organic compounds

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

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In the title compound, $C_6H_9N_2S^+ \cdot Cl^- \cdot CH_4N_2S$, 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 N—H···Cl hydrogen bonds. The amino groups of each thiourea adduct interact with the chloride anions through a pair of N—H···Cl hydrogen bonds and the S atom of another thiourea adduct through a pair of N—H···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).
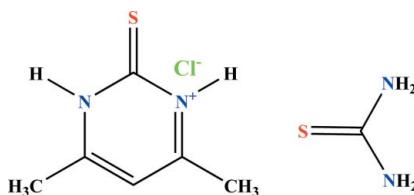
Experimental

Crystal data

$C_6H_9N_2S^+ \cdot Cl^- \cdot CH_4N_2S$	V = 1204.88 (12) Å^3
M_r = 252.78	Z = 4
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
a = 6.6459 (4) Å	μ = 0.63 mm^{-1}
b = 21.6144 (14) Å	T = 293 K
c = 8.3878 (5) Å	$0.10 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	636 independent reflections
Absorption correction: none	447 reflections with $I > 2\sigma(I)$
1080 measured reflections	R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055	49 parameters
$wR(F^2)$ = 0.175	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
636 reflections	$\Delta\rho_{min}$ = -0.51 e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···Cl1^i	0.86	2.46	3.310 (4)	171
N2—H2A···Cl1	0.86	2.50	3.297 (5)	154
N2—H2B···S2^{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*.

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

References

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supporting information

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

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S1. Comment

The title compound, $C_6H_9N_2S.CH_4N_2SCl$, 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-(bi-phenyl-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/>, 2005). All atoms, except H5B and H5C, lie on a mirror plane, similar to the observed structure of 4,6-dimethyl-pyrimidine-2(1H</>)-thione (Seth & Sur, 1995). The molecular adduct forms hydrogen bonds with two chloride anions by N1—H1···Cl1(-x + 1/2, -y + 1/2, -z + 1) (Fig. 2). Each thiourea molecule is linked to two other thioura molecule by hydrogen bonds and one chloride anion respectively by N2—H2B···S2(-x, -y, -z + 1) and N2—H2A···Cl1 (Table. 2).

S2. 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 10*M* 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 (*v* C=N), 1187 (*v* C=S). ^1H NMR (200 MHz, D$_2$O, δ, p.p.m.): 2.40 (s, 6H, –CH$_3$); 6.83 (s, 1H, –CH). ^{13}C NMR (200 MHz, D$_2$O, δ, p.p.m.): 19.26 (–CH$_3$); 118.32 (–CH); 168.02 (N=C); 172.90 (N=C—S—H).

S3. 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).
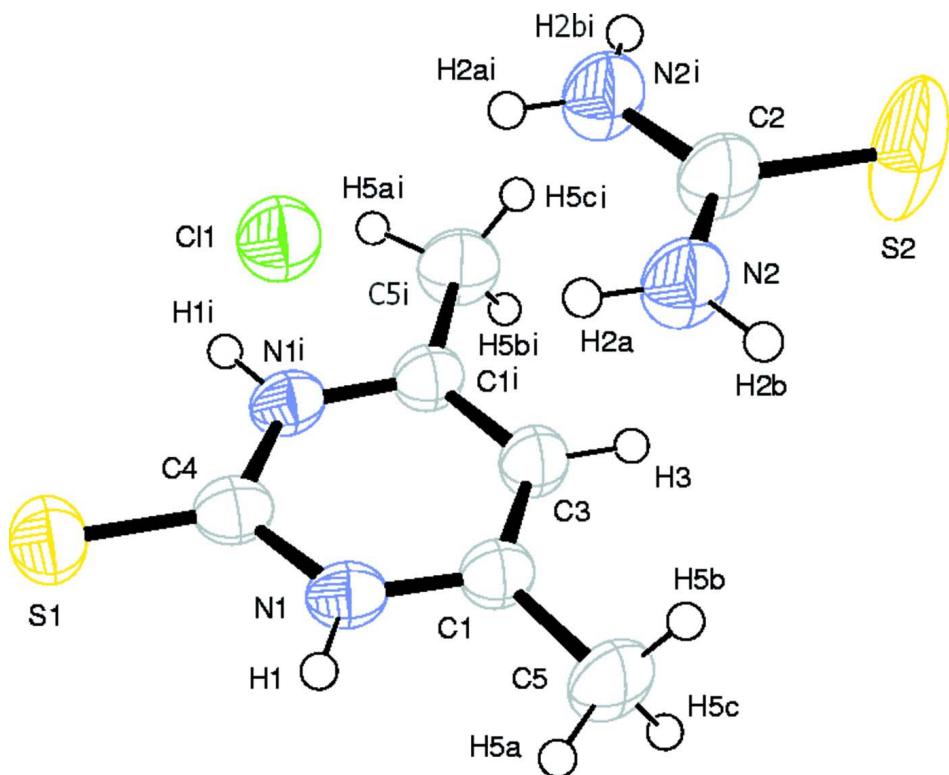
Figure 1

