



HAL
open science

Synthesis and crystal structure of (E)-2-(2-[azaniumylidene(methylsultanyl)methyl]hydrazinyl-idenemethyl)benzene-1,4-diol hydrogen sulfate

Oussama Nehar, Samira Louhibi, Thierry Roisnel

► **To cite this version:**

Oussama Nehar, Samira Louhibi, Thierry Roisnel. Synthesis and crystal structure of (E)-2-(2-[azaniumylidene(methylsultanyl)methyl]hydrazinyl-idenemethyl)benzene-1,4-diol hydrogen sulfate. *Acta crystallographica Section E: Crystallographic communications* [2015-..], 2019, 75 (11), pp.1738-+. 10.1107/S2056989019014233 . hal-02391899

HAL Id: hal-02391899

<https://univ-rennes.hal.science/hal-02391899>

Submitted on 9 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Synthesis and crystal structure of (*E*)-2-([2-[azaniumylidene(methylsulfanyl)methyl]hydrazinylidene]methyl)benzene-1,4-diol hydrogen sulfate

Oussama Nehar,^{a*} Samira Louhibi^a and Thierry Roisnel^b

Received 26 September 2019

Accepted 17 October 2019

Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; thiosemicarbazone; hydrogen bonding; organic salt.**CCDC reference:** 1960006**Supporting information:** this article has supporting information at journals.iucr.org/e

^aLaboratoire de Chimie Inorganique et Environnement, Université de Tlemcen, BP 119, 13000 Tlemcen, Algeria, and ^bCentre de Diffractométrie X, UMR 6226 CNRS, Unit Sciences Chimiques de Rennes, Université de Rennes I, 263 Avenue du General Leclerc, 35042 Rennes, France. *Correspondence e-mail: oussamanehar@gmail.com

The title molecular salt, C₉H₁₂N₃O₂S⁺·HSO₄⁻, was obtained through the protonation of the azomethine N atom in a sulfuric acid medium. The crystal comprises two entities, a thiosemicarbazide cation and a hydrogen sulfate anion. The cation is essentially planar and is further stabilized by a strong intramolecular O—H···N hydrogen bond. In the crystal, a three-dimensional network is established through O—H···O and N—H···O hydrogen bonds. A weak intermolecular C—H···O hydrogen bond is also observed. The hydrogen sulfate anion exhibits disorder over two sets of sites and was modelled with refined occupancies of 0.501 (6) and 0.499 (6).

1. Chemical context

Thiosemicarbazones and their complexes are well known for their pharmacological properties, as antimicrobial (Plech *et al.*, 2011; Pandeya *et al.*, 1999; Küçükgülzel *et al.*, 2006), anti-inflammatory (Palaska *et al.*, 2002) and antitumoural (de Oliveira *et al.*, 2015) agents. Complexes of thiosemicarbazones are studied in the literature as drug candidates, biomarkers and biocatalysts (Hayne *et al.*, 2014; Lim *et al.*, 2010). It is believed that the biological activity of these compounds has a strong relationship with the nature of the aldehydes and ketones from which those thiosemicarbazones were obtained (Teoh *et al.*, 1999), and also on the substituents attached at the ⁺NH₂ N atom (Beraldo & Gambino, 2004). An interesting attribute of thiosemicarbazones is their ability to exhibit thione–thiol tautomerism and they can also exist as *E* and *Z* isomers. Thiosemicarbazones have an excellent capacity to complex transition metals, acting as chelating agents; this process usually takes place *via* dissociation of the acidic proton (Pal *et al.*, 2002). The crystal structure of the title molecular salt was determined in order to investigate its biological and catalytic activities.

2. Structural commentary

The molecular structure of the title molecular salt is illustrated in Fig. 1. It comprises two entities, *i.e.* a thiosemicarbazone cation and a hydrogen sulfate anion. The cation is essentially planar and shows an *E* conformation with regard to the C6–N5 bond, the maximum deviation from the mean plane through the 15 non-H atoms being 0.1 (2) Å for atom C6. This planarity is due to electron delocalization along the cation backbone, which is further stabilized by an intramolecular O13–H13···N5 hydrogen bond (Zhu *et al.*, 2004). The bond

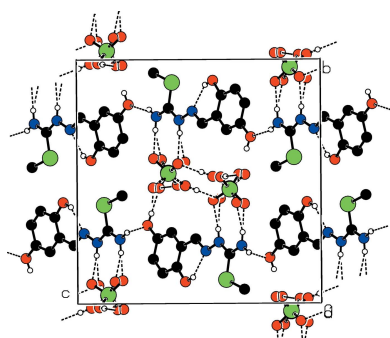
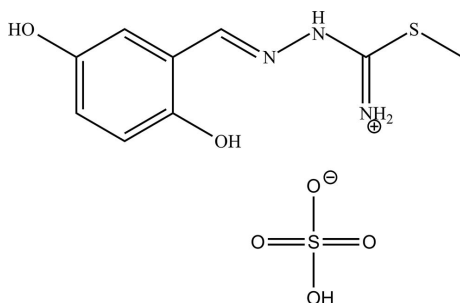


Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C10-H10\cdots O12A^i$	0.95	2.60	3.541 (10)	170
$N3-H3A\cdots O12A^{ii}$	0.89 (2)	1.85 (2)	2.738 (12)	178 (3)
$N3-H3A\cdots O12B^{ii}$	0.89 (2)	1.98 (2)	2.841 (11)	163 (3)
$N3-H3B\cdots O14^{iii}$	0.86 (2)	2.05 (2)	2.874 (3)	160 (3)
$N4-H4\cdots O13A^{ii}$	0.86 (3)	2.00 (3)	2.849 (5)	167 (3)
$N4-H4\cdots O13B^{ii}$	0.86 (3)	2.00 (3)	2.841 (5)	164 (3)
$O13-H13\cdots N5$	0.78 (3)	2.03 (3)	2.685 (3)	142 (3)
$O14-H14\cdots O11A^{iv}$	0.83 (4)	1.90 (4)	2.716 (16)	167 (3)
$O14-H14\cdots O11B^{iv}$	0.83 (4)	1.82 (4)	2.62 (2)	162 (3)
$O14A-H14A\cdots O11A^{iv}$	0.84	2.28	3.123 (17)	180
$O14B-H14B\cdots S2B^{ii}$	0.84	2.73	3.490 (9)	152
$O14B-H14B\cdots O13B^{ii}$	0.84	1.73	2.567 (7)	180

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - 1, y, z$.

lengths and angles resemble those observed for similar thiosemicarbazone derivatives (Gangadharan *et al.*, 2015; Joseph *et al.*, 2004; Nehar *et al.*, 2016; Houari *et al.*, 2013). The anion (hydrogen sulfate) is disordered, split over two sets of sites with relative occupancies of 0.501 (6) and 0.499 (6), and labelled with *A* and *B* suffixes.



3. Supramolecular features

In the crystal, the three-dimensional structure is established through an extensive network of $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds. Also within this network exists a weak $C-H\cdots O$ intermolecular hydrogen bond (Table 1 and Fig. 2). The crystal packing is shown in Fig. 2.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.4, May 2019 update; Groom *et al.*, 2016) for the *S*-methyl-(methylidene)thiosemicarbazidium cation yielded three results, *viz.* *S*-methyl-*N*-(pyrrolyl-2-methylene)isothiosemicarbazidium iodide monohydrate (CSD refcode JIHZUV; Bourosh *et al.*, 1990), 8-quinolinealdehyde *S*-methylthiosemicarbazone hydrochloride dihydrate (RUJXOK; Botoshansky *et al.*, 2009) and ((*E*)-{2-[(*E*)-(4-hydroxynaphthalen-1-yl)methylidene]hydrazin-1-yl}(methylsulfanyl)methylidene)azanium hydrogen sulfate monohydrate. The three-dimensional coordinates for the first structure are unavailable. A comparison of the structures reveals that the cation in the RUJXOK structure is less planar than the cation in ESOTIR, the latter being more similar to the cation of the title compound. However, for structures RUJXOK and ESOTIR, the

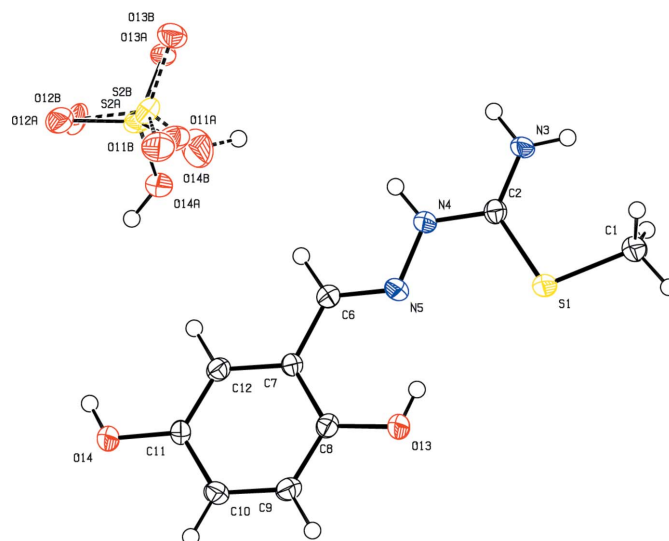


Figure 1
 The molecular structure of the title molecular salt, showing the labelling and with displacement ellipsoids drawn at the 50% probability level. The disordered hydrogen sulfate anion is shown.

bond lengths and angles are similar to those of the title molecular salt.

