respectively by $N2—H2B \cdots S2(-x, -y, -z + 1)$ and $N2—H2A \cdots Cl1$ (Table. 2).

Experimental

Thiourea (2 g, 26 mmol) was reacted with 2,4-pentadione (2.6 g, 26 mmol) in C_3H_6O (20 ml) solution, to give the corresponding 1:1 adduct after two hour under refluxing. After cooling to room temperature, 3.4 ml HCl 10M was added dropwise to the solution and the resulting mixture was refluxed for one hour before left standing overnight. The filtrate gave yellowish crystal suitable for X-ray analyses after four days of slow evaporation. Yield: 87.69%. m.p. 190 ± 2 °C. Anal. Calc. for $C_7H_{13}N_4S_2Cl$ (%): C, 33.26; H, 5.18; N, 22.16. Found: C, 33.37; H, 5.15; N, 22.25. Selected IR data (cm^{-1} , KBr pellet): 1599 (ν C=N), 1187 (ν C=S). 1H NMR (200 MHz, D_2O , δ , p.p.m.): 2.40 (s, 6H, $-CH_3$); 6.83 (s, 1H, $-CH$). ^{13}C NMR (200 MHz, D_2O , δ , p.p.m.): 19.26 ($-CH_3$); 118.32 ($-CH$); 168.02 (N=C); 172.90 (N=C—S—H).

Refinement

The H atoms of the NH_2 groups were located in the Fourier difference maps and refined by riding motion. Others H atoms were placed geometrically and refined with a riding model. $U_{iso}(H)$ for H was assigned as $1.2U_{eq}$ of the attached C atoms (1.5 for methyl C atoms).

Figures

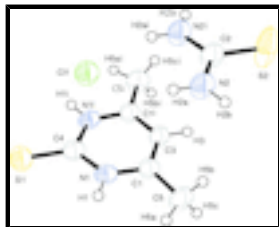


Fig. 1. An *ORTEP* view of the asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. Symmetry code: (i) $-x, y, -z + 1/2$

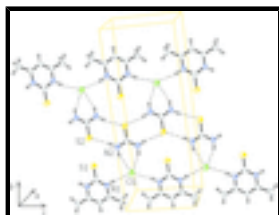


Fig. 2. Molecular representation of the compound showing hydrogen bonds. The broken lines stand for hydrogen bonds.

4,6-Dimethyl-2-thioxo-1,2-dihydropyrimidin-3-ium chloride–thiourea (1/1)

Crystal data

$C_6H_9N_2S^+ \cdot Cl^- \cdot CH_4N_2S$

$M_r = 252.78$

Orthorhombic, *Cmcm*

Hall symbol: $-C\ 2c\ 2$

$a = 6.6459\ (4)\ \text{\AA}$

$b = 21.6144\ (14)\ \text{\AA}$

$c = 8.3878\ (5)\ \text{\AA}$

$V = 1204.88\ (12)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 528$

$D_x = 1.393\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 653 reflections

$\theta = 1.0\text{--}25.4^\circ$

$\mu = 0.63\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, yellow

$0.10 \times 0.10 \times 0.10\ \text{mm}$

Data collection

Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

φ scans

Absorption correction: none

1080 measured reflections

636 independent reflections

447 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 25.3^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -7 \rightarrow 7$

$k = -25 \rightarrow 25$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.055$$

$$wR(F^2) = 0.175$$

$$S = 1.05$$

636 reflections

49 parameters

Primary atom site location: structure-invariant direct methods

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 1.9948P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.004$$

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.0000	0.22960 (8)	0.7500	0.0492 (6)	
S1	0.5000	0.32187 (9)	0.7500	0.0582 (7)	
S2	0.0000	-0.02324 (10)	0.7500	0.1135 (15)	
N1	0.5000	0.21069 (18)	0.6134 (5)	0.0424 (10)	
H1	0.5000	0.2302	0.5240	0.051*	
N2	0.0000	0.0864 (2)	0.6144 (5)	0.0558 (12)	
H2A	0.0000	0.1262	0.6154	0.067*	
H2B	0.0000	0.0669	0.5251	0.067*	
C1	0.5000	0.1485 (2)	0.6079 (6)	0.0423 (11)	
C2	0.0000	0.0553 (4)	0.7500	0.0526 (19)	
C3	0.5000	0.1172 (3)	0.7500	0.0448 (17)	
H3	0.5000	0.0741	0.7500	0.054*	
C4	0.5000	0.2456 (3)	0.7500	0.0431 (16)	
C5	0.5000	0.1187 (3)	0.4493 (6)	0.0589 (15)	
H5A	0.5000	0.1499	0.3679	0.088*	
H5B	0.3821	0.0934	0.4385	0.088*	0.50
H5C	0.6179	0.0934	0.4385	0.088*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0583 (11)	0.0481 (11)	0.0412 (10)	0.000	0.000	0.000
S1	0.0680 (13)	0.0463 (11)	0.0602 (14)	0.000	0.000	0.000
S2	0.267 (5)	0.0420 (14)	0.0316 (11)	0.000	0.000	0.000