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
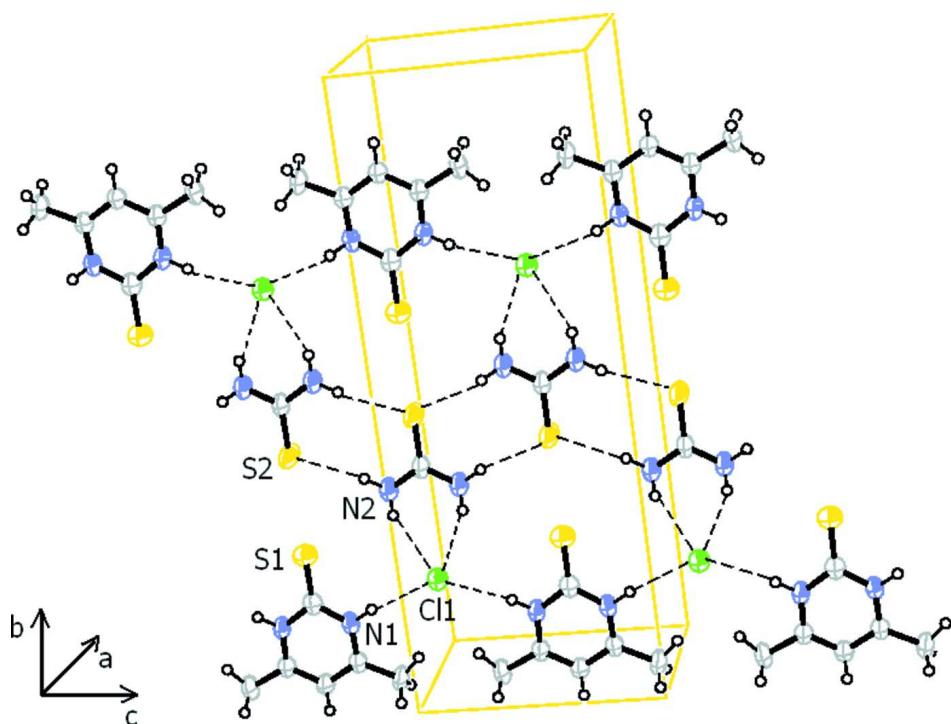
Figure 2

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
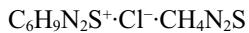
$C_6H_9N_2S^+ \cdot Cl^- \cdot CH_4N_2S$	$F(000) = 528$
$M_r = 252.78$	$D_x = 1.393$ Mg m^{-3}
Orthorhombic, *Cmcm*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2c 2	Cell parameters from 653 reflections
$a = 6.6459$ (4) Å	$\theta = 1.0–25.4°$
$b = 21.6144$ (14) Å	$\mu = 0.63$ mm^{-1}
$c = 8.3878$ (5) Å	$T = 293$ K
$V = 1204.88$ (12) Å^3	Prism, yellow
$Z = 4$	$0.10 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	447 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.024$
Graphite monochromator	$\theta_{max} = 25.3°$, $\theta_{min} = 3.1°$
φ scans	$h = -7 \rightarrow 7$
1080 measured reflections	$k = -25 \rightarrow 25$
636 independent reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$S = 1.05$
Least-squares matrix: full	636 reflections
$R[F^2 > 2\sigma(F^2)] = 0.055$	49 parameters
$wR(F^2) = 0.175$	0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 1.9948P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.44$ e Å^{-3}

$\Delta\rho_{min} = -0.51$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å^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
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, º)

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 code: (i) *x*, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{ii}	0.86	2.46	3.310 (4)	171
N2—H2*A*···Cl1	0.86	2.50	3.297 (5)	154
N2—H2*B*···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.