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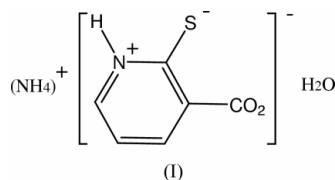
Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.040
wR factor = 0.174
Data-to-parameter ratio = 17.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Ammonium 2-mercaptopyridine-3-carboxylate hydrate

The crystal structure of ammonium 2-mercaptopyridine-3-carboxylate hydrate, $\text{NH}_4^+ \cdot \text{C}_6\text{H}_4\text{NO}_2\text{S}^- \cdot \text{H}_2\text{O}$, contains a zwitterionic anion with the pyridine-N atom protonated. All potential donor and acceptor atoms are involved in hydrogen-bonding, resulting in a three-dimensional network structure.Received 3 March 2003
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Comment

2-Mercapto-substituted alcohols and acids have considerable utility as bidentate ligands in coordination chemistry (Harris & Livingstone, 1964; McAuliffe, 1986). These ligands may act as either mono- or di-anionic species and, with bismuth(III) often give octahedral complexes (Agoes *et al.*, 1997; Sagatys *et al.*, 2003). The ammonium tris(2-mercaptobenzoato-*O,S*) bismuth(III) dihydrate complex (Sagatys *et al.*, 2003) is readily formed, while the complex with the analogous ligand thionicotinic acid (2-mercaptopyridine-3-carboxylic acid) is less so. The structure of the ionic species formed from the latter acid under aqueous ammoniacal conditions was therefore determined in an attempt to explain this anomaly.

The crystal structure of ammonium 2-mercaptopyridine-3-carboxylate hydrate, (I), confirms the presence of a zwitterionic anion species with protonation at the pyridine-N atom and deprotonation of the carboxylate and thiolate residues (Fig. 1). The plane of the carboxylate group at C3 is anti-clinally related to that of the pyridine ring [torsion angle C2—C3—C7—O71 = 75.1 (4)°]. The formation of the stable zwitterion probably accounts for the different behaviour of thionicotinic acid compared to thiosalicylic acid as a complexing agent.

The crystal packing of (I) shows that all ammonium H atoms, together with the zwitterionic pyridinium H atom, are involved in hydrogen-bonding interactions to carboxylate and water O atoms, as well as to a thiol-S atom [N11—H14...S2 = 3.350 (3) Å] (Fig. 2 and Table 1). The water molecule is also hydrogen bonded to two carboxylate O atoms, giving a three-dimensional network structure.

Experimental

The title compound, (I), was prepared by dissolving 5.0 g (3.2 mmol) of thionicotinic acid (2-mercaptopyridine-3-carboxylic acid) in 150 ml of 28% ammonia solution at room temperature and allowing the

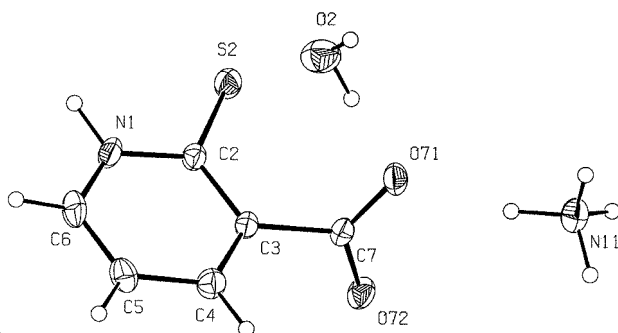


Figure 1
The molecular structure and atom-numbering scheme for (I). Ellipsoids are shown at the 30% probability level.

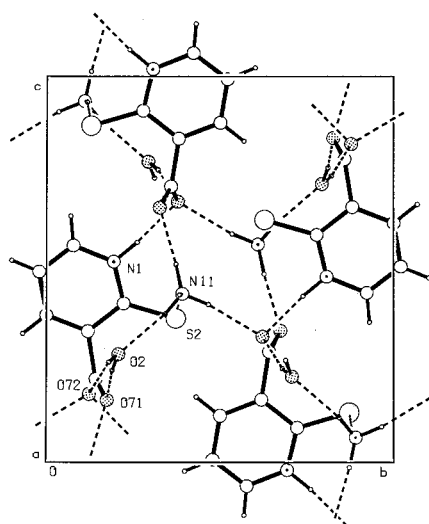


Figure 2
The packing of (I) in the unit cell, viewed down *a*, with hydrogen-bonding interactions shown as dashed lines.

filtered solution to evaporate to dryness at room temperature over a period of *ca* 3 weeks.

Crystal data

$\text{H}_4\text{N}^+\cdot\text{C}_6\text{H}_4\text{NO}_2\text{S}^-\cdot\text{H}_2\text{O}$
 $M_r = 190.22$
 Monoclinic, $P2_1/n$
 $a = 6.8327$ (4) Å
 $b = 10.8017$ (12) Å
 $c = 12.2436$ (5) Å
 $\beta = 100.854$ (5)°
 $V = 887.47$ (12) Å³
 $Z = 4$

$D_x = 1.424$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.8\text{--}18.9^\circ$
 $\mu = 0.34$ mm⁻¹
 $T = 296$ (2) K
 Plate, colourless
 $0.35 \times 0.35 \times 0.12$ mm

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: none
 2631 measured reflections
 2451 independent reflections
 1113 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

$\theta_{\text{max}} = 29.5^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 13$
 $l = -15 \rightarrow 15$
 3 standard reflections every 150 reflections
 intensity decay: 0.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.174$
 $S = 1.00$
 2451 reflections
 138 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.1032P)^2 + 0.154P]$$

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

$$(\Delta/\sigma)_{\text{max}} < 0.001$$

$$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$$

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O72 ⁱ	0.97 (4)	1.83 (4)	2.801 (4)	174 (4)
N11—H11...O72 ⁱⁱ	0.96 (6)	1.97 (6)	2.892 (4)	159 (5)
N11—H12...O71	1.01 (6)	1.85 (6)	2.839 (3)	166 (4)
N11—H13...O2 ⁱⁱⁱ	0.91 (5)	1.94 (5)	2.774 (4)	151 (4)
N11—H14...S2 ^{iv}	0.90 (4)	2.47 (4)	3.350 (3)	164 (5)
O2—H21...O71	0.94 (5)	1.84 (5)	2.767 (3)	173 (6)
O2—H22...O72 ^v	0.84 (5)	1.98 (6)	2.806 (3)	167 (7)

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

H atoms involved in hydrogen-bonding interactions (*i.e.* H1, H11, H12, H13, H14, H21 and H22) were located by difference methods, and both positional and displacement parameters were refined. Other H atoms were included in the riding-model approximation.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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