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4-Methylpyridinium Hydrogen Sulfide

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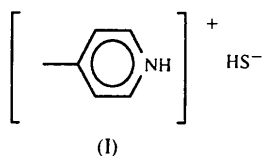
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Abstract

4-Methylpyridinium hydrogen sulfide, $C_6H_7NH^+ \cdot HS^-$, was obtained as a by-product of the reaction between $GaCl_3$ and thioglycolic acid in a 4-methylpyridine solution. The compound consists of heterocyclic $C_6H_7NH^+$ cationic rings and HS^- anions. Both the $C_6H_7NH^+$ cation and the HS^- anion lie on crystallographic mirror planes with the N, S, two C and two H atoms positioned in the planes. The H atom of the HS^- anion was not located.

Comment

As part of our program to study the reactions of indium and gallium compounds in nitrogen-donor solvents, we have isolated, crystallized and structurally characterized a number of by-products derived from reactions of the solvents, including piperidinium hydrogen sulfide (Andras, Hepp, Fanwick, Duraj & Gordon, 1994), 4-methylpyridinium bromide (Andras, Hepp, Fanwick, Martuch & Duraj, 1993) and 4-methylpyridinium hydrogen sulfide, (I), the structure of which is reported here.



† This work was performed while the author held a National Research Council–NASA Research Associateship.

4-Methylpyridinium hydrogen sulfide, also known as γ -picolinium hydrogen sulfide, retains the basic structure of the 4-methylpyridine ring (Ohms *et al.*, 1985), but its structure varies from that of 4-methylpyridine in several small ways. These variations include an increase in the C—N—C bond angle as the lone pair on the N atom of 4-methylpyridine is replaced with the N—H bond of the 4-methylpyridinium ring and a slight shortening (0.03 Å) of the C(2)—C(3) bond length between the neutral and protonated rings.

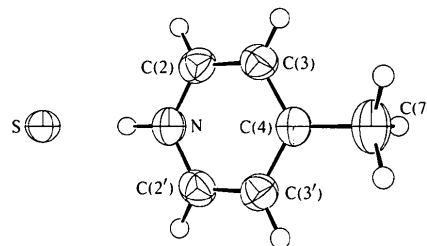


Fig. 1. ORTEP (Johnson, 1965) drawing of the title molecule (without the undetected H atom of HS^-) showing the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level, while isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

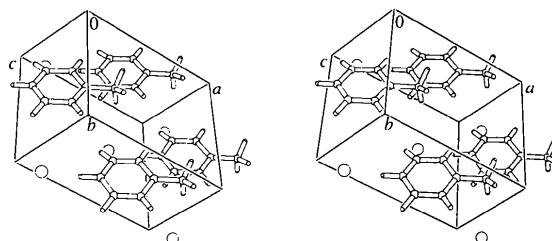


Fig. 2. Packing diagram of the title compound.

Experimental

4-Methylpyridinium hydrogen sulfide was obtained as a by-product of the reaction between $GaCl_3$ and thioglycolic acid ($HSCH_2CO_2H$) in a 4-methylpyridine solution. The reaction was carried out under an argon atmosphere. 2.0 ml (18.7 mmol) of $HSCH_2CO_2H$ was slowly added to a solution of 0.87 g of $GaCl_3$ in 30 ml of 4-methylpyridine. After reacting for 24 h, the precipitate which formed was removed by filtration. The filtrate solution was layered with 30 ml of freshly distilled hexanes. This produced colorless crystals of 4-methylpyridinium hydrogen sulfide which were allowed to grow for 80 d. The crystals were then collected, washed with three 10 ml aliquots of hexanes and dried *in vacuo*.

