Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Hydrazine carbodithioic acid pyridinium-2-yl methyl ester chloride

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.096
Data-to-parameter ratio = 18.9

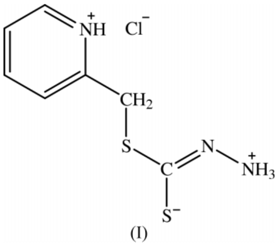
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[C_7H_{10}N_3S_2]^+\cdot Cl^-$, exists as an ionic compound of a dithiocarbazate system, with a zwitterionic $^+H_3NNCS^-$ moiety and a protonated pyridine ring. The C—S thione bond distance of the zwitterionic moiety [1.708 (2) Å] is longer than the normal double bond and the C—N of the carbazate moiety has double-bond character. The crystal packing is stabilized by intramolecular hydrogen bonds, which form a two-dimensional network perpendicular to *b*.

Received 12 December 2002
Accepted 2 January 2003
Online 17 January 2003

Comment

Unlike many dithiocarbazate compounds, such as *S*-methyldithiocarbazate (Mattes & Waber, 1980) and *S*-benzyldithiocarbazate (Shanmuga Sundara Raj *et al.*, 2000), the title compound, (I), exists in ionic form, with a zwitterionic N3/N2/C7/S2 moiety, the protonated N1 as cation and a chloride anion (Fig. 1). However, the organic cation maintains the preferred configuration, which is *cis* for the ammonium group across the C═N bond, and *trans* for the pyridiniummethylene group across the C—S bond, both relative to the terminal thiono S atom. The C7—N2 bond length of 1.296 (2) Å indicates its double-bond character, while C7—S2 [1.708 (2) Å] is longer than the normal C═S bond of between 1.65 and 1.68 Å for dithiocarbazate (Mattes & Waber, 1980; Shanmuga Sundara Raj *et al.*, 2000; Tarafder *et al.*, 2001), but close to the zwitterionic C—S bond length in dithiocarbamic acid [1.712 (2) Å; Yamin *et al.*, 2002]. Although the N2—N3 bond length of 1.437 (2) Å is within the normal range, it is longer than the normal N—N distance for a carbazate system [1.396 Å for *S*-benzyldithiocarbazate; Shanmuga Sundara Raj *et al.*, 2000]. The bond lengths and angles of the picolyl group are within normal ranges (Allen *et al.*, 1987).



(I)

All H atoms bonded to N atoms (one at N1 and three at N3) participate in hydrogen bonding (Table 2). Two of them are intramolecular (N1—H1*n*···N2 and N3—H3*n*2···S2). Intermolecular N—H···Cl hydrogen bonds connect the molecules into a two-dimensional network perpendicular to the *b* axis (Fig. 2).

DOI: 10.1107/S160053680300014X

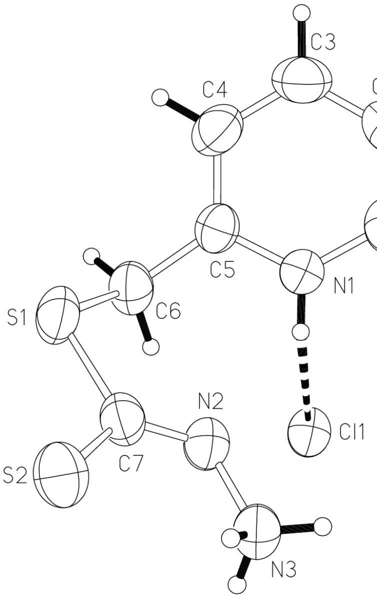


Figure 1
*ORTEP*II (Johnson, 1976) view of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as circles of arbitrary radii.

