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N-Hydroxy-4,5-dimethylthiazole-2(3*H*)-thione hemihydrate

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Key indicators

Single-crystal X-ray study
T = 300 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.119
Data-to-parameter ratio = 16.7

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

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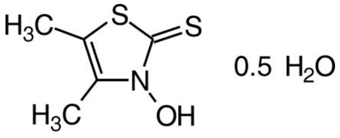
The geometry of the title compound, $C_5H_7NOS_2 \cdot 0.5H_2O$, is characterized by a planar *N*,*S*-heterocyclic core that is distorted from a regular pentagon. Solvent water participates in non-chelated hydrogen bonds and acts as a twofold donor (O—H···S═C) and a twofold acceptor [O···H—O(—N)].

Comment

N-Hydroxy-4,5-dimethylthiazole-2(3*H*)-thione was prepared in order to probe the effect of substituents on the spectroscopic location and intensity of absorption bands caused by visible to near-UV light excitations of thiazole-2(3*H*)-thiones (Hartung *et al.*, 2005). The compound crystallizes as the hemihydrate, (I). It was investigated by X-ray diffraction in order to compare the computed equilibrium geometry (Hartung *et al.*, 2005) with data originating from a crystal structure analysis.



(I)

The thiazole-2(3*H*)-thione core in (I) is virtually planar [deviation of 0.043 (5) Å for C2 and 0.022 (5) Å for N3 from the plane of C4/C5/S1]. The endocyclic bond angle C2—S1—C5 measures 93.4 (1)°, which leads to a distortion of the heterocyclic core from a regular pentagon (Fig. 1). The two endocyclic heteroatoms, N3 and S1, form single bonds with the

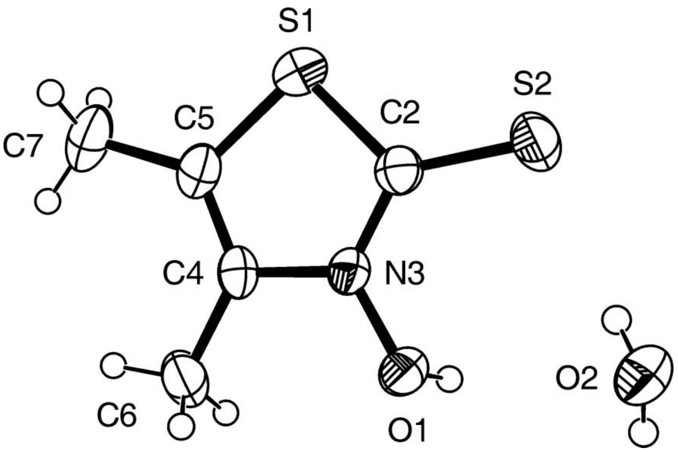


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

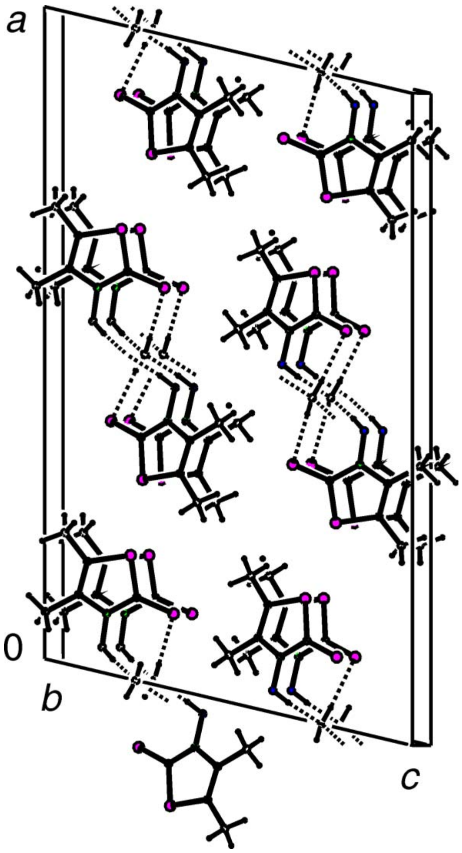


Figure 2
Visualization of the hydrogen bonding between *N*-hydroxy-4,5-dimethylthiazole-2(3*H*)-thione and H_2O in (I), viewed approximately along [010].

adjacent C atoms (Table 1). The N3—C4 distance, however, exceeds the mean value of 1.34 (2) Å for an Nsp^2 —Csp^2 single bond. The lengths of the other two bonds agree with the reported mean values for Nsp^2 —Csp^2 and S—Csp^2 bond lengths (Allen *et al.*, 1987). The geometric parameters of the thiohydroxamic acid functional group (HO—N—C═S) are similar to the bond lengths and angles which have recently been reported for structurally related heterocyclic compounds (Hartung *et al.*, 1996, 2003, 2005; Hartung, Kneuer *et al.*, 1999; Hartung, Schwarz *et al.*, 1999; Bond *et al.*, 2000).

