5-Chloro-2-hydroxybenzaldehyde thiosemicarbazone

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In the title compound, $C_8H_8ClN_3OS$, the whole molecule assumes a planar structure, with an r.m.s. deviation of 0.108 (2) Å, and an intramolecular O—H···N hydrogen bond generates and $S(6)$ and ring motif. In the crystal structure, each of two pairs of intermolecular N—H···S hydrogen bonds connects two molecules, forming inversion dimers with $R_2^2(8)$ motifs.

Related literature

For the biological activities and pharmaceutical properties of thiosemicarbazones and their derivatives, see: Casas *et al.* (2000); Ferrari *et al.* (2000); Maccioni *et al.* (2003). For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).

Experimental

Crystal data

$C_8H_8ClN_3OS$	$V = 1014.99$ (12) Å^3
$M_r = 229.69$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.8303$ (4) Å	$\mu = 0.55$ mm^{-1}
$b = 23.6579$ (17) Å	$T = 296$ K
$c = 7.5893$ (5) Å	$0.52 \times 0.33 \times 0.08$ mm
$\beta = 104.164$ (6)°	

Data collection

Stoe IPDS II diffractometer	4469 measured reflections
Absorption correction: integration	1895 independent reflections
(X-RED32; Stoe & Cie, 2002)	1524 reflections with $I > 2\sigma(I)$
$T_{min} = 0.763$, $T_{max} = 0.957$	$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	128 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
1895 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···S1^i	0.86	2.70	3.491 (2)	153
N3—H3A···S1^{ii}	0.86	2.87	3.387 (2)	120
N3—H3A···N1	0.86	2.36	2.693 (3)	103
N3—H3B···S1^{iii}	0.86	2.55	3.390 (2)	167

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2621).

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supporting information

5-Chloro-2-hydroxybenzaldehyde thiosemicarbazone

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S1. Comment

Thiosemicarbazones constitute an important class of *N*,*S* donor ligands due to their propensity to react with a wide range of metals (Casas *et al.*, 2000). Thiosemicarbazones exhibit various biological activities and have therefore attracted considerable pharmaceutical interest (Maccioni *et al.*, 2003; Ferrari *et al.*, 2000). We here report the crystal structure of the title compound (I).

The title molecule (I) shown in Fig. 1 is planar with an r.m.s. deviation of 0.108 Å and all bond lengths agree with standard values (Allen *et al.*, 1987). Intramolecular O—H⋯N and N—H⋯N hydrogen bonds (Table 1) generate the *S*(6) and *S*(5) ring motifs, respectively (Bernstein *et al.*, 1995).

In the crystal structure, molecules are linked by N—H⋯S hydrogen bonds, forming $R_2^2(8)$ dimers (Table 1 and Fig. 2).

S2. Experimental

A mixture of 5-chlorosalicylalehyde (0.01 mol) and hydrazinecarbothioamide (0.01 mol) in 20 ml of ethanol was refluxed for about 2 h. On cooling, the solid separated was filtered and recrystallized from ethanol. Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of ethanol.

S3. Refinement

All H atoms were geometrically placed (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$ and $1.5U_{eq}(O)$.
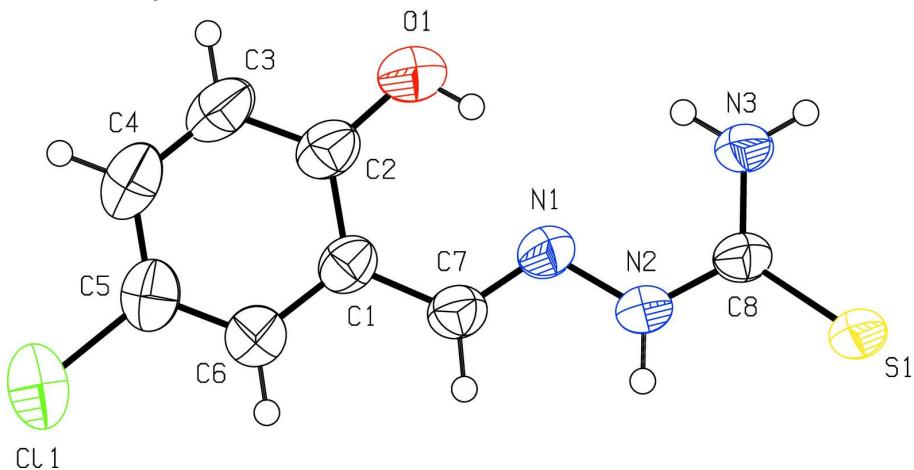
Figure 1