5. Synthesis and crystallization

An equimolar amount of thiosemicarbazide (10 mmol, 0.91 g) and 2,5-dihydroxybenzaldehyde (10 mmol, 1.38 g) were dissolved in a methanol–water solution in the presence of sulfuric acid. The mixture was then refluxed for 3 h. The solution was filtered and left to evaporate at room temperature. After slow evaporation, brown crystals suitable for X-ray diffraction analysis were obtained.

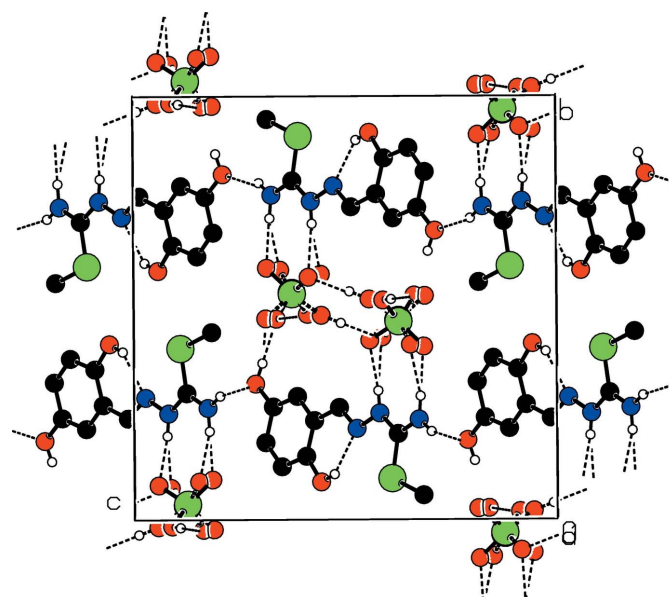


Figure 2
 Projection along the *a* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen sulfate anion is disordered and had to be modelled as two conformations *A* and *B*, with relative occupancies of 0.501 (6) and 0.499 (6), respectively. H atoms were located in difference Fourier maps, but were subsequently included in calculated positions and treated as riding on their parent atoms with constrained thermal parameters: $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and $\text{C}-\text{H} = 0.98 \text{ \AA}$ for methyl H atoms, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $\text{C}-\text{H} = 0.95 \text{ \AA}$ or $\text{N}-\text{H} = 0.88 \text{ \AA}$ otherwise.

Acknowledgements

The authors are grateful for the support provided by the Algerian Ministry for Education and Research.

References

- Beraldo, H. & Gambino, D. (2004). *Mini Rev. Med. Chem.* **4**, 159–165.
- Botoshansky, M., Bourosh, P. N., Revenco, M. D., Korja, I. D., Simonov, Yu. A. & Panfilie, T. (2009). *Zh. Strukt. Khim.* **50**, 188–191.
- Bourosh, P. N., Jampolskaia, M. A., Dvorkin, A. A., Gerbelev, N. V., Simonov, Yu. A. & Malinovskii, T. I. (1990). *Dokl. Akad. Nauk SSSR*, **311**, 1119–1122.
- Bruker (2015). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gangadharan, R., Haribabu, J., Karvembu, R. & Sethusankar, K. (2015). *Acta Cryst.* **E71**, 305–308.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hayne, D. J., Lim, S. & Donnelly, P. S. (2014). *Chem. Soc. Rev.* **43**, 6701–6715.
- Houari, B., Louhibi, S., Boukli-Hacene, L., Roisnel, T. & Taleb, M. (2013). *Acta Cryst.* **E69**, o1469.
- Joseph, M., Suni, V., Nayar, C. R., Kurup, M. R. P. & Fun, H.-K. (2004). *J. Mol. Struct.* **705**, 63–70.
- Küçükgülzel, G., Kocatepe, A., De Clercq, E., Şahin, F. & Güllüce, M. (2006). *Eur. J. Med. Chem.* **41**, 353–359.
- Lim, S., Paterson, B. M., Fodero-Tavoletti, M. T., O’Keefe, G. J., Cappai, R., Barnham, K. J., Villemagne, V. L. & Donnelly, P. S. (2010). *Chem. Commun.* **46**, 5437–5439.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Nehar, O., Louhibi, S., Boukli-Hacene, L. & Roisnel, T. (2016). *Acta Cryst.* **E72**, 1326–1329.
- Oliveira, J. F. de, da Silva, A. L., Vendramini-Costa, D. B., da Cruz Amorim, C. A., Campos, J. F., Ribeiro, A. G., Olímpio de Moura,

