Crystal structure and Hirshfeld surface analysis of (Z)-4-chloro-N′-(4-oxothiazolidin-2-ylidene)-benzenesulfonohydrazide monohydrate

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The asymmetric unit of the title thiazole derivative containing a sulfonyl-hydrazinic moiety, $C_9H_8ClN_3O_3S_2 \cdot H_2O$, consists of two independent molecules and two water molecules. The central parts of the molecules are twisted as both the molecules are bent at both the S and N atoms. In the crystal, N—H···N, N—H···O, C—H···O and O—H···O hydrogen-bonding interactions connect the molecules, forming layers parallel to the ab plane. Two-dimensional fingerprint plots associated with the Hirshfeld surface show that the largest contributions to the crystal packing come from O···H/H···O (32.9%) and H···H (22.6%) interactions.

1. Chemical context

Sulfonamides are of interest as this class of compounds exhibits a wide array of biological activities such as antitumor, antibacterial, diuretic and hypoglycaemic activities (Kamal et al., 2007). It has been reported that incorporation of hydrazine moieties increases the carbonic anhydrase inhibition activity (Winum et al., 2005). Along with the sulfonamide group, the presence of the 2-hydrazino-thiazole moiety enhances the pharmacological activities. The thiozoyl group is of interest because of its medicinal use in antitumor (Holla et al., 2003; Kappe et al., 2004), hyposensitive (Dash et al., 1980), anti-HIV (Patt et al., 1992), antimicrobial and anticancer agents (Frère et al., 2003). Sulfonylhydrazines and their derivatives can easily be prepared and are stable. We report herein the synthesis and structure of the title compound, which is a new thiazole compound containing a sulfonylhydrazinic moiety.
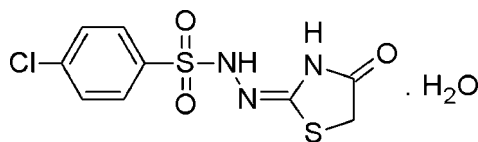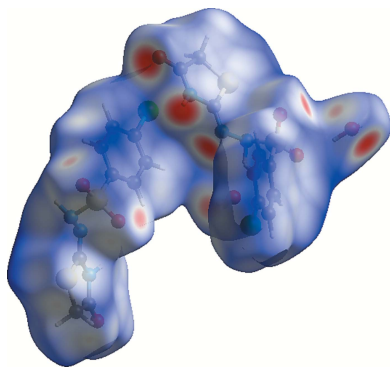
2. Structural commentary

The asymmetric unit of the title compound contains two independent molecules and two water molecules (Fig. 1). The C8—O3 and C17—O6 bond lengths of 1.202 (5) Å, 1.218 (6) Å, respectively, are consistent with C=O double-bond character. Similarly, the values of the C7—N2 and C16—N5 bond lengths [1.285 (5) and 1.276 (5) Å, respectively] are
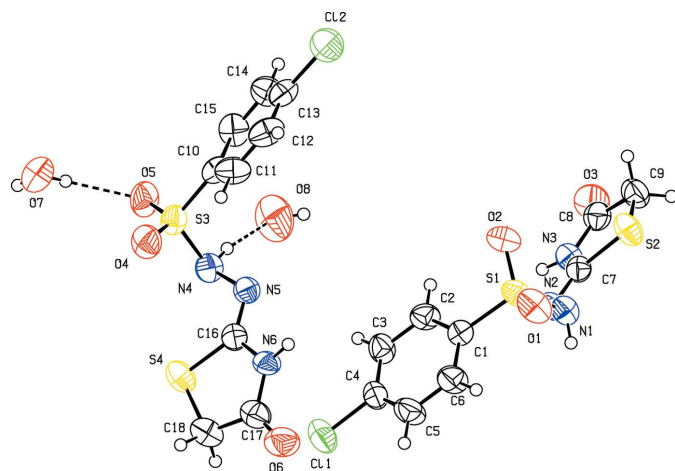
Figure 1
The molecular structure of the title compound showing displacement ellipsoids at the 50% probability level.

close to that of a typical C=N double bond, while the longer C7—N3 and C16—N6 bond lengths of 1.370 (5) and 1.381 (5) Å, respectively, are consistent with the normal C—N single bonds, indicating that the compound exists in the Schiff base form. Further, the N1—N2 and N4—N5 bond lengths of 1.440 (5) and 1.442 (5) Å, respectively, and the S1—N1 and S3—N4 bond lengths of 1.644 (4) and 1.649 (4) Å, respectively, are in agreement with single-bond character.

The central parts of both molecules are twisted as they are bent at the S (S1 and S3) and N (N2 and N5) atoms as indicated by the C1—S1—N1—N2 and S1—N1—N2—C7 torsion angles of 57.0 (3) and 111.8 (3)°, respectively, and by the C10—S3—N4—N5 and S3—N4—N5—C16 torsion angles of 57.6 (3) and 109.7 (3)°, respectively. The sulfonylhydrazide bond exists in the synclinal conformation preferred by aromatic sulfonamides (Purandara *et al.*, 2017), with C—S—N—N torsion angles of 57.0 (3) and 57.6 (3)° in the two independent molecules. The geometrical parameters for the thiazole and benzene rings are within the expected ranges and comparable with those of other substituted thiazoles or benzenesulfonylhydrazide derivatives (Zaharia *et al.*, 2010). The C7—S2—C9 and C16—S4—C18 angles in the two molecules have the same value of 91.4 (2)°, and it is similar to the angles typically observed in thiazole derivatives (Form *et al.*, 1974). The thiazole rings are approximately planar (r.m.s. deviations of 0.011 and 0.029 Å for S2/N3/C7–C9 and S4/N6/C16–C18, respectively), and form dihedral angles of 26.18 (15) and 37.19 (12)° with the aromatic ring of the *p*-chlorophenylsulfonyl groups.

