Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Methyl-1-(3-pyridylmethylene)thiosemicarbazone hemihydrate

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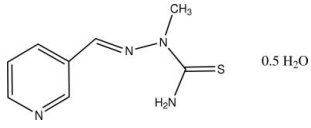
Received 20 June 2007; accepted 24 June 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.089; data-to-parameter ratio = 13.8.

The asymmetric unit of the title compound, $C_8H_{10}N_4S\cdot0.5H_2O$, contains one 2-methyl-1-(3-pyridylmethylene)thiosemicarbazone molecule and one half of a water molecule with its O atom lying on a twofold rotation axis. The thiosemicarbazone molecule exhibits an *anti* arrangement between the thione S atom and the hydrazine N atom. The thiosemicarbazone molecules are interconnected into a chain by N—H···N hydrogen bonds. The chains are interconnected by N—H···O and O—H···S hydrogen bonds involving water molecules into a three-dimensional network.

Related literature

For general background, see: Soliman *et al.* (2007); Beraldo *et al.* (2004); Quiroga *et al.* (2004); Casas *et al.* (2000). For related structures, see: Beraldo *et al.* (2000, 2001); Mendes *et al.* (2001); Lovejoy *et al.* (2000); Valdés-Martínez *et al.* (1991, 1995, 1996, 1997); Ali *et al.* (2006).



Experimental

Crystal data

$C_8H_{10}N_4S\cdot0.5H_2O$
M_r = 203.27
Monoclinic, $C2/c$
a = 16.901 (2) Å
b = 10.091 (1) Å
c = 12.681 (1) Å
β = 112.077 (1)°
V = 2004.2 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 298 (2) K
0.21 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: analytical (*SHELXTL*; Sheldrick, 2000)
T_{min} = 0.924, T_{max} = 0.961
8695 measured reflections
1830 independent reflections
1402 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.089
S = 0.94
1830 reflections
133 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O1	0.86 (2)	2.41 (2)	3.036 (2)	129 (2)
N4—H4B···N1^{i}	0.86 (2)	2.11 (2)	2.969 (2)	175 (2)
O1—H1···S1^{ii}	0.846 (5)	2.53 (1)	3.347 (2)	162 (3)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2007).

The authors are grateful to CONACYT (grant No. 40332-Q) and DGAPA–UNAM (grant No. IN216806) for financial support, and to the CSCI, Spain, for a licence to use the Cambridge Structural Database.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2398).

References

Ali, M. A., Mirza, A. H., Ejau, W. B. & Bernhardt, P. V. (2006). *Polyhedron*, **25**, 3337–3342.
Beraldo, H. & Gambino, D. (2004). *Mini-Rev. Med. Chem.* **4**, 31–39.
Beraldo, H., Lima, R., Teixeira, L. R., Moura, A. A. & West, D. X. (2000). *J. Mol. Struct.* **553**, 43–48.
Beraldo, H., Lima, R., Teixeira, L. R., Moura, A. A. & West, D. X. (2001). *J. Mol. Struct.* **559**, 99–106.
Bruker (1999). *SMART* (Version 5.625) and *SAINT* (Version 6.23c). Bruker AXS Inc., Madison, Wisconsin, USA.
Casas, J. S., Garcia-Tasende, M. S. & Sordo, J. (2000). *Coord. Chem. Rev.* **209**, 197–261.
Lovejoy, D. B., Richardson, D. R. & Bernhardt, P. V. (2000). *Acta Cryst.* C**56**, 341–342.
Mendes, I. C., Teixeira, L. R., Lima, R., Beraldo, H., Speziali, N. L. & West, D. X. (2001). *J. Mol. Struct.* **559**, 355–360.
Quiroga, A. G. & Ranninger, C. N. (2004). *Coord. Chem. Rev.* **248**, 119–133.
Sheldrick, G. M. (2000). *SHELXTL* (Windows Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Soliman, A. A. & Linert, W. (2007). *Monatsh. Chem.* **138**, 175–189.
Valdés-Martínez, J., Rubio, M., Rosado, R. C., Salcedo-Loaiza, J., Toscano, R. A., Espinosa-Pérez, G., Hernández-Ortega, S. & Ebert, K. (1997). *J. Chem. Crystallogr.* **27**, 627–634.
Valdés-Martínez, J., Toscano, R. A. & Cea-Olivares, R. (1991). *Acta Cryst.* C**47**, 2666–2668.
Valdés-Martínez, J., Toscano, R. A. & Ramírez-Ortiz, J. (1995). *Polyhedron*, **14**, 579–584.
Valdés-Martínez, J., Toscano, R. A., Zentella-Dehesa, A., Salberg, M. M., Bain, G. A. & West, D. X. (1996). *Polyhedron*, **15**, 427–432.
Westrip, S. P. (2007). *publCIF*. In preparation.