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N1	0.048 (2)	0.052 (3)	0.0276 (19)	0.000	0.000	0.0029 (18)
N2	0.084 (3)	0.053 (3)	0.030 (2)	0.000	0.000	0.0004 (19)
C1	0.048 (3)	0.046 (3)	0.033 (3)	0.000	0.000	0.000 (2)
C2	0.078 (5)	0.053 (4)	0.027 (4)	0.000	0.000	0.000
C3	0.059 (4)	0.041 (4)	0.035 (4)	0.000	0.000	0.000
C4	0.036 (3)	0.053 (4)	0.040 (4)	0.000	0.000	0.000
C5	0.086 (4)	0.063 (3)	0.028 (3)	0.000	0.000	-0.007 (2)

Geometric parameters (Å, °)

S1—C4	1.649 (7)	C1—C5	1.479 (7)
S2—C2	1.698 (8)	C2—N2 ⁱ	1.322 (6)
N1—C1	1.345 (6)	C3—C1 ⁱ	1.371 (6)
N1—C4	1.371 (5)	C3—H3	0.9300
N1—H1	0.8600	C4—N1 ⁱ	1.371 (5)
N2—C2	1.322 (6)	C5—H5A	0.9600
N2—H2A	0.8600	C5—H5B	0.9600
N2—H2B	0.8600	C5—H5C	0.9600
C1—C3	1.371 (6)		
C1—N1—C4	125.3 (4)	C1 ⁱ —C3—C1	120.8 (6)
C1—N1—H1	117.4	C1 ⁱ —C3—H3	119.6
C4—N1—H1	117.4	C1—C3—H3	119.6
C2—N2—H2A	120.0	N1 ⁱ —C4—N1	113.3 (6)
C2—N2—H2B	120.0	N1 ⁱ —C4—S1	123.3 (3)
H2A—N2—H2B	120.0	N1—C4—S1	123.3 (3)
N1—C1—C3	117.7 (5)	C1—C5—H5A	109.5
N1—C1—C5	117.8 (4)	C1—C5—H5B	109.5
C3—C1—C5	124.5 (5)	H5A—C5—H5B	109.5
N2 ⁱ —C2—N2	118.8 (7)	C1—C5—H5C	109.5
N2 ⁱ —C2—S2	120.6 (3)	H5A—C5—H5C	109.5
N2—C2—S2	120.6 (3)	H5B—C5—H5C	109.5
C4—N1—C1—C3	0.000 (1)	C5—C1—C3—C1 ⁱ	180.0
C4—N1—C1—C5	180.000 (1)	C1—N1—C4—N1 ⁱ	0.000 (2)
N1—C1—C3—C1 ⁱ	0.000 (2)	C1—N1—C4—S1	180.0

Symmetry codes: (i) $x, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots C11 ⁱⁱ	0.86	2.46	3.310 (4)	171
N2—H2A \cdots C11	0.86	2.50	3.297 (5)	154
N2—H2B \cdots S2 ⁱⁱⁱ	0.86	2.49	3.347 (5)	173

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

Fig. 1

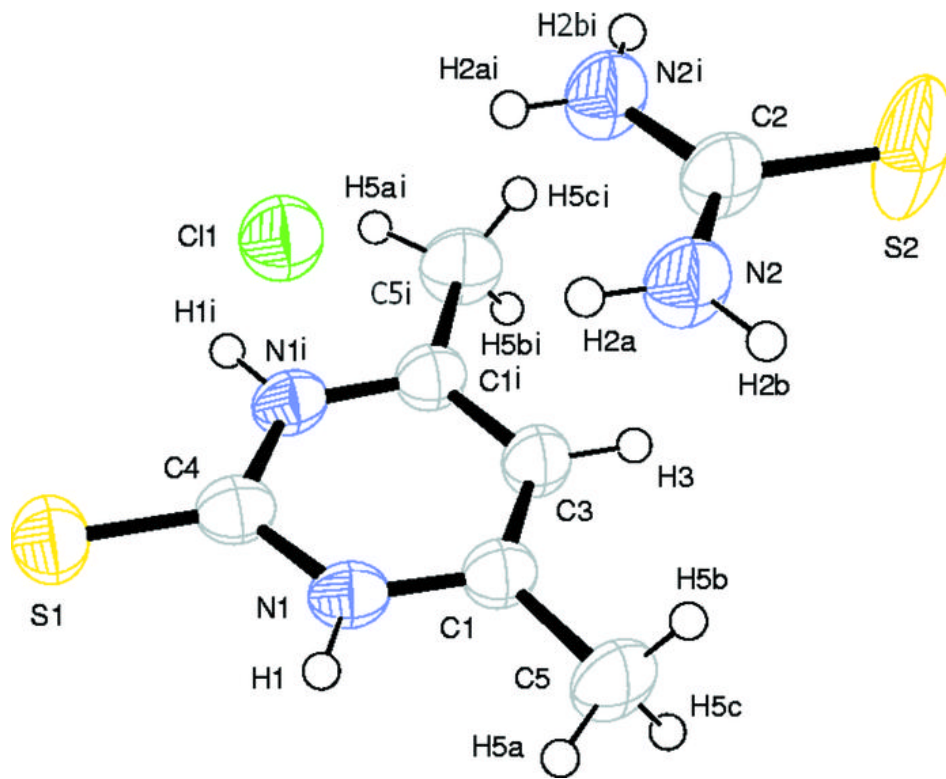


Fig. 2