3. Supramolecular features

In the crystal, the two independent molecules are linked into dimers by pairs of N—H···N hydrogen bonds, forming rings with an $R_2^2(8)$ graph-set motif. These dimers are connected by C—H···O hydrogen bonds involving the thiazole C—H and a sulfonyl O atom into chains running parallel to the *a* axis
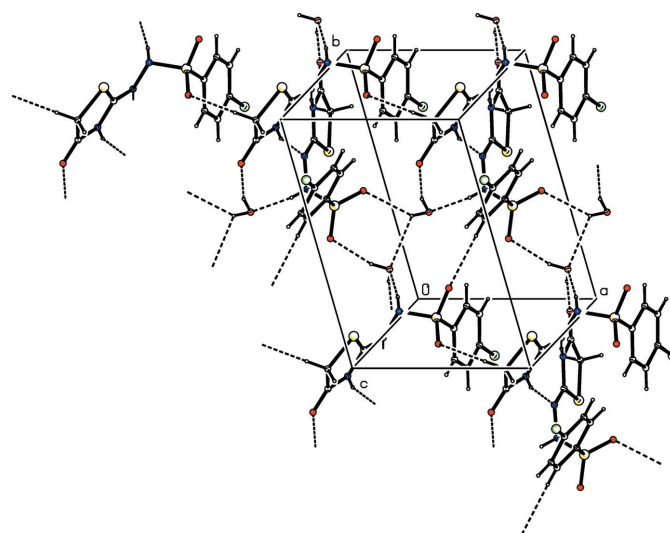
Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O7[i]	0.84 (2)	2.07 (2)	2.900 (6)	168 (4)
N3—H3N···N5[ii]	0.85 (2)	2.07 (2)	2.895 (5)	162 (4)
C9—H9B···O2[ii]	0.97	2.42	3.236 (6)	141
N4—H4N···O8	0.85 (2)	1.95 (2)	2.788 (6)	168 (4)
N6—H6N···N2[iii]	0.85 (2)	1.97 (2)	2.808 (5)	170 (4)
C15—H15···O1[iv]	0.93	2.55	3.355 (5)	145
O7—H71···O5	0.82 (3)	2.08 (3)	2.868 (6)	162 (6)
O7—H72···O6[iv]	0.82 (2)	1.99 (2)	2.810 (5)	174 (6)
O8—H81···O4[ii]	0.82 (2)	2.35 (6)	2.987 (6)	136 (7)
O8—H81···O7[ii]	0.82 (2)	2.50 (7)	3.034 (7)	124 (7)
O8—H82···O3[iii]	0.83 (2)	2.37 (3)	3.159 (7)	159 (8)

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

(Table 1, Fig. 2). The water molecules are involved both in the enforcement of the dimers through N—H···O and O—H···O hydrogen bonds, forming $R_3^3(9)$ rings, and in inter-chain O—H···O hydrogen-bonding interactions, forming layers parallel to the *ab* plane.

4. Database survey

Although a search in the Cambridge. Structural Database (CSD, Version 5.39, update of August 2018; Groom *et al.*, 2016) revealed several reports of the crystal structure of sulfonamides and thiazole (Gowda *et al.*, 2008, 2009), there are only a few reports on the crystal structures of sulfonylhydrazides functionalized by thiazole groups (Zaharia *et al.*, 2010). Comparison of the structure of the title compound with that of N′-(5-acetyl-4-methyl-4,5-dihydrothiazol-2-yl)benzenesulfonohydrazide (Zaharia *et al.*, 2010) indicates that the electron-withdrawing chloro group does not impart sufficient inductive effect to reduce the electron density on the benzene ring, and that the ability of the aromatic C—H groups to participate in C—H···O interactions is very much reduced.
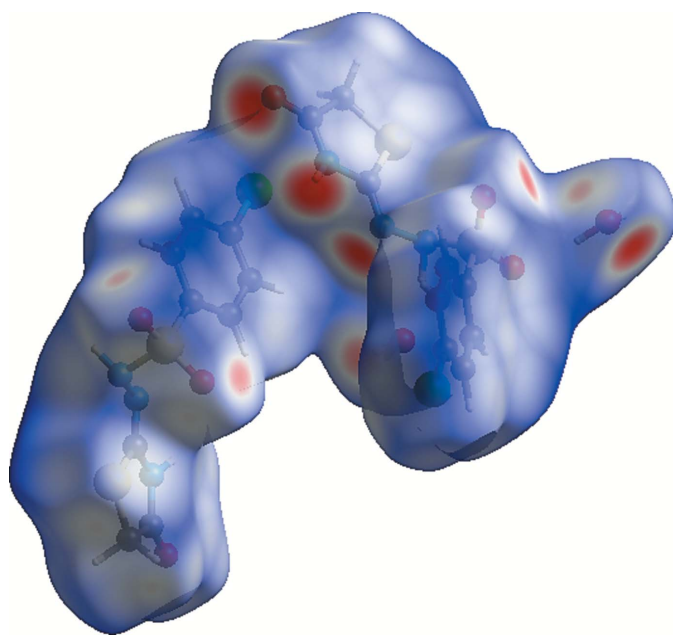