  doi:10.1107/S1600536807030760

supplementary materials

Acta Cryst. (2007). E**63**, o3334 [**doi:10.1107/S1600536807030760**]

2-Methyl-1-(3-pyridylmethylene)thiosemicarbazone hemihydrate

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Comment

Due to their pharmacological versatility (Beraldo *et al.* 2004; Quiroga *et al.* 2004) there has been a continuous interest in the chemistry and structure of thiosemicarbazones and their metal complexes (Soliman *et al.* 2007; Casas *et al.* 2000; Beraldo *et al.* 2000, 2001; Mendes *et al.* 2001; Lovejoy *et al.* 2000; Valdés-Martínez *et al.* 1991, 1995, 1996, 1997; Ali *et al.* 2006).

The 3-formyl-*N*(2)-methylthiosemicarbazone molecule in the title compound, (I), presents an *anti* arrangement between the thione S atom and the hydrazinic N atom with respect to the N3—C8 bond (see Fig. 1). The molecule is approximately planar with the S1 [0.220 (1) Å] and N4 [−0.132 (2) Å] showing the greater deviation from the mean plane of the molecule.

The thiosemicarbazone molecules are interconnected by N4—H4B···N1($x - 1/2$, $y - 1/2$, z) hydrogen bonds into a chain. Two of these chains are interconnected by water molecules forming an $R_4^4(12)$ motif through N4–H4A···O1 and O1—H1···S1($1 - x$, $-y$, $1 - z$) hydrogen bonds (Table 1) as shown in Fig 2. These double chains are interconnected into a three-dimensional network by N4—H4A···O1 hydrogen bonds as shown in Fig.3.

Experimental

The title compound was obtained from the reaction of 3-pyridinecarboxaldehyde (1.07 g, 10 mmol) and 2-methyl-3-thiosemicarbazide (1.05 g, 10 mmol) in boiling ethanol (200 ml) containing 1 ml of acetic acid. Crystal were obtained by slow evaporation of the solution at room temperature.

Refinement

C-bound H atoms were placed in geometrically idealized positions and refined using a riding model, with C—H = 0.93 Å (aromatic) or 0.96 Å (methyl). H atoms on N and O atoms were located in a difference map and their positional parameters were refined with distance restraints [N–H = 0.90 (1) Å, O–H = 0.85 (1) Å]. The U_{iso}(H) values were set at $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C,*N*) for other H atoms.

Figures

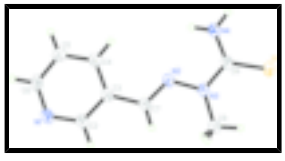

Fig. 1. The molecular structure of 3-formyl-*N*(2)-methylthiosemicarbazone in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Fig. 2. The hydrogen bonding (dashed lines) in the chains of (I).

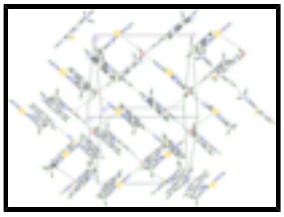

Fig. 3. The crystal packing of (I). Hydrogen bonds are shown as dashed lines.

2-Methyl-1-(3-pyridylmethylene)thiosemicarbazone hemihydrate

Crystal data

$C_8H_{10}N_4S·0.5H_2O$	F_{000} = 856
M_r = 203.27	D_x = 1.347 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3795 reflections
a = 16.901 (2) Å	θ = 2.4–25.3º
b = 10.091 (1) Å	μ = 0.29 mm^{-1}
c = 12.681 (1) Å	*T* = 298 (2) K
β = 112.077 (1)º	Prism, colourless
V = 2004.2 (3) Å^3	0.21 × 0.18 × 0.16 mm
Z = 8	

Data collection

Bruker SMART APEX CCD diffractometer	1830 independent reflections
Radiation source: fine-focus sealed tube	1402 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.040
Detector resolution: 0.661 pixels mm^{-1}	θ_{max} = 25.4º
T = 298(2) K	θ_{min} = 2.4º
ω scans	*h* = −20→20
Absorption correction: analytical (SHELXTL; Sheldrick, 2000)	*k* = −12→12
T_{min} = 0.924, T_{max} = 0.961	*l* = −15→15
8695 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.036	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.089	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.94	$(\Delta/\sigma)_{max}$ = 0.001

