

Pyridine-2-carbaldehyde thiosemicarbazone
1.75-hydrateZhi Min Jin,^{a*} Liang Shen,^b
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Key indicators

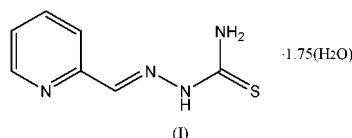
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.040
 wR factor = 0.095
Data-to-parameter ratio = 15.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The structure of the title compound, $\text{C}_7\text{H}_8\text{N}_4\text{S}\cdot 1.75\text{H}_2\text{O}$, is similar to that of pyridine-2-carbaldehyde thiosemicarbazone dihydrate [Huang (1993). *J. X. Univ. (Nat. Sci.)*, **32**, 741–744], except for the disorder in a water molecule and presence of another water molecule at special position (1/2, 3/4, 1/8).

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Comment

Thiosemicarbazones and their metal compounds exhibit a wide range of biological activity (French *et al.*, 1974; Easmon *et al.*, 1992; Agrawal *et al.*, 1975). The crystal structures of pyridine-2-carbaldehyde thiosemicarbazone monohydrate (PCT·H₂O; Biyushkin *et al.*, 1987) and pyridine-2-carbaldehyde thiosemicarbazone dihydrate [PCT·2H₂O (Huang, 1993); Cambridge Structural Database (Allen, 2002) refcode YODYUL] have been reported previously. PCT·H₂O crystallizes in the monoclinic space group $P2_1/b$, with $a = 9.161(6)$, $b = 16.042(5)$, $c = 6.496(5)\text{ \AA}$ and $\gamma = 90.85^\circ$. PCT·2H₂O crystallizes in the tetragonal space group $I4_1/a$, with $a = b = 13.671(1)\text{ \AA}$ and $c = 22.176(3)\text{ \AA}$. The title compound, PCT·1.75H₂O, (I), is also found to crystallize in the tetragonal space group $I4_1/a$, with cell parameters essentially the same as those of PCT·2H₂O.The X-ray structure determination of (I) shows that there is no difference between it and the crystal structure of PCT·2H₂O (Huang, 1993), except for the disorder in a water molecule (O2) and the presence of another water molecule at the special position (1/2, 3/4, 1/8) in (I). The water molecule O2 is found to be disordered over two mutually incompatible symmetry-related sites and hence the occupancy of each site is 0.5. The total number of water molecules in the unit cell is 28.The bond lengths and angles in the PCT molecule are comparable with the corresponding values in PCT·2H₂O (Huang, 1993). The C7–N4 bond length [1.314(2) Å] is shorter than that of a normal C–N single bond, due to the p - π conjugation between atom N4 and the C7=S bond. The C5–C6 bond length of 1.457(3) Å indicates conjugation between the pyridine ring and the side chain. As a result of extensive electron delocalization over the entire molecule, the PCT molecule is almost planar. The dihedral angle between the pyridine ring and the plane through the side-chain atoms (S, N2, N3, N4, C6 and C7) is 6.18(8)°.

In the crystal structure, the molecules at (x, y, z) and $(-x, 1 - y, -z)$, and (x, y, z) and $(-x, \frac{1}{2} - y, z)$ are arranged as anti-parallel pairs (Fig. 2) at perpendicular distances of 3.277 (1) and 3.390 (1) Å, respectively, with significant π - π interactions between the thiourea moiety and the pyridine ring. The symmetry-related molecular columns are interlinked by N3—H3N \cdots N1ⁱ and N4—H4A \cdots Sⁱⁱⁱ hydrogen bonds (see Table 2 for details). The water molecules are involved in an extensive O—H \cdots O, O—H \cdots S and N—H \cdots O hydrogen-bonding network (Table 2).

Experimental

To an aqueous solution (20 ml) of thiosemicarbazone (0.107 g, 1 mmol), a methanol solution (10 ml) containing pyridine-2-carbaldehyde (0.18 g, 3 mmol) was added with stirring. The mixture was then refluxed for 2 h, yielding a yellow solution. Yellow single crystals of (I) were obtained from the solution by slow evaporation.

Crystal data

$C_7H_8N_4S \cdot 1.75H_2O$	Mo $K\alpha$ radiation
$M_r = 211.76$	Cell parameters from 39 reflections
Tetragonal, $I4_1/a$	$\theta = 2.8$ – 14.9°
$a = 13.676$ (1) Å	$\mu = 0.29$ mm $^{-1}$
$c = 22.192$ (3) Å	$T = 293$ (2) K
$V = 4150.6$ (7) Å 3	Plate, yellow
$Z = 16$	$0.48 \times 0.48 \times 0.44$ mm
$D_x = 1.356$ Mg m $^{-3}$	

Data collection

Siemens P4 diffractometer	$R_{int} = 0.020$
$\theta/2\theta$ scans	$\theta_{max} = 26.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 17$
$T_{min} = 0.831$, $T_{max} = 0.880$	$k = 0 \rightarrow 17$
2473 measured reflections	$l = -1 \rightarrow 27$
2158 independent reflections	3 standard reflections
1437 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 2.8%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} = 0.001$
2158 reflections	$\Delta\rho_{max} = 0.13$ e Å $^{-3}$
144 parameters	$\Delta\rho_{min} = -0.18$ e Å $^{-3}$

Table 1

Selected geometric parameters (Å, °).