Figure 2
The molecular packing of the title compound, with hydrogen bonds (Table 1) shown as dashed lines.
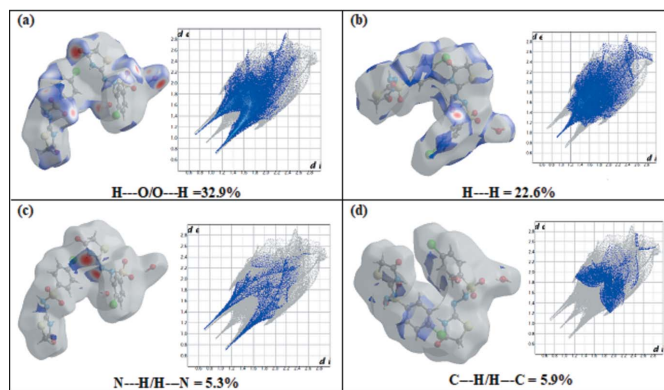
Partial double-bond character is observed between the hydrazinyl N atom and the adjacent benzothiazole moiety in 2-[2-(3-nitrobenzenesulfonyl)hydrazinyl]-1,3-benzothiazole (Morscher *et al.*, 2018). The orientation of the thiazole ring in the title compound is similar to that of (*Z*)-methyl 2-[(*Z*)-4-oxo-2-(2-tosylhydrazono)thiazolidin-5-ylidene]acetate and (*Z*)-methyl-2-[(*Z*)-2-(ethylimino)-4-oxo-3-(phenylamino)thiazolidin-5-ylidene]acetate (Hassan *et al.*, 2016). The molecule of *N*′-{3-[3-(trifluoromethyl)phenyl]-1,3-thiazol-2(3*H*)-ylidene}benzenesulfonohydrazide (Chen *et al.*, 2015) is observed to have a Schiff base conformation.

5. Hirshfeld Surface Analysis

In order to explore the role of weak intermolecular interactions in the crystal packing, Hirshfeld surfaces (d_{norm}) and related fingerprint plots were generated using *CrystalExplorer17.5* (McKinnon *et al.*, 2007; Spackman *et al.*, 2008; Spackman & Jayatilaka, 2009; Wolff *et al.*, 2012). The three-dimensional molecular Hirshfeld surfaces were generated using a high standard surface resolution over a colour scale of −0.6355 to 1.5137 a.u. for d_{norm}. To identify the normalized contacts, the d_{norm} function is used, which is expressed as; $d_{norm} = (d_i - r_i^{vdw})/r_i^{vdw} + (d_e - r_e^{vdw})/r_e^{vdw}$ (Shit *et al.*, 2016), where d_i and d_e are the distances from internal and external atoms to the Hirshfeld surface and r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms inside and outside the surface. On the Hirshfeld surfaces mapped over d_{norm} (Fig. 3), strong N—H···N and S—O···H interactions are observed as red spots close to atoms N5, N6 and O6. Furthermore, the two-dimensional fingerprint plots indicate that the largest contributions are from O···H/H···O contacts, which contribute 32.9% to the Hirshfeld surface (Fig. 4*a*) with $d_i + d_e \sim 1.9$ Å. The

Figure 4
The two dimensional fingerprint (FP) plot for the title compound, delineated into (*a*) O···H/H···O, (*b*) H···H, (*c*) N···H/H···N and (*d*) C···H/H···C interactions. d_{norm} surfaces for each plot indicating the relevant surface patches associated with the specific contacts are shown on the left.

presence of water molecules in the unit cell provides the largest contribution to the stability of the crystal packing. The next largest contributor is from H···H interactions, which contribute 22.6%. A single sharp spike can be seen in the middle region of the plot, at $d_i = d_e = 0.9$ Å (Fig. 4*b*). The N···H contacts, which refer to N—H···N interactions, contribute 5.3% to the surface. Two sharp spikes having $d_i + d_e = 1.8$ Å (Fig. 4*c*) are observed. The C···H contacts contribute 5.9% to the Hirshfeld surface, featuring a wide region with $d_i + d_e = 3.1$ Å (Fig. 4*d*). The different interatomic contacts and percentage contributions to the Hirshfeld surface are Cl···H/H···Cl (8.3%), S···H/H···S (6.1%), Cl···O/O···Cl (3.0%), Cl···C/C···Cl (2.4%), S···O/O···S (1.7%), and C···O/O···C (1.6%) as depicted in the fingerprint plots (Fig. 5*a*–*f*).

Figure 3
View of the Hirshfeld surface mapped over d_{norm}.
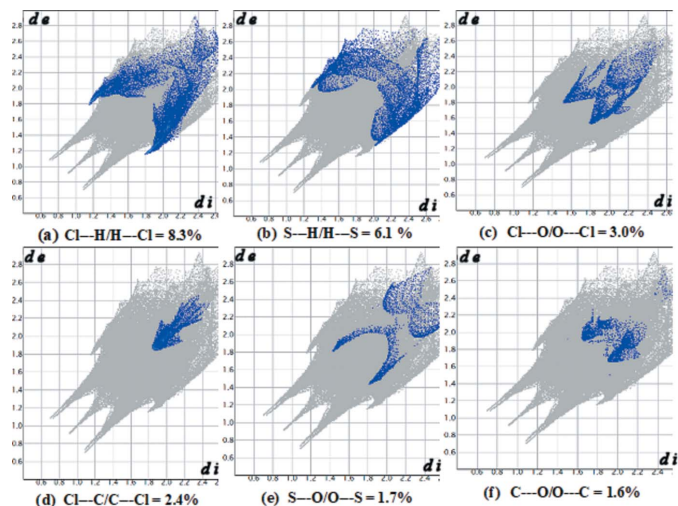
Figure 5
Fingerprint plots of interactions, listing their percentage contributions: (*a*) Cl···H/H···Cl, (*b*) S···H/H···S, (*c*) Cl···O/O···Cl, (*d*) Cl···C/C···Cl, (*e*) S···O/O···S and (*f*) C···O/O···C.