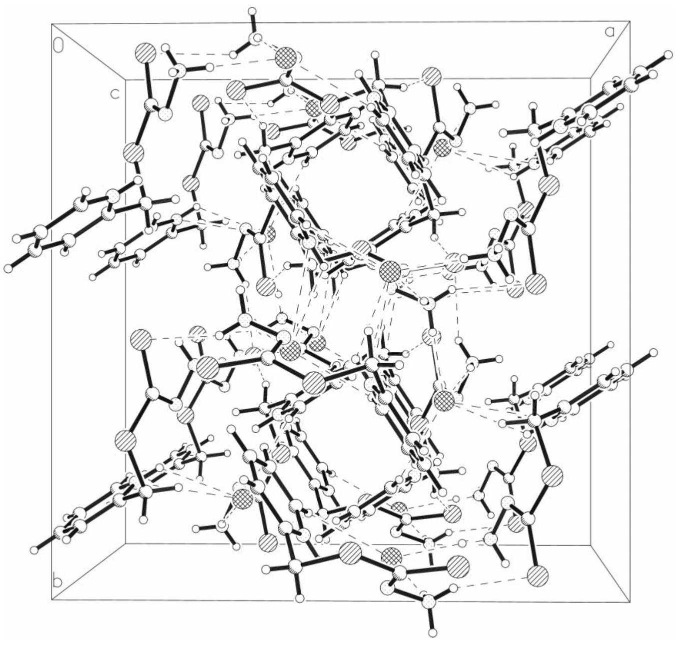


Figure 2
Packing diagram of the title compound, viewed down the *c* axis. Dashed lines denote the N—H···Cl and N—H···S interactions.

The picolyl N1/C1/C2/C3/C4/C5/C6/C7 and zwitterionic N3/N2/S1/S2 moieties are planar, with maximum deviations of 0.017 (2) Å at N1 and 0.034 (1) Å at S1, respectively. The two planes make a dihedral angle of 64.16 (6)°.

Experimental

Potassium hydroxide (11.4 g, 0.2 mol) was completely dissolved in 70 ml of 90% ethanol and cooled in ice. To the cooled solution hydrazine hydrate (10 g, 0.2 mol) was added slowly with stirring. A solution of carbon disulfide (15.2 g, 0.2 mol) in ethanol (23 ml) was added dropwise from a burette, with constant stirring, for about 1 h. The temperature of the mixture was kept below 263 K during the addition. During this time, two layers formed. The yellow oil in the lower layer was then separated using a separation funnel, dissolved in 40% ethanol (100 ml) and cooled in ice. 2–Picolylchloride hydrochloride (32.8 g, 0.2 mol) was completely dissolved in 100 ml of 80% ethanol and added slowly to the above solution with vigorous mechanical stirring. The resulting light-green product was filtered, washed with distilled water and dried. The product was recrystallized from absolute ethanol.

Crystal data

$C_7H_{10}N_3S_2^+\cdot Cl^-$
$M_r = 235.75$
Tetragonal, $I4_1/a$
$a = 16.5700\ (8)$ Å
$c = 15.3576\ (7)$ Å
$V = 4216.7\ (3)$ Å^3
$Z = 16$
$D_x = 1.485$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6222 reflections
$\theta = 1.8$–28.3°
$\mu = 0.72$ mm^{-1}
$T = 293\ (2)$ K
Block, yellow
0.55 × 0.49 × 0.38 mm

Data collection

Bruker Smart APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.694$, $T_{max} = 0.773$
12702 measured reflections
2545 independent reflections
1920 reflections with $I > 2\ s(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.3°$
$h = -21 \rightarrow 21$
$k = -21 \rightarrow 21$
$l = -10 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.096$
$S = 0.93$
2545 reflections
135 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.820 (2)	N1—C1	1.335 (2)
S1—C7	1.764 (2)	N2—C7	1.296 (2)
S2—C7	1.708 (2)	N2—N3	1.437 (2)
N1—C5	1.337 (2)		
C6—S1—C7	103.9 (1)	N2—C7—S2	129.5 (1)
C5—N1—C1	124.1 (2)	N2—C7—S1	116.7 (1)
C7—N2—N3	112.2 (2)	S2—C7—S1	113.8 (1)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*n*···N2	0.83 (1)	2.35 (2)	2.934 (2)	128 (2)
N1—H1*n*···Cl1	0.83 (1)	2.66 (2)	3.237 (2)	127 (2)
N1—H1*n*···Cl1^{i}	0.83 (1)	3.13 (2)	3.580 (2)	117 (2)
N3—H3*n*1···Cl1^{i}	0.86 (1)	2.35 (1)	3.162 (2)	158 (2)
N3—H3*n*2···S2	0.88 (1)	2.33 (2)	2.925 (2)	126 (2)
N3—H3*n*3···Cl1^{ii}	0.86 (1)	2.26 (1)	3.108 (2)	170 (2)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$.

The N—H distances were restrained to 0.85 (1) Å. The other H atoms were included using a riding model, with fixed C—H bond lengths of 0.93 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The authors thank the Universiti Putra Malaysia and Universiti Kebangsaan Malaysia for research facilities, and the Malaysian Government for research grants Nos. 09-02-04-0296 and 09-02-02-0163.

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