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1-(4-Nitrobenzoyl)thiosemicarbazide monohydrate: a three-dimensional hydrogen-bonded framework structure

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.091
Data-to-parameter ratio = 14.1

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

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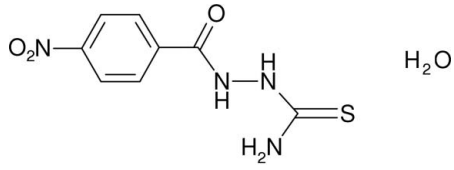
In the title compound, $C_8H_8N_4O_3S\cdot H_2O$, strong hydrogen bonding results in the formation of a number of chains and dimers, which combine to give a three-dimensional hydrogen-bonded framework.

Comment

Acylthiosemicarbazides are versatile compounds, having a large spectrum of biological properties (Bhat *et al.*, 1967; Guersoy & Karali, 1995; Plumitallo *et al.*, 2004). They are, in addition, useful precursors of various biologically active heterocyclic compounds, including triazoles (Kane *et al.*, 1994; Palaska *et al.*, 2002), thiadiazoles (Oruc *et al.*, 2004; Palaska *et al.*, 2002) and oxadiazoles (Palaska *et al.*, 2002; Yale & Losee, 1966). Certain acylthiosemicarbazide–transition metal complexes have also been shown to possess useful biological activities (Shen *et al.*, 1997; Singh & Singh, 2001). As part of our interest in acylthiosemicarbazide compounds, we now report the crystal structure of 1-(4-nitrobenzoyl)thiosemicarbazide monohydrate, (I).



(I)

Within the asymmetric unit of (I), the O atom of the solvent water molecule acts as an H-atom acceptor for the amide group of the organic molecule (Fig. 1). The *p*-nitro group is rotated from the essentially planar aryl group by an angle of 13.07 (12)°, whereas the CN(O) group is twisted by 10.77 (12)°.

The hydrogen bonding (Table 2) at the basic level produces a mixture of chains and dimers. The combination of the hydrogen bond described above, together with O1*W*—H1*WA*···O7^{ii} [symmetry code: (ii) $x+1, y, z$] leads to a $C_2^2(9)$ chain (Bernstein *et al.*, 1995) along [010]. Another chain, *C*(12), forms along [100] *via* the N9—H9*A*···O42^{v} hydrogen bond [symmetry code: (v) $x, y, z-1$]. These combine to form an $R_5^6(34)$ ring (Fig. 2); the disparity between the number of donors and acceptors results from the amide acting as a double donor. The rings link to create a sheet normal to [010] (Fig. 2).

All other hydrogen bonds involve S as an acceptor and result in dimers. In the first, the hydrogen bond within the asymmetric unit combines with O1*W*—H1*WA*···S1^{1}

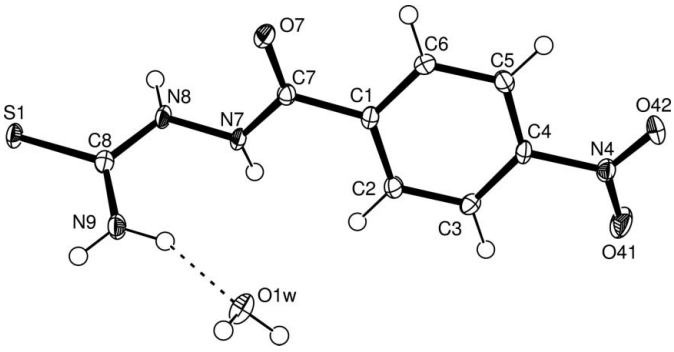


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radius. The dashed line indicates a hydrogen bond.

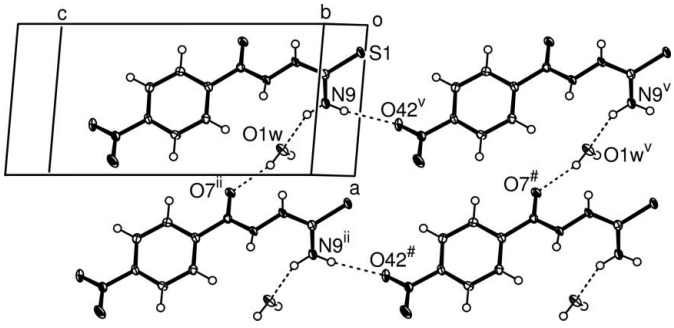


Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $R_5^6(34)$ ring which links with others to give sheets. Atoms marked with (ii), (v) or a hash (#) are at the symmetry positions $(1 + x, y, z)$, $(x, y, -1 + z)$ and $(1 + x, y, -1 + z)$, respectively. Dashed lines indicate hydrogen bonds.