6. Synthesis and crystallization

4-Chloro-N'-(4-oxo-4,5-dihydro-1,3-thiazol-2-yl)benzene-1-sulfonohydrazide was prepared by adding 4-chloro benzene-sulfonyl chloride (0.02 mol) under stirring to a solution of thiosemicarbazide (0.02 mol) in 5% aqueous NaOH solution (20 ml). The reaction mixture was stirred at room temperature for 1 h, then diluted twofold with water and neutralized with glacial acetic acid. The solid 2-(4-chlorobenzene-1-sulfonyl)-hydrazine-1-carbothioamide (A) obtained was crystallized from acetic acid. Monochloroacetic acid (0.01 mol) and anhydrous sodium acetate (0.04 mol) were added to A (0.01 mol) in glacial acetic acid. The reaction mixture was refluxed for 8–10 h and the completion of the reaction was checked by TLC. The reaction mixture was then poured into cold water. The resulted precipitate of the title compound was separated by vacuum filtration. Prismatic colourless single crystals of the title compound were grown from a mixture of acetonitrile-DMF (5:1 v/v) by slow evaporation of the solvent. The purity of the compound was checked by TLC and characterized by IR spectroscopy. The characteristic IR absorptions observed at 3095.9, 1639.5, 1458.7, 1343.2, 1139.4, and 1215.7 cm^{-1} correspond to N—H, C=O, C=N, S=O asymmetric and symmetric, and C—S absorptions, respectively. The ^{1}H and ^{13}C spectra of the title compound are as follows: ^{1}H (400MHz, DMSO-d_6); δ 3.45 (d, 2H, –CH$_2$), 7.68–7.86 (m, 4H, Ar—H), 10.01 (s, 1H), 11.96 (s, 1H). ^{13}C NMR (400 MHz, DMSO-d_6); δ 36.8, 128.4, 129.1, 131.1,132.5, 133.9, 137.2, 165.4, 185.5.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bonded to C were positioned with idealized geometry using a riding model with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene). The H atoms of the NH groups and the H atoms of the water molecules were located in a difference-Fourier map and later refined with the N—H and O—H bond lengths constrained to be 0.86 (2) and 0.82 (2) Å, respectively. All H atoms were refined with isotropic displacement parameters set at $1.2U_{eq}$ of the parent atom.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_8ClN_3O_3S_2 \cdot H_2O$
M_r	323.77
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	7.6276 (6), 11.090 (1), 17.116 (2)
α, β, γ (°)	96.95 (1), 99.49 (1), 106.08 (1)
V (Å^3)	1350.8 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.60
Crystal size (mm)	$0.42 \times 0.20 \times 0.06$
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Single Crystal X-ray diffractometer with a Sapphire CCD detector
Absorption correction	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.785, 0.965
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8631, 4935, 3375
R_{int}	0.026
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.161, 1.05
No. of reflections	4935
No. of parameters	367
No. of restraints	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.52, −0.25

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

References

Chen, W., Wang, H.-A., Wei, W., Li, Y.-X., Hua, X.-W., Song, H.-B., Yu, S.-J. & Li, Z.-M. (2015). *Chin. J. Struct. Chem.* **34**, 503–509.

Dash, B., Patra, M. & Praharaj, S. (1980). *Indian J. Chem.* **19B**, 894–897.

Form, G. R., Raper, E. S. & Downie, T. C. (1974). *Acta Cryst.* **B30**, 342–348.

Frère, S., Thiéry, V., Bailly, C. & Besson, T. (2003). *Tetrahedron*, **59**, 773–779.

Gowda, B. T., Foro, S., Babitha, K. S. & Fuess, H. (2008). *Acta Cryst.* E**64**, o2190.

Gowda, B. T., Foro, S., Nirmala, P. G. & Fuess, H. (2009). *Acta Cryst.* E**65**, o2763.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hassan, A. A., Mohamed, N. K., El-Shaieb, K. M. A., Tawfeek, H. N., Bräse, S. & Nieger, M. (2016). *J. Heterocycl. Chem.* **53**, 46–50.

Holla, B. S., Malini, V. K., Rao, B. S., Sarojini, K. B. & Kumari, N. S. (2003). *Eur. J. Med. Chem.* **38**, 313–318.

Kamal, A., Khan, M. N. A., Srinivasa Reddy, K. & Rohini, K. (2007). *Bioorg. Med. Chem.* **15**, 1004–1013.

Kappe, O. C. (2004). *Angew. Chem. Int. Ed.* **43**, 6250–6284.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Morscher, A., de Souza, M. V. N., Wardell, J. L. & Harrison, W. T. A. (2018). *Acta Cryst.* E**74**, 673–677.

Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd., Abingdon, England.

Patt, W. C., Hamilton, H. W., Taylor, M. D., Ryan, M. J., Taylor, D. G. Jr, Connolly, C. J. C., Doherty, A. M., Klutchko, S. R., Sircar, I., Steinbaugh, B. A., Batley, B. L., Painchaud, C. A., Rapundalo, S. T., Michniewicz, B. M. & Oslon, S. C. (1992). *J. Med. Chem.* **35**, 2562–2572.

Purandara, H., Foro, S. & Thimme Gowda, B. (2017). *Acta Cryst.* E**73**, 1683–1686.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Shit, S., Marschner, C. & Mitra, S. (2016). *Acta Chim. Slovenica*, **63**, 129–137.