1830 reflections	$\Delta\rho_{max}$ = 0.20 e Å^{-3}
133 parameters	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
2 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\text{sigma}(F^2)$ 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}
S1	0.40483 (3)	0.25286 (5)	0.58184 (4)	0.05486 (19)
N1	0.81555 (9)	0.47029 (15)	0.36753 (13)	0.0500 (4)
C2	0.76726 (11)	0.46750 (17)	0.42982 (15)	0.0463 (4)
H2	0.7807	0.5260	0.4908	0.056*
C3	0.69838 (10)	0.38351 (16)	0.41005 (13)	0.0379 (4)
C4	0.67824 (11)	0.29788 (18)	0.31816 (15)	0.0456 (4)
H4	0.6326	0.2393	0.3014	0.055*
C5	0.72671 (12)	0.30095 (18)	0.25238 (16)	0.0508 (5)
H5	0.7139	0.2452	0.1898	0.061*
C6	0.79457 (11)	0.38766 (18)	0.28005 (16)	0.0484 (5)
H6	0.8272	0.3882	0.2351	0.058*
C7	0.65111 (10)	0.39031 (16)	0.48553 (14)	0.0400 (4)
H7	0.6666	0.4522	0.5442	0.048*
C8	0.47507 (10)	0.23971 (17)	0.51628 (14)	0.0378 (4)
C9	0.56853 (11)	0.41704 (19)	0.63545 (15)	0.0494 (5)
H9A	0.5315	0.4072	0.6768	0.074*
H9B	0.5637	0.5054	0.6057	0.074*
H9C	0.6265	0.4008	0.6855	0.074*
N2	0.58876 (8)	0.31211 (13)	0.47160 (11)	0.0379 (3)
N3	0.54415 (8)	0.32252 (13)	0.54211 (11)	0.0389 (3)
N4	0.46463 (9)	0.15186 (16)	0.43554 (13)	0.0448 (4)
H4A	0.5011 (11)	0.1461 (18)	0.4028 (15)	0.054*
H4B	0.4233 (11)	0.0955 (16)	0.4182 (15)	0.054*
O1	0.5000	0.0027 (2)	0.2500	0.0960 (9)
H1	0.526 (2)	−0.049 (2)	0.3048 (19)	0.144*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0516 (3)	0.0664 (4)	0.0605 (3)	−0.0126 (2)	0.0370 (3)	−0.0099 (2)
N1	0.0453 (9)	0.0490 (9)	0.0649 (10)	−0.0103 (7)	0.0312 (8)	−0.0028 (8)
C2	0.0434 (10)	0.0456 (11)	0.0539 (11)	−0.0115 (8)	0.0229 (8)	−0.0063 (9)
C3	0.0339 (9)	0.0379 (10)	0.0431 (9)	−0.0026 (7)	0.0157 (7)	0.0039 (8)
C4	0.0398 (10)	0.0475 (11)	0.0501 (11)	−0.0100 (8)	0.0179 (8)	−0.0032 (8)
C5	0.0521 (12)	0.0543 (12)	0.0489 (11)	−0.0050 (9)	0.0223 (9)	−0.0077 (9)
C6	0.0481 (11)	0.0525 (12)	0.0550 (11)	0.0003 (9)	0.0311 (9)	0.0039 (9)
C7	0.0385 (9)	0.0398 (10)	0.0424 (9)	−0.0064 (8)	0.0161 (7)	−0.0015 (8)
C8	0.0372 (9)	0.0375 (9)	0.0394 (9)	−0.0017 (7)	0.0153 (7)	0.0045 (8)
C9	0.0512 (11)	0.0530 (12)	0.0475 (10)	−0.0122 (9)	0.0225 (8)	−0.0090 (9)
N2	0.0349 (7)	0.0406 (8)	0.0420 (8)	−0.0028 (6)	0.0186 (6)	0.0024 (6)
N3	0.0374 (8)	0.0424 (8)	0.0413 (8)	−0.0070 (6)	0.0200 (6)	−0.0034 (7)
N4	0.0410 (9)	0.0456 (9)	0.0562 (10)	−0.0122 (7)	0.0280 (8)	−0.0089 (8)
O1	0.167 (3)	0.0559 (15)	0.102 (2)	0.000	0.093 (2)	0.000

Geometric parameters (Å, °)

S1—C8	1.691 (2)	C7—N2	1.275 (2)
N1—C6	1.325 (2)	C7—H7	0.93
N1—C2	1.332 (2)	C8—N4	1.315 (2)
C2—C3	1.385 (2)	C8—N3	1.372 (2)
C2—H2	0.93	C9—N3	1.454 (2)
C3—C4	1.386 (2)	C9—H9A	0.96
C3—C7	1.461 (2)	C9—H9B	0.96
C4—C5	1.372 (3)	C9—H9C	0.96
C4—H4	0.93	N2—N3	1.373 (2)
C5—C6	1.379 (2)	N4—H4A	0.86 (2)
C5—H5	0.93	N4—H4B	0.86 (2)
C6—H6	0.93	O1—H1	0.846 (5)
C6—N1—C2	116.89 (15)	C3—C7—H7	119.8
N1—C2—C3	124.49 (17)	N4—C8—N3	116.7 (2)
N1—C2—H2	117.8	N4—C8—S1	121.5 (1)
C3—C2—H2	117.8	N3—C8—S1	121.8 (1)
C2—C3—C4	117.25 (16)	N3—C9—H9A	109.5
C2—C3—C7	118.83 (15)	N3—C9—H9B	109.5
C4—C3—C7	123.92 (15)	H9A—C9—H9B	109.5
C5—C4—C3	118.88 (16)	N3—C9—H9C	109.5
C5—C4—H4	120.6	H9A—C9—H9C	109.5
C3—C4—H4	120.6	H9B—C9—H9C	109.5
C4—C5—C6	119.30 (17)	C7—N2—N3	119.4 (1)
C4—C5—H5	120.4	C8—N3—N2	115.1 (1)
C6—C5—H5	120.4	C8—N3—C9	123.3 (1)
N1—C6—C5	123.20 (16)	N2—N3—C9	121.6 (1)
N1—C6—H6	118.4	C8—N4—H4A	120.5 (13)