[symmetry code: (i) $1 - x, 1 - y, -z$] to form an $R_4^4(12)$ ring. The other two are simpler motifs; N7—H7···S1^{iii} [symmetry code: (iii) $1 - x, 2 - y, -z$] giving an $R_2^2(10)$ ring and N8—H8···S1^{iv} [symmetry code: (iv) $-x, 2 - y, -z$] forming an $R_2^2(8)$ motif. The former two dimers combine with the above-described hydrogen bond to give a chain along [010] (Fig. 3). The sheet shown in Fig. 2 and the chain shown in Fig. 3 thus combine to give a three-dimensional hydrogen-bonded framework.

Experimental

A solution of potassium thiocyanate (0.73 g, 12.5 mmol) and concentrated HCl (1.25 ml) was added to a stirred solution of 4-nitrobenzoylhydrazide (1.5 g, 8.3 mmol) (Hosamani & Pattanashettar, 2004) in methanol (21 ml). The mixture was evaporated to dryness on a steam bath, further methanol (21 ml) was added and the mixture heated for 1 h on a steam bath. The resulting solid was successively washed with water and a small volume of ethanol, and recrystallized from acetone, yielding 2.1 g (70%) of yellow 1-(4-nitrobenzoyl)thiosemicarbazide (m.p. 489 K). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.71 (*s*, 1H, CONHNH), 9.44 (*s*, 1H, CONH), 8.33 (*d*, 2H, J = 8.5 Hz, Ar—H), 8.13 (*d*, 2H, J = 8.5 Hz, Ar—H), 7.95 (*s*, 1H, $CSNH_2$), 7.79 (*s*, 1H, $CSNH_2$).

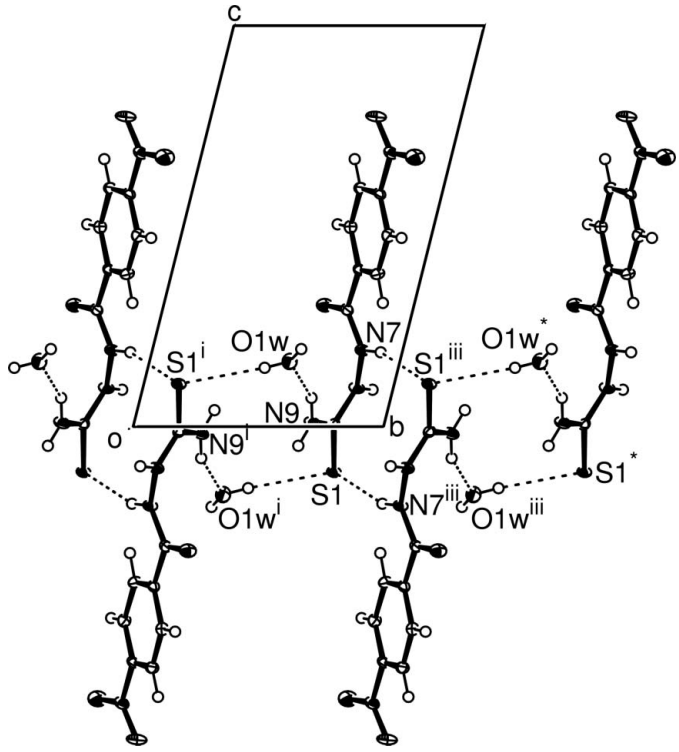


Figure 3
Part of the crystal structure of (I), showing the formation of hydrogen-bonded dimers linked to form a chain. Atoms marked with (i), (iii) or an asterisk (*) are at the symmetry positions $(1 - x, 1 - y, -z)$, $(1 - x, 2 - y, -z)$ and $(x, 1 + y, z)$ respectively. Dashed lines indicate hydrogen bonds.

Crystal data

$C_8H_8N_4O_3S\cdot H_2O$
M_r = 258.26
Triclinic, $P\overline{1}$
a = 6.0621 (2) Å
b = 7.3991 (3) Å
c = 12.2661 (5) Å
α = 75.9684 (16)°
β = 85.112 (2)°
γ = 88.903 (2)°
V = 531.83 (4) Å^3
Z = 2
D_x = 1.613 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 120 (2) K
Slab, pale yellow
0.45 × 0.45 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.688, T_{max} = 0.928
8670 measured reflections
2425 independent reflections
2178 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.091
S = 1.12
2425 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.2095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···S1^{i}	0.79 (2)	2.61 (2)	3.3472 (13)	156.5 (18)
O1W—H1WA···O7^{ii}	0.81 (2)	2.01 (2)	2.7944 (15)	162.7 (19)
N7—H7···S1^{iii}	0.831 (19)	2.608 (19)	3.4096 (13)	162.4 (16)
N8—H8···S1^{iv}	0.854 (19)	2.49 (2)	3.3382 (13)	172.0 (16)
N9—H9A···O42^{v}	0.84 (2)	2.26 (2)	3.0834 (17)	164.8 (18)
N9—H9B···O1W	0.89 (2)	1.94 (2)	2.7754 (16)	153.8 (17)

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

All H atoms were located in difference maps; those in the aryl ring were then treated as riding atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). All other H atoms were refined freely.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997) and *PLATON* (Spek, 2003).

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