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Winum, J. Y., Dogné, J. M., Casini, A., de Leval, X., Montero, J. L., Scozzafava, A., Vullo, D., Innocenti, A. & Supuran, C. T. (2005). *J. Med. Chem.* **48**, 2121–2125.

Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer3.1.* University of Western Australia.

Zaharia, V., Curticapenan, M., Palibroda, N., Vlasa, M. & Silvestru, A. (2010). *Rev. Roum. Chim.* **55**, 831–841.

supporting information

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Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

(*Z*)-4-Chloro-*N*′-(4-oxothiazolidin-2-ylidene)benzenesulfonohydrazide monohydrate

Crystal data

$C_9H_8ClN_3O_3S_2 \cdot H_2O$	$Z = 4$
$M_r = 323.77$	$F(000) = 664$
Triclinic, $P\bar{1}$	$D_x = 1.592$ Mg m^{-3}
$a = 7.6276$ (6) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.090$ (1) Å	Cell parameters from 2682 reflections
$c = 17.116$ (2) Å	$\theta = 2.8–27.8°$
$\alpha = 96.95$ (1)°	$\mu = 0.60$ mm^{-1}
$\beta = 99.49$ (1)°	$T = 293$ K
$\gamma = 106.08$ (1)°	Prism, colourless
$V = 1350.8$ (2) Å^3	$0.42 \times 0.20 \times 0.06$ mm

Data collection

Oxford Diffraction Xcalibur Single Crystal X-ray diffractometer with a Sapphire CCD detector	8631 measured reflections
	4935 independent reflections
	3375 reflections with $I > 2\sigma(I)$
Radiation source: Enhance (Mo) X-ray Source	$R_{int} = 0.026$
Rotation method data acquisition using ω scans	$\theta_{max} = 25.4°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan	$h = -9 \rightarrow 5$
(*CrysAlis RED*; Oxford Diffraction, 2009)	$k = -13 \rightarrow 13$
$T_{min} = 0.785$, $T_{max} = 0.965$	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.058$	
$wR(F^2) = 0.161$	$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 1.1929P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
4935 reflections	$(\Delta/\sigma)_{max} = 0.001$
367 parameters	$\Delta\rho_{max} = 0.52$ e Å^{-3}
8 restraints	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.33684 (17)	0.77231 (13)	0.00096 (7)	0.0689 (4)
S1	0.23228 (14)	1.01774 (10)	0.33163 (6)	0.0479 (3)
S2	−0.21540 (16)	0.96967 (12)	0.42899 (7)	0.0594 (3)
O1	0.3605 (4)	1.1427 (3)	0.35513 (19)	0.0659 (9)
O2	0.2255 (4)	0.9268 (3)	0.38508 (18)	0.0626 (8)
O3	−0.6004 (5)	0.6450 (3)	0.3600 (2)	0.0732 (10)
N1	0.0248 (5)	1.0382 (3)	0.3165 (2)	0.0484 (8)
H1N	0.024 (6)	1.086 (4)	0.282 (2)	0.058*
N2	−0.1246 (4)	0.9225 (3)	0.2827 (2)	0.0471 (8)
N3	−0.3702 (4)	0.7765 (3)	0.3134 (2)	0.0460 (8)
H3N	−0.380 (6)	0.721 (3)	0.2726 (19)	0.055*
C1	0.2676 (5)	0.9482 (4)	0.2392 (2)	0.0421 (9)
C2	0.2102 (6)	0.8168 (4)	0.2167 (3)	0.0515 (10)
H2	0.1557	0.7651	0.2505	0.062*
C3	0.2345 (6)	0.7627 (4)	0.1432 (3)	0.0523 (11)
H3	0.1967	0.6747	0.1273	0.063*
C4	0.3146 (5)	0.8409 (4)	0.0946 (2)	0.0475 (10)
C5	0.3755 (7)	0.9718 (5)	0.1168 (3)	0.0617 (12)
H5	0.4315	1.0231	0.0831	0.074*
C6	0.3514 (7)	1.0250 (4)	0.1899 (3)	0.0577 (12)
H6	0.3920	1.1131	0.2060	0.069*
C7	−0.2275 (5)	0.8889 (4)	0.3335 (2)	0.0419 (9)
C8	−0.4741 (6)	0.7422 (5)	0.3700 (3)	0.0522 (11)
C9	−0.4074 (6)	0.8429 (5)	0.4445 (3)	0.0600 (12)
H9A	−0.3669	0.8068	0.4905	0.072*
H9B	−0.5080	0.8761	0.4549	0.072*
Cl2	0.8418 (2)	0.63805 (14)	0.57661 (8)	0.0805 (4)
S3	0.78365 (15)	0.43436 (10)	0.21411 (7)	0.0511 (3)
S4	0.74715 (17)	0.59857 (12)	0.02143 (7)	0.0603 (3)
O4	0.9602 (4)	0.4892 (3)	0.1948 (2)	0.0670 (9)
O5	0.7003 (5)	0.2980 (3)	0.1978 (2)	0.0691 (9)
O6	0.8569 (5)	0.9655 (4)	0.0519 (2)	0.0762 (10)
N4	0.6297 (5)	0.4853 (3)	0.1590 (2)	0.0501 (9)
H4N	0.541 (5)	0.458 (4)	0.183 (3)	0.060*
N5	0.6762 (5)	0.6224 (3)	0.1738 (2)	0.0468 (8)
N6	0.7780 (5)	0.8026 (3)	0.12079 (19)	0.0473 (8)
H6N	0.804 (6)	0.847 (4)	0.1678 (15)	0.057*
C10	0.8011 (5)	0.4900 (4)	0.3167 (3)	0.0461 (10)
C11	0.9365 (6)	0.6028 (4)	0.3554 (3)	0.0593 (12)