The water molecule in (I), lying on a twofold rotation axis, participates in non-chelated hydrogen bonds, and acts as a twofold hydrogen-bond donor and a twofold acceptor (Table 2). This arrangement leads to the formation of two types of hydrogen-bonded columns along the *b* axis (Fig. 2). Each column contains molecules of *N*-(hydroxy)-4,5-dimethylthiazole-2(3*H*)-thione of identical absolute configuration with respect to the geometry about the stereogenic N3—O1 axis (Hartung *et al.*, 2003). This mode of interaction between H_2O and *N*-(hydroxy)-4,5-dimethylthiazole-2(3*H*)-thione is distinctly different from those observed in *N*-(hydroxy)-4-methylthiazole-2(3*H*)-thione hemihydrate (Bond *et al.*, 2000). In the latter case, the water molecule is protonated by one molecule of *N*-(hydroxy)-4-methylthiazole-2(3*H*)-thione to furnish the corresponding anion and the H_3O^+ cation.

Experimental

Crystals of (I) suitable for X-ray diffraction were obtained by slow addition of petroleum ether to a solution of *N*-(hydroxy)-4,5-dimethylthiazole-2(3*H*)-thione in diethyl ether under ambient conditions [for further details, see Hartung *et al.* (2005)].

Crystal data

$C_5H_7NOS_2 \cdot 0.5H_2O$
$M_r = 170.24$
Monoclinic, $C2/c$
$a = 25.564$ (1) Å
$b = 4.141$ (2) Å
$c = 15.000$ (2) Å
$\beta = 103.08$ (2)°
$V = 1546.7$ (8) Å^3
$Z = 8$

$D_x = 1.462$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1854 reflections
$\theta = 2.9$–18.6°
$\mu = 0.62$ mm^{-1}
$T = 300$ (2) K
Prism, pale yellow
0.60 × 0.48 × 0.36 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD area-detector
ω scans
Absorption correction: analytical *CrysAlisRED* (Oxford Diffraction, 2002)
$T_{\min} = 0.708$, $T_{\max} = 0.808$

4701 measured reflections
1553 independent reflections
1405 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 26.4°$
$h = -31 \rightarrow 31$
$k = -3 \rightarrow 5$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.119$
$S = 1.06$
1553 reflections
93 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 1.7712P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.012$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C5	1.751 (2)	S2—C2	1.672 (2)
S1—C2	1.729 (2)	C4—C5	1.341 (3)
N3—C4	1.406 (3)	C4—C6	1.489 (3)
N3—C2	1.350 (3)	C5—C7	1.501 (3)
N3—O1	1.380 (2)		
N3—C2—S1	106.8 (2)	C4—C5—C7	128.4 (2)
S2—C2—S1	125.0 (1)	C4—C5—S1	110.3 (2)
N3—C2—S2	128.2 (2)	N3—O1—H1	104.9 (2)
C5—C4—N3	111.3 (2)	C2—N3—C4	118.2 (2)
N3—C4—C6	119.0 (2)	C2—N3—O1	121.5 (2)
S2—C2—N3—O1	5.3 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2$^{\rm i}$	0.86 (3)	1.82 (3)	2.680 (2)	176 (3)
O2—H2···S2	0.84 (1)	2.41 (1)	3.246 (2)	171 (3)

Symmetry codes: (i) $x, y-1, z$.

o1742 Hartung *et al.* • $C_5H_7NOS_2 \cdot 0.5H_2O$ *Acta Cryst.* (2005). E**61**, o1741–o1743

Atoms H1 and H2 were located in a difference Fourier map and their atomic coordinates were refined, with $U_{\rm iso}$(H) set at $1.2U_{\rm eq}$ of O1 or O2, respectively. All other H atoms were positioned geometrically and treated as riding atoms, with C—H distances in the range 0.93–0.96 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP3* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bond, A. D., Feeder, N., Teat, S. J. & Jones, W. (2000). *Tetrahedron*, **56**, 6617–6624.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (2005). *ORTEP3 for Windows*. University of Glasgow, Scotland.

Hartung, J., Hiller, M., Schwarz, M., Svoboda, I. & Fuess, H. (1996). *Liebigs Ann. Chem.* pp. 2091–2097.

Hartung, J., Kneuer, R., Schwarz, M., Svoboda, I. & Fuess, H. (1999). *Eur. J. Org. Chem.* pp. 97–106.

Hartung, J., Schwarz, M., Svoboda, I., Fuess, H. & Duarte, M. T. (1999). *Eur. J. Org. Chem.* pp. 1275–1290.

Hartung, J., Schwarz, M., Svoboda, I. & Fuess, H. (2003). *Acta Cryst.* C**59**, o682–o684.

Hartung, J., Špehar, K., Svoboda, I., Fuess, H., Arnone, M. & Engels, B. (2005). *Eur. J. Org. Chem.* pp. 869–891.

Oxford Diffraction (2002). *CrysAlisCCD* and *CrysAlisRED*. Versions 1.170.14. Oxford Diffraction, Oxford, England.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Acta Cryst. (2005). E**61**, o1741–o1743 Hartung *et al.* • $C_5H_7NOS_2{\cdot}0.5H_2O$ **o1743**