The title molecule with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.
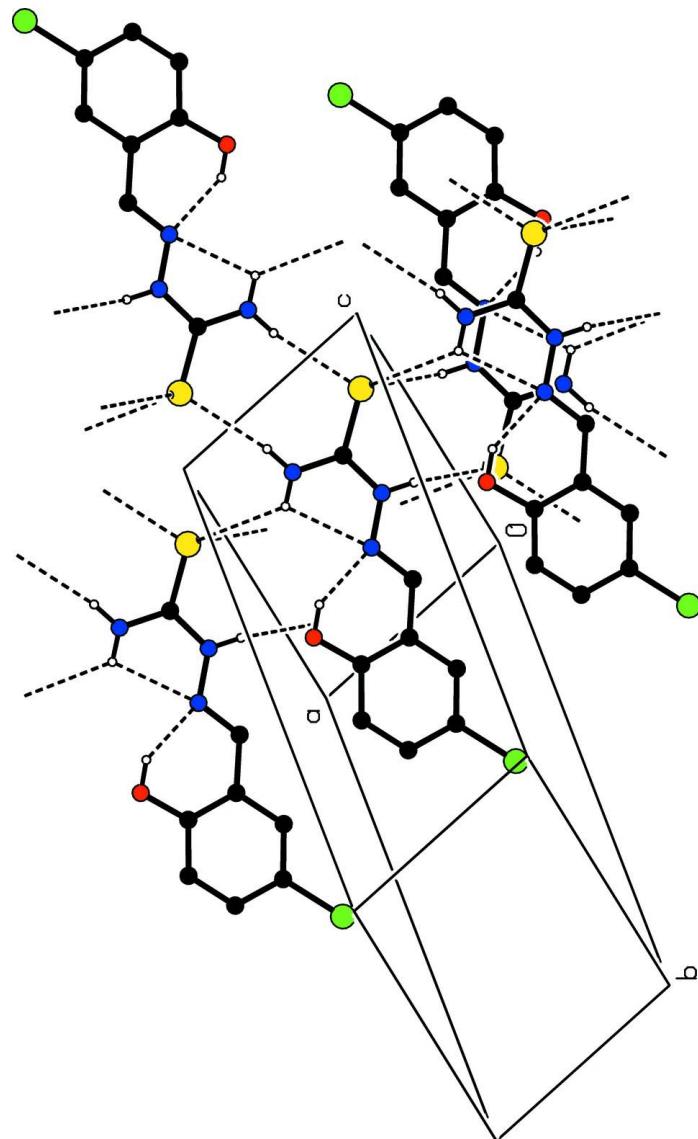
Figure 2

View of the packing and hydrogen bonding interactions of (I), showing dimer formation by $R^2_2(8)$ ring motif. All H atoms not involved in hydrogen bonding have been omitted for clarity.

5-Chloro-2-hydroxybenzaldehyde thiosemicarbazone

Crystal data

$C_8H_8ClN_3OS$	$F(000) = 472$
$M_r = 229.69$	$D_x = 1.503$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8344 reflections
$a = 5.8303$ (4) Å	$\theta = 1.7–26.2°$
$b = 23.6579$ (17) Å	$\mu = 0.55$ mm^{-1}
$c = 7.5893$ (5) Å	$T = 296$ K
$\beta = 104.164$ (6)°	Prism, colourless
$V = 1014.99$ (12) Å^3	$0.52 \times 0.33 \times 0.08$ mm
$Z = 4$	

Data collection

Stoe IPDS II diffractometer	$T_{min} = 0.763$, $T_{max} = 0.957$
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	4469 measured reflections
	1895 independent reflections
Plane graphite monochromator	1524 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm⁻¹	$R_{int} = 0.051$

Stoe IPDS II diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm^{-1}

ω scans

Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)

$T_{min} = 0.763$, $T_{max} = 0.957$

4469 measured reflections

1895 independent reflections

1524 reflections with $I > 2\sigma(I)$

$R_{int} = 0.051$

$\theta_{max} = 25.6°$, $\theta_{min} = 1.7°$

$h = -5 \rightarrow 7$

$k = -28 \rightarrow 26$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.120$

$S = 1.04$

1895 reflections

128 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.120P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.20$ e Å⁻³