H11	1.0191	0.6482	0.3273	0.071*
C12	0.9484 (6)	0.6473 (4)	0.4349 (3)	0.0605 (12)
H12	1.0383	0.7233	0.4607	0.073*
C13	0.8276 (6)	0.5797 (4)	0.4762 (3)	0.0540 (11)
C14	0.6935 (6)	0.4666 (5)	0.4392 (3)	0.0611 (12)
H14	0.6137	0.4207	0.4682	0.073*
C15	0.6792 (6)	0.4226 (4)	0.3595 (3)	0.0566 (11)
H15	0.5875	0.3474	0.3339	0.068*
C16	0.7281 (5)	0.6717 (4)	0.1146 (2)	0.0438 (9)
C17	0.8171 (6)	0.8523 (5)	0.0550 (3)	0.0575 (12)
C18	0.8040 (7)	0.7499 (5)	−0.0134 (3)	0.0652 (13)
H18A	0.9219	0.7657	−0.0308	0.078*
H18B	0.7080	0.7488	−0.0586	0.078*
O7	0.9751 (5)	0.1699 (4)	0.1821 (3)	0.0766 (10)
H71	0.880 (5)	0.191 (6)	0.182 (4)	0.092*
H72	0.933 (8)	0.112 (4)	0.143 (3)	0.092*
O8	0.3062 (6)	0.4099 (6)	0.2195 (4)	0.1111 (16)
H81	0.195 (4)	0.390 (7)	0.199 (4)	0.133*
H82	0.303 (12)	0.472 (5)	0.250 (4)	0.133*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0697 (8)	0.0852 (9)	0.0517 (7)	0.0274 (7)	0.0175 (6)	−0.0042 (6)
S1	0.0486 (6)	0.0477 (6)	0.0378 (6)	0.0020 (5)	0.0078 (4)	0.0023 (5)
S2	0.0572 (7)	0.0670 (8)	0.0452 (6)	0.0120 (6)	0.0114 (5)	−0.0085 (5)
O1	0.0601 (19)	0.057 (2)	0.059 (2)	−0.0078 (15)	0.0119 (15)	−0.0071 (15)
O2	0.070 (2)	0.072 (2)	0.0449 (18)	0.0156 (17)	0.0139 (15)	0.0183 (16)
O3	0.059 (2)	0.068 (2)	0.088 (3)	0.0044 (18)	0.0237 (18)	0.0185 (19)
N1	0.049 (2)	0.039 (2)	0.049 (2)	0.0029 (16)	0.0122 (17)	−0.0008 (15)
N2	0.0460 (19)	0.046 (2)	0.0420 (19)	0.0047 (16)	0.0111 (16)	−0.0001 (15)
N3	0.0411 (18)	0.049 (2)	0.042 (2)	0.0083 (16)	0.0061 (15)	0.0010 (16)
C1	0.039 (2)	0.041 (2)	0.044 (2)	0.0106 (17)	0.0078 (17)	0.0082 (18)
C2	0.057 (3)	0.042 (2)	0.053 (3)	0.007 (2)	0.015 (2)	0.014 (2)
C3	0.058 (3)	0.041 (2)	0.055 (3)	0.011 (2)	0.018 (2)	0.002 (2)
C4	0.046 (2)	0.056 (3)	0.043 (2)	0.019 (2)	0.0111 (18)	0.002 (2)
C5	0.079 (3)	0.058 (3)	0.052 (3)	0.013 (2)	0.030 (2)	0.017 (2)
C6	0.077 (3)	0.037 (2)	0.056 (3)	0.006 (2)	0.025 (2)	0.010 (2)
C7	0.038 (2)	0.046 (2)	0.039 (2)	0.0147 (18)	0.0014 (17)	0.0022 (18)
C8	0.044 (2)	0.060 (3)	0.057 (3)	0.020 (2)	0.011 (2)	0.014 (2)
C9	0.056 (3)	0.080 (3)	0.052 (3)	0.027 (2)	0.021 (2)	0.013 (2)
Cl2	0.0968 (10)	0.0802 (10)	0.0634 (8)	0.0332 (8)	0.0091 (7)	0.0040 (7)
S3	0.0483 (6)	0.0431 (6)	0.0643 (7)	0.0136 (5)	0.0182 (5)	0.0104 (5)
S4	0.0632 (7)	0.0641 (8)	0.0448 (6)	0.0112 (6)	0.0121 (5)	−0.0066 (5)
O4	0.0518 (18)	0.073 (2)	0.084 (2)	0.0203 (16)	0.0285 (17)	0.0204 (19)
O5	0.084 (2)	0.0379 (17)	0.087 (3)	0.0158 (16)	0.0302 (19)	0.0047 (16)
O6	0.097 (3)	0.066 (2)	0.071 (2)	0.021 (2)	0.028 (2)	0.0261 (19)
N4	0.052 (2)	0.041 (2)	0.050 (2)	0.0078 (17)	0.0055 (16)	−0.0003 (16)