C5—C6—H6	118.4	C8—N4—H4B	120.1 (12)
N2—C7—C3	120.5 (2)	H4A—N4—H4B	119.2 (18)
N2—C7—H7	119.8		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4A···O1	0.86 (2)	2.41 (2)	3.036 (2)	129 (2)
N4—H4B···N1^{i}	0.86 (2)	2.11 (2)	2.969 (2)	175 (2)
O1—H1···S1^{ii}	0.846 (5)	2.53 (1)	3.347 (2)	162 (3)

Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) −*x*+1, −*y*, −*z*+1.

Fig. 1

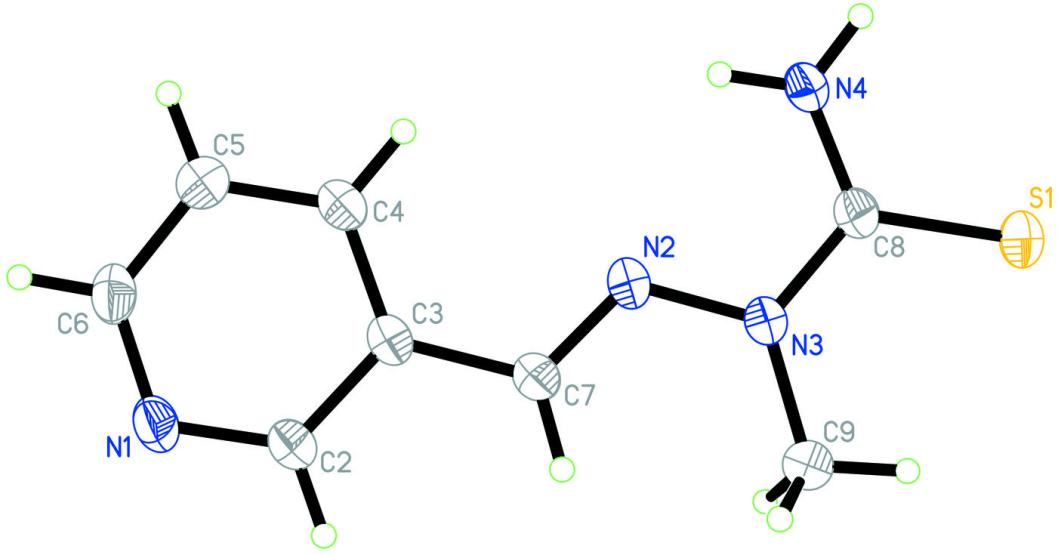

Fig. 2

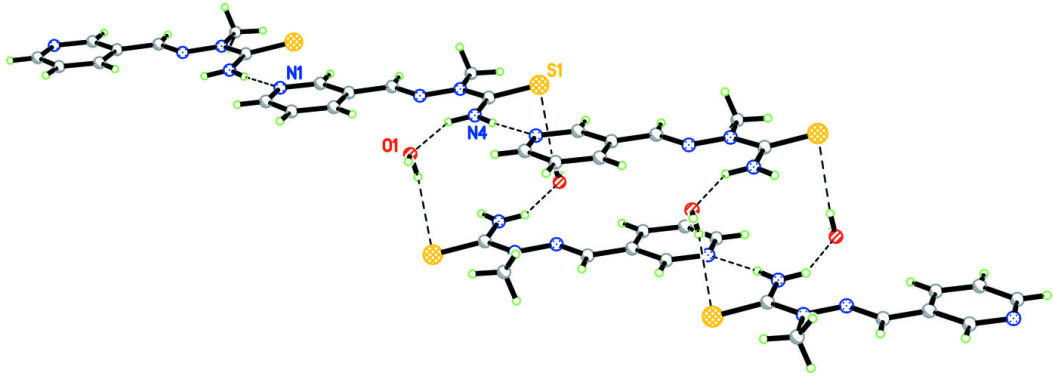

Fig. 3