$\Delta\rho_{min} = -0.37$ e Å⁻³

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.36123 (17)	0.20555 (4)	−0.30970 (10)	0.0868 (3)
S1	0.15507 (9)	0.01021 (3)	0.79551 (8)	0.0559 (2)
O1	0.8537 (3)	0.13549 (11)	0.4272 (3)	0.0750 (8)
N1	0.4525 (3)	0.08332 (9)	0.4467 (3)	0.0489 (6)
N2	0.3002 (3)	0.05468 (10)	0.5260 (3)	0.0523 (6)
N3	0.5874 (3)	0.04298 (10)	0.7883 (3)	0.0524 (7)
C1	0.4996 (4)	0.13306 (11)	0.1830 (3)	0.0493 (8)
C2	0.7333 (4)	0.15067 (12)	0.2573 (4)	0.0573 (8)
C3	0.8480 (5)	0.18395 (14)	0.1559 (4)	0.0687 (10)
C4	0.7368 (6)	0.20095 (13)	−0.0164 (4)	0.0702 (10)
C5	0.5049 (5)	0.18372 (12)	−0.0912 (4)	0.0604 (9)
C6	0.3886 (5)	0.15099 (11)	0.0062 (3)	0.0542 (8)
C7	0.3665 (4)	0.09979 (11)	0.2818 (3)	0.0507 (8)
C8	0.3636 (4)	0.03756 (11)	0.6999 (3)	0.0454 (7)
H1	0.76270	0.12040	0.48000	0.1120*
H2	0.15960	0.04740	0.46260	0.0630*

H3	1.00350	0.19500	0.20550	0.0830*
H3A	0.68790	0.05710	0.73440	0.0630*
H3B	0.63280	0.03240	0.89980	0.0630*
H4	0.81520	0.22370	−0.08260	0.0840*
H6	0.23310	0.14030	−0.04510	0.0650*
H7	0.21210	0.08970	0.22430	0.0610*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1118 (7)	0.0820 (6)	0.0700 (4)	0.0054 (5)	0.0287 (4)	0.0188 (4)
S1	0.0349 (3)	0.0795 (5)	0.0526 (3)	−0.0048 (3)	0.0096 (2)	0.0063 (3)
O1	0.0458 (10)	0.0951 (17)	0.0791 (12)	−0.0077 (10)	0.0058 (9)	0.0132 (11)
N1	0.0379 (9)	0.0554 (12)	0.0544 (10)	−0.0011 (8)	0.0131 (8)	0.0019 (9)
N2	0.0336 (9)	0.0683 (14)	0.0529 (10)	−0.0059 (9)	0.0065 (8)	0.0074 (9)
N3	0.0334 (9)	0.0742 (15)	0.0485 (10)	−0.0031 (9)	0.0079 (7)	0.0017 (9)
C1	0.0447 (12)	0.0466 (14)	0.0597 (13)	0.0017 (10)	0.0189 (10)	−0.0007 (10)
C2	0.0453 (12)	0.0558 (16)	0.0729 (15)	0.0009 (11)	0.0186 (11)	0.0020 (12)
C3	0.0489 (14)	0.0623 (18)	0.100 (2)	−0.0044 (12)	0.0281 (14)	0.0079 (15)
C4	0.0725 (17)	0.0577 (18)	0.0926 (19)	0.0020 (14)	0.0438 (15)	0.0108 (15)
C5	0.0729 (17)	0.0490 (15)	0.0653 (14)	0.0056 (13)	0.0283 (12)	0.0030 (11)
C6	0.0540 (13)	0.0505 (15)	0.0595 (12)	0.0029 (11)	0.0168 (10)	−0.0014 (11)
C7	0.0403 (12)	0.0544 (15)	0.0570 (12)	0.0002 (10)	0.0111 (10)	0.0015 (11)
C8	0.0344 (10)	0.0510 (14)	0.0505 (11)	0.0009 (9)	0.0096 (9)	−0.0029 (10)

Geometric parameters (Å, º)

Cl1—C5	1.743 (3)	C1—C2	1.404 (4)
S1—C8	1.690 (2)	C1—C6	1.405 (3)
O1—C2	1.357 (4)	C1—C7	1.438 (3)
O1—H1	0.8200	C2—C3	1.383 (4)
N1—N2	1.368 (3)	C3—C4	1.370 (4)
N1—C7	1.289 (3)	C4—C5	1.393 (5)
N2—C8	1.343 (3)	C5—C6	1.361 (4)
N3—C8	1.319 (3)	C3—H3	0.9300
N2—H2	0.8600	C4—H4	0.9300
N3—H3A	0.8600	C6—H6	0.9300
N3—H3B	0.8600	C7—H7	0.9300
Cl1···C5^i	3.606 (3)	C7···C8^{vi}	3.598 (4)
S1···N3^{ii}	3.387 (2)	C7···N3^{vi}	3.440 (4)
S1···N2^{iii}	3.491 (2)	C7···C3^{ii}	3.550 (4)
S1···N3^{iv}	3.390 (2)	C8···C7^{vi}	3.598 (4)
S1···H3A^{ii}	2.8700	C8···C6^{vii}	3.530 (3)
S1···H2^{iii}	2.7000	C8···N1^{vi}	3.339 (3)
S1···H3B^{iv}	2.5500	C3···H7^v	3.0300
S1···H7^{iii}	3.1700	C3···H4^{viii}	2.9900
O1···N1	2.681 (3)	C7···H3^{ii}	3.0500