N5	0.052 (2)	0.044 (2)	0.042 (2)	0.0137 (16)	0.0069 (16)	0.0037 (16)
N6	0.057 (2)	0.051 (2)	0.0315 (18)	0.0168 (17)	0.0033 (16)	0.0056 (16)
C10	0.038 (2)	0.039 (2)	0.058 (3)	0.0082 (18)	0.0031 (18)	0.0137 (19)
C11	0.056 (3)	0.050 (3)	0.061 (3)	−0.003 (2)	0.008 (2)	0.020 (2)
C12	0.059 (3)	0.039 (3)	0.068 (3)	−0.001 (2)	−0.006 (2)	0.013 (2)
C13	0.057 (3)	0.047 (3)	0.058 (3)	0.021 (2)	0.001 (2)	0.014 (2)
C14	0.057 (3)	0.059 (3)	0.063 (3)	0.007 (2)	0.017 (2)	0.015 (2)
C15	0.043 (2)	0.047 (3)	0.072 (3)	0.0000 (19)	0.016 (2)	0.006 (2)
C16	0.038 (2)	0.050 (3)	0.040 (2)	0.0146 (18)	0.0011 (17)	0.0015 (19)
C17	0.052 (3)	0.072 (3)	0.047 (3)	0.016 (2)	0.010 (2)	0.011 (2)
C18	0.072 (3)	0.073 (3)	0.049 (3)	0.016 (3)	0.018 (2)	0.011 (2)
O7	0.077 (3)	0.065 (2)	0.093 (3)	0.030 (2)	0.013 (2)	0.0167 (19)
O8	0.056 (2)	0.146 (5)	0.131 (4)	0.030 (3)	0.029 (3)	0.013 (3)

Geometric parameters (Å, º)

Cl1—C4	1.744 (4)	S3—O5	1.441 (3)
S1—O1	1.422 (3)	S3—N4	1.649 (4)
S1—O2	1.438 (3)	S3—C10	1.759 (5)
S1—N1	1.644 (4)	S4—C16	1.746 (4)
S1—C1	1.770 (4)	S4—C18	1.812 (5)
S2—C7	1.741 (4)	O6—C17	1.218 (6)
S2—C9	1.808 (5)	N4—N5	1.442 (5)
O3—C8	1.202 (5)	N4—H4N	0.850 (19)
N1—N2	1.440 (5)	N5—C16	1.276 (5)
N1—H1N	0.842 (19)	N6—C17	1.353 (6)
N2—C7	1.285 (5)	N6—C16	1.381 (5)
N3—C7	1.370 (5)	N6—H6N	0.851 (19)
N3—C8	1.374 (5)	C10—C11	1.389 (6)
N3—H3N	0.851 (19)	C10—C15	1.390 (6)
C1—C6	1.377 (6)	C11—C12	1.369 (7)
C1—C2	1.385 (6)	C11—H11	0.9300
C2—C3	1.389 (6)	C12—C13	1.368 (6)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.366 (6)	C13—C14	1.380 (6)
C3—H3	0.9300	C14—C15	1.368 (6)
C4—C5	1.379 (6)	C14—H14	0.9300
C5—C6	1.381 (6)	C15—H15	0.9300
C5—H5	0.9300	C17—C18	1.498 (7)
C6—H6	0.9300	C18—H18A	0.9700
C8—C9	1.503 (6)	C18—H18B	0.9700
C9—H9A	0.9700	O7—H71	0.82 (2)
C9—H9B	0.9700	O7—H72	0.82 (2)
Cl2—C13	1.737 (5)	O8—H81	0.82 (2)
S3—O4	1.426 (3)	O8—H82	0.83 (2)
O1—S1—O2	120.4 (2)	O4—S3—N4	107.3 (2)
O1—S1—N1	105.18 (19)	O5—S3—N4	103.2 (2)

O2—S1—N1	105.77 (19)	O4—S3—C10	107.8 (2)
O1—S1—C1	108.45 (19)	O5—S3—C10	108.6 (2)
O2—S1—C1	107.88 (19)	N4—S3—C10	109.61 (18)
N1—S1—C1	108.64 (18)	C16—S4—C18	91.4 (2)
C7—S2—C9	91.4 (2)	N5—N4—S3	112.3 (3)
N2—N1—S1	113.6 (3)	N5—N4—H4N	106 (3)
N2—N1—H1N	106 (3)	S3—N4—H4N	97 (3)
S1—N1—H1N	107 (3)	C16—N5—N4	112.6 (3)
C7—N2—N1	111.2 (3)	C17—N6—C16	117.8 (4)
C7—N3—C8	117.6 (4)	C17—N6—H6N	124 (3)
C7—N3—H3N	122 (3)	C16—N6—H6N	117 (3)
C8—N3—H3N	119 (3)	C11—C10—C15	119.4 (4)
C6—C1—C2	120.4 (4)	C11—C10—S3	120.0 (3)
C6—C1—S1	119.8 (3)	C15—C10—S3	120.6 (3)
C2—C1—S1	119.8 (3)	C12—C11—C10	120.1 (4)
C1—C2—C3	119.6 (4)	C12—C11—H11	119.9
C1—C2—H2	120.2	C10—C11—H11	119.9
C3—C2—H2	120.2	C13—C12—C11	119.7 (4)
C4—C3—C2	119.0 (4)	C13—C12—H12	120.1
C4—C3—H3	120.5	C11—C12—H12	120.1
C2—C3—H3	120.5	C12—C13—C14	121.2 (5)
C3—C4—C5	122.1 (4)	C12—C13—Cl2	119.4 (4)
C3—C4—Cl1	118.6 (3)	C14—C13—Cl2	119.4 (4)
C5—C4—Cl1	119.2 (3)	C15—C14—C13	119.4 (4)
C4—C5—C6	118.7 (4)	C15—C14—H14	120.3
C4—C5—H5	120.7	C13—C14—H14	120.3
C6—C5—H5	120.7	C14—C15—C10	120.3 (4)
C1—C6—C5	120.2 (4)	C14—C15—H15	119.9
C1—C6—H6	119.9	C10—C15—H15	119.9
C5—C6—H6	119.9	N5—C16—N6	118.7 (4)
N2—C7—N3	119.3 (4)	N5—C16—S4	129.9 (3)
N2—C7—S2	128.6 (3)	N6—C16—S4	111.3 (3)
N3—C7—S2	112.1 (3)	O6—C17—N6	124.2 (4)
O3—C8—N3	123.9 (4)	O6—C17—C18	124.6 (4)
O3—C8—C9	125.7 (4)	N6—C17—C18	111.2 (4)
N3—C8—C9	110.4 (4)	C17—C18—S4	108.0 (3)
C8—C9—S2	108.4 (3)	C17—C18—H18A	110.1
C8—C9—H9A	110.0	S4—C18—H18A	110.1
S2—C9—H9A	110.0	C17—C18—H18B	110.1
C8—C9—H9B	110.0	S4—C18—H18B	110.1
S2—C9—H9B	110.0	H18A—C18—H18B	108.4
H9A—C9—H9B	108.4	H71—O7—H72	98 (6)
O4—S3—O5	119.9 (2)	H81—O8—H82	94 (7)
O1—S1—N1—N2	172.9 (3)	O4—S3—N4—N5	−59.2 (3)
O2—S1—N1—N2	−58.6 (3)	O5—S3—N4—N5	173.2 (3)
C1—S1—N1—N2	57.0 (3)	C10—S3—N4—N5	57.6 (3)
S1—N1—N2—C7	111.8 (3)	S3—N4—N5—C16	109.7 (3)