Crystal data

$C_6H_8N^+ \cdot HS^-$
 $M_r = 127.21$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic	Cell parameters from 25 reflections
<i>Cm</i>	$\theta = 18\text{--}23^\circ$
$a = 8.679 (2) \text{ \AA}$	$\mu = 0.364 \text{ mm}^{-1}$
$b = 7.964 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.860 (2) \text{ \AA}$	Chunk
$\beta = 101.10 (2)^\circ$	$0.47 \times 0.32 \times 0.22 \text{ mm}$
$V = 329.6 (3) \text{ \AA}^3$	Colorless
$Z = 2$	
$D_x = 1.28 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	385 observed reflections
$\omega/2\theta$ scans	$[F > 3.0\sigma(F)]$
Absorption correction: empirical, ΔF (Walker & Stuart, 1983)	$\theta_{\max} = 27.5^\circ$
$T_{\min} = 0.421$, $T_{\max} = 1.000$	$h = 0 \rightarrow 11$
413 measured reflections	$k = 0 \rightarrow 10$
413 independent reflections	$l = -6 \rightarrow 6$
	3 standard reflections
	frequency: 83 min
	intensity decay: none

Refinement

Refinement on F	$w = 1/\sigma^2(F)$
$R = 0.039$	$(\Delta/\sigma)_{\max} = 0.02$
$wR = 0.048$	$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
$S = 1.617$	$\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
385 reflections	Extinction correction: none
59 parameters	Atomic scattering factors
All H-atom parameters refined; anion H atom not located	from Cromer & Waber (1974)

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

$$B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
S	0.16570	1	0.95320	3.86 (2)
N	0.4327 (5)	1	0.6516 (9)	3.61 (8)
C(2)	0.4863 (5)	0.8540 (5)	0.5731 (9)	3.93 (7)
C(3)	0.5969 (5)	0.8508 (5)	0.4101 (8)	3.72 (6)
C(4)	0.6555 (6)	1	0.323 (1)	3.23 (8)
C(7)	0.7805 (7)	1	0.152 (1)	4.8 (1)
H(1)	0.349 (9)	1	0.77 (2)	6 (2)
H(21)	0.459 (7)	0.756 (9)	0.68 (1)	8 (2)
H(31)	0.632 (8)	0.754 (9)	0.35 (1)	9 (2)
H(71)	0.872 (9)	1	0.30 (2)	6 (2)
H(72)	0.77 (1)	0.89 (1)	0.01 (2)	12 (2)

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

S—H(1)	1.98 (9)	C(3)—C(4)	1.390 (5)
N—C(2)	1.335 (5)	C(3)—H(31)	0.90 (8)
N—H(1)	1.00 (9)	C(4)—C(7)	1.488 (8)
C(2)—C(3)	1.357 (7)	C(7)—H(71)	1.0 (1)
C(2)—H(21)	0.98 (8)	C(7)—H(72)	1.1 (1)
C(2)—N—C(2')	121.1 (6)	C(3)—C(4)—C(3')	117.5 (5)
C(2)—N—H(1)	119.4 (3)	C(3)—C(4)—C(7)	121.2 (3)
N—C(2)—C(3)	120.5 (4)	C(4)—C(7)—H(71)	99 (6)
N—C(2)—H(21)	114 (4)	C(4)—C(7)—H(72)	113 (5)
C(3)—C(2)—H(21)	124 (4)	H(71)—C(7)—H(72)	115 (6)
C(2)—C(3)—C(4)	120.2 (4)	H(72)—C(7)—H(72')	103 (11)
C(2)—C(3)—H(31)	121 (5)	S—H(1)—N	173 (8)
C(4)—C(3)—H(31)	118 (5)		

Symmetry code: (i) $x, 2 - y, z$.

The crystal for analysis was sealed in a glass capillary. Intensity data were collected with a variable scan rate of $2\text{--}16^\circ \text{ min}^{-1}$ and an ω -scan width of $(0.74 + 0.350 \tan \theta)^\circ$. Intensities were corrected for Lorentz and polarization effects. Atoms were located in succeeding difference Fourier syntheses. With the exception of the H atom of the HS⁻ ion, H atoms were located and their positions and isotropic displacement parameters refined. The structure was refined by full-matrix least-squares methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w , was defined by the Killean & Lawrence (1969) method with terms of 0.020 and 0.1. Anomalous dispersion effects were included in F_c (Ibers & Hamilton, 1964) and the values of f' and f'' were those of Cromer (1974). Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta$ and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *MolEN* (Fair, 1990). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *WordPerfect for Windows* (Version 5.2).

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Lists of structure factors, anisotropic displacement parameters and torsion angles have been deposited with the IUCr (Reference: BK1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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