O1···N2ᵛ	3.168 (3)	C7···H1	2.4800
O1···H2ᵛ	2.7100	H1···N1	1.9700
N1···O1	2.681 (3)	H1···C7	2.4800
N1···N3	2.693 (3)	H1···H3A	2.5600
N1···C8ᵛⁱ	3.339 (3)	H2···O1ⁱⁱ	2.7100
N2···O1ⁱⁱ	3.168 (3)	H2···H7	2.1500
N2···S1ⁱⁱⁱ	3.491 (2)	H2···S1ⁱⁱⁱ	2.7000
N3···C6ᵛⁱⁱ	3.398 (3)	H3···C7ᵛ	3.0500
N3···S1ⁱᵛ	3.390 (2)	H3A···S1ᵛ	2.8700
N3···S1ᵛ	3.387 (2)	H3A···N1	2.3600
N3···N1	2.693 (3)	H3A···H1	2.5600
N3···C7ᵛⁱ	3.440 (4)	H3B···S1ⁱᵛ	2.5500
N1···H1	1.9700	H4···C3ⁱ	2.9900
N1···H3A	2.3600	H6···H7	2.4000
C3···C7ᵛ	3.550 (4)	H7···C3ⁱⁱ	3.0300
C5···Cl1ᵛⁱⁱⁱ	3.606 (3)	H7···H2	2.1500
C6···N3ⁱˣ	3.398 (3)	H7···H6	2.4000
C6···C8ⁱˣ	3.530 (3)	H7···S1ⁱⁱⁱ	3.1700
C2—O1—H1	109.00	Cl1—C5—C4	119.6 (2)
N2—N1—C7	115.9 (2)	Cl1—C5—C6	119.9 (2)
N1—N2—C8	122.0 (2)	C4—C5—C6	120.5 (3)
C8—N2—H2	119.00	C1—C6—C5	121.1 (3)
N1—N2—H2	119.00	N1—C7—C1	122.7 (2)
H3A—N3—H3B	120.00	N2—C8—N3	118.1 (2)
C8—N3—H3A	120.00	S1—C8—N2	118.92 (18)
C8—N3—H3B	120.00	S1—C8—N3	123.01 (18)
C2—C1—C6	118.0 (2)	C2—C3—H3	119.00
C6—C1—C7	118.8 (2)	C4—C3—H3	119.00
C2—C1—C7	123.2 (2)	C3—C4—H4	120.00
O1—C2—C1	121.9 (2)	C5—C4—H4	120.00
C1—C2—C3	120.0 (3)	C1—C6—H6	119.00
O1—C2—C3	118.1 (2)	C5—C6—H6	119.00
C2—C3—C4	121.2 (3)	N1—C7—H7	119.00
C3—C4—C5	119.2 (3)	C1—C7—H7	119.00
C7—N1—N2—C8	−176.7 (2)	C6—C1—C2—C3	−0.9 (4)
N2—N1—C7—C1	176.5 (2)	C7—C1—C2—O1	2.5 (4)
N1—N2—C8—S1	171.99 (18)	O1—C2—C3—C4	−179.8 (3)
N1—N2—C8—N3	−8.0 (4)	C1—C2—C3—C4	0.9 (5)
C7—C1—C2—C3	−178.2 (3)	C2—C3—C4—C5	−0.8 (5)
C2—C1—C6—C5	1.0 (4)	C3—C4—C5—Cl1	179.5 (2)
C7—C1—C6—C5	178.3 (3)	C3—C4—C5—C6	0.8 (5)
C2—C1—C7—N1	−0.3 (4)	Cl1—C5—C6—C1	−179.6 (2)

| C6—C1—C7—N1 | −177.6 (2) | C4—C5—C6—C1 | −0.9 (4) |
| C6—C1—C2—O1 | 179.8 (2) | | |

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2; (ii) *x*−1, *y*, *z*; (iii) −*x*, −*y*, −*z*+1; (iv) −*x*+1, −*y*, −*z*+2; (v) *x*+1, *y*, *z*; (vi) −*x*+1, −*y*, −*z*+1; (vii) *x*, *y*, *z*+1; (viii) *x*, −*y*+1/2, *z*+1/2; (ix) *x*, *y*, *z*−1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.97	2.681 (3)	144
N2—H2···S1ⁱⁱⁱ	0.86	2.70	3.491 (2)	153
N3—H3*A*···S1ᵛ	0.86	2.87	3.387 (2)	120
N3—H3*A*···N1	0.86	2.36	2.693 (3)	103
N3—H3*B*···S1ⁱᵛ	0.86	2.55	3.390 (2)	167

Symmetry codes: (iii) −*x*, −*y*, −*z*+1; (iv) −*x*+1, −*y*, −*z*+2; (v) *x*+1, *y*, *z*.