O1—S1—C1—C6	−22.2 (4)	O4—S3—C10—C11	23.0 (4)
O2—S1—C1—C6	−154.2 (4)	O5—S3—C10—C11	154.4 (3)
N1—S1—C1—C6	91.6 (4)	N4—S3—C10—C11	−93.5 (4)
O1—S1—C1—C2	158.0 (3)	O4—S3—C10—C15	−157.6 (3)
O2—S1—C1—C2	26.0 (4)	O5—S3—C10—C15	−26.3 (4)
N1—S1—C1—C2	−88.2 (4)	N4—S3—C10—C15	85.8 (4)
C6—C1—C2—C3	−1.2 (6)	C15—C10—C11—C12	−0.4 (7)
S1—C1—C2—C3	178.6 (3)	S3—C10—C11—C12	179.0 (4)
C1—C2—C3—C4	−0.1 (6)	C10—C11—C12—C13	0.6 (7)
C2—C3—C4—C5	1.2 (7)	C11—C12—C13—C14	0.2 (7)
C2—C3—C4—Cl1	−177.7 (3)	C11—C12—C13—Cl2	−179.1 (3)
C3—C4—C5—C6	−1.1 (7)	C12—C13—C14—C15	−1.2 (7)
Cl1—C4—C5—C6	177.9 (4)	Cl2—C13—C14—C15	178.1 (4)
C2—C1—C6—C5	1.4 (7)	C13—C14—C15—C10	1.3 (7)
S1—C1—C6—C5	−178.4 (4)	C11—C10—C15—C14	−0.6 (7)
C4—C5—C6—C1	−0.3 (7)	S3—C10—C15—C14	−179.9 (4)
N1—N2—C7—N3	−176.1 (3)	N4—N5—C16—N6	−179.6 (3)
N1—N2—C7—S2	5.0 (5)	N4—N5—C16—S4	0.8 (5)
C8—N3—C7—N2	178.3 (4)	C17—N6—C16—N5	−174.4 (4)
C8—N3—C7—S2	−2.6 (5)	C17—N6—C16—S4	5.3 (5)
C9—S2—C7—N2	−179.0 (4)	C18—S4—C16—N5	174.5 (4)
C9—S2—C7—N3	2.0 (3)	C18—S4—C16—N6	−5.1 (3)
C7—N3—C8—O3	−178.6 (4)	C16—N6—C17—O6	177.6 (4)
C7—N3—C8—C9	1.6 (5)	C16—N6—C17—C18	−2.1 (5)
O3—C8—C9—S2	−179.7 (4)	O6—C17—C18—S4	178.5 (4)
N3—C8—C9—S2	0.0 (5)	N6—C17—C18—S4	−1.8 (5)
C7—S2—C9—C8	−1.1 (3)	C16—S4—C18—C17	3.9 (3)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯O7[i]	0.84 (2)	2.07 (2)	2.900 (6)	168 (4)
N3—H3N⋯N5[ii]	0.85 (2)	2.07 (2)	2.895 (5)	162 (4)
C9—H9B⋯O2[ii]	0.97	2.42	3.236 (6)	141
N4—H4N⋯O8	0.85 (2)	1.95 (2)	2.788 (6)	168 (4)
N6—H6N⋯N2[iii]	0.85 (2)	1.97 (2)	2.808 (5)	170 (4)
C15—H15⋯O1[iv]	0.93	2.55	3.355 (5)	145
O7—H71⋯O5	0.82 (2)	2.08 (3)	2.868 (5)	162 (6)
O7—H72⋯O6[iv]	0.82 (2)	1.99 (2)	2.810 (5)	174 (6)
O8—H81⋯O4[ii]	0.82 (2)	2.35 (6)	2.987 (6)	136 (7)
O8—H81⋯O7[ii]	0.82 (2)	2.50 (7)	3.034 (7)	124 (7)
O8—H82⋯O3[iii]	0.83 (2)	2.37 (3)	3.159 (7)	159 (8)

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