S—C7	1.6895 (18)	N4—C7	1.314 (2)
N1—C1	1.338 (2)	C1—C2	1.368 (3)
N1—C5	1.347 (2)	C2—C3	1.371 (3)
N2—C6	1.271 (2)	C3—C4	1.375 (3)
N2—N3	1.372 (2)	C4—C5	1.384 (3)
N3—C7	1.351 (2)	C5—C6	1.457 (3)
C1—N1—C5	117.18 (17)	N1—C5—C4	122.56 (18)
C6—N2—N3	115.51 (15)	N1—C5—C6	114.42 (16)
C7—N3—N2	120.11 (15)	C4—C5—C6	123.02 (18)
N1—C1—C2	123.7 (2)	N2—C6—C5	122.18 (17)
C1—C2—C3	118.5 (2)	N4—C7—N3	117.77 (16)
C2—C3—C4	119.59 (19)	N4—C7—S	123.74 (15)
C3—C4—C5	118.47 (19)	N3—C7—S	118.48 (14)

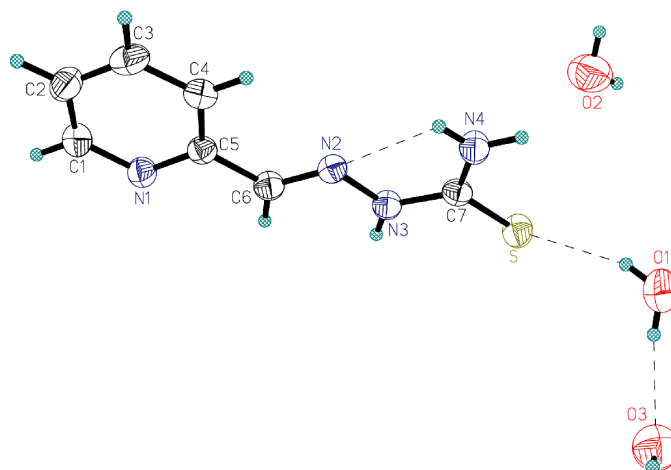


Figure 1

A view of (I), showing 40% probability displacement ellipsoids. O2 is disordered equally over this and a symmetry-related site, and O3 lies on a special position.

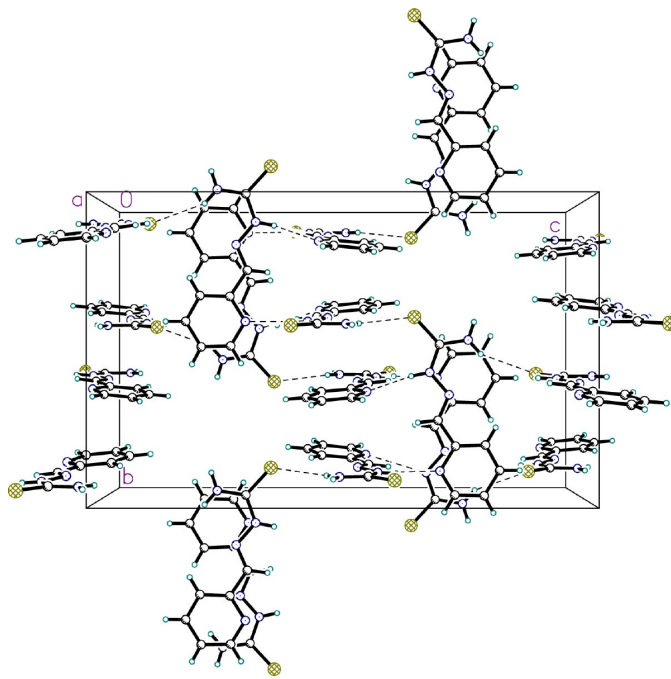


Figure 2

A view of the molecular packing, viewed down the a axis. Water molecules have been omitted for clarity.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4A \cdots N2	0.86	2.31	2.653 (2)	104
O1—H1O1 \cdots O3	0.80 (3)	2.00 (3)	2.777 (2)	166 (3)
O1—H2O1 \cdots S	0.81 (2)	2.56 (3)	3.325 (2)	158 (3)
N3—H3N \cdots N1 ⁱ	0.86	2.15	2.998 (2)	171
O3—H1O3 \cdots O1 ⁱⁱ	0.82 (4)	2.00 (3)	2.777 (2)	160 (9)
N4—H4A \cdots S ⁱⁱⁱ	0.86	2.73	3.488 (2)	148
N4—H4B \cdots O1 ^{iv}	0.86	2.07	2.924 (2)	173
O2—H1O2 \cdots O1 ^v	0.83 (4)	1.98 (5)	2.796 (6)	168 (6)
O2—H2O2 \cdots S ^{vi}	0.83 (5)	2.56 (7)	3.277 (7)	145 (7)

Symmetry codes: (i) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $1 - x, \frac{3}{4} - y, z$; (iii) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$; (iv) $1 - x, 1 - y, -z$; (v) $x, y - \frac{1}{2}, -z$; (vi) $1 - x, \frac{1}{2} - y, z$.

Water H atoms were located in a difference Fourier map and their positional parameters were refined with the O–H distances restrained to 0.82 (1) Å. The remaining H atoms were positioned geometrically (N–H = 0.86 Å and C–H = 0.93 Å) and allowed to ride on their parent atoms. The isotropic displacement parameters of the H atoms were set equal to 1.2–1.5 times U_{eq} of the parent atoms. There is conflict between some of the alternative positions for the disordered H atoms on water molecules O1 and O3.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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