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_9\text{H}_{12}\text{N}_3\text{O}_2\text{S}^+\text{HSO}_4^-$
M_r	323.34
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	4.9411 (8), 16.139 (2), 16.426 (3)
β (°)	100.440 (7)
V (Å ³)	1288.2 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.44
Crystal size (mm)	0.38 × 0.15 × 0.12
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
$T_{\text{min}}, T_{\text{max}}$	0.838, 0.948
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7962, 2846, 2014
R_{int}	0.045
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.644
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.147, 1.03
No. of reflections	2846
No. of parameters	243
No. of restraints	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.46

Computer programs: *APEX2* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *SXGRAPH* (Farrugia, 1999), *Mercury* (Macrae *et al.*, 2008) and *CRYSCALC* (T. Roisnel, local program).

- R., Neves, J. L., Ruiz, A. L., Ernesto de Carvalho, J. & Alves de Lima, M. C. (2015). *Eur. J. Med. Chem.* **104**, 148–156.
- Pal, I., Basuli, F. & Bhattacharya, S. (2002). *J. Chem. Sci.* **114**, 255–268.
- Palaska, E., Şahin, G., Kelicen, P., Durlu, N. T. & Altinok, G. (2002). *Farmaco*, **57**, 101–107.
- Pandeya, S. N., Sriram, D., Nath, G. & DeClercq, E. (1999). *Eur. J. Pharm. Sci.* **9**, 25–31.
- Plech, T., Wujec, M., Siwek, A., Kosikowska, U. & Malm, A. (2011). *Eur. J. Med. Chem.* **46**, 241–248.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Teoh, S.-G., Ang, S.-H., Fun, H.-K. & Ong, C.-W. (1999). *J. Organomet. Chem.* **580**, 17–21.
- Zhu, J., Wang, X.-Z., Chen, Y.-Q., Jiang, X.-K., Chen, X.-Z. & Li, Z.-T. (2004). *J. Org. Chem.* **69**, 6221–6227.

supporting information

Acta Cryst. (2019). E75, 1738-1740 [https://doi.org/10.1107/S2056989019014233]

Synthesis and crystal structure of (*E*)-2-({2-[azaniumylidene(methylsulfanyl)methyl]hydrazinylidene}methyl)benzene-1,4-diol hydrogen sulfate

Oussama Nehar, Samira Louhibi and Thierry Roisnel

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *APEX2* (Bruker, 2014); data reduction: *APEX2* (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: SXGRAPH (Farrugia, 1999) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: CRYSCALC (T. Roisnel, local program, 2019).

(*E*)-2-({2-[Azaniumylidene(methylsulfanyl)methyl]hydrazinylidene} \ methyl)benzene-1,4-diol sulfate

Crystal data

$C_9H_{12}N_3O_2S^+HSO_4^-$
 $M_r = 323.34$
 Monoclinic, $P2_1/n$
 $a = 4.9411$ (8) Å
 $b = 16.139$ (2) Å
 $c = 16.426$ (3) Å
 $\beta = 100.440$ (7)°
 $V = 1288.2$ (3) Å³
 $Z = 4$

$F(000) = 672$
 $D_x = 1.667$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2859 reflections
 $\theta = 2.5$ – 27.0 °
 $\mu = 0.44$ mm⁻¹
 $T = 150$ K
 Prism, colourless
 $0.38 \times 0.15 \times 0.12$ mm

Data collection

Bruker APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 CCD rotation images, thin slices scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2014)
 $T_{\min} = 0.838$, $T_{\max} = 0.948$

7962 measured reflections
 2846 independent reflections
 2014 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.3$ °, $\theta_{\text{min}} = 3.6$ °
 $h = -6 \rightarrow 4$
 $k = -19 \rightarrow 20$
 $l = -21 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.147$
 $S = 1.03$
 2846 reflections
 243 parameters
 8 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.086P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ 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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.99180 (14)	0.09724 (4)	0.39012 (4)	0.0247 (2)	
C1	1.1843 (6)	0.05832 (18)	0.31564 (19)	0.0283 (7)	
H1A	1.103765	0.079127	0.260512	0.042*	
H1B	1.178644	-0.002377	0.315474	0.042*	
H1C	1.375761	0.076956	0.330229	0.042*	
C2	1.0137 (5)	0.20289 (18)	0.37549 (16)	0.0196 (6)	
N3	1.1584 (4)	0.23722 (15)	0.32555 (15)	0.0212 (5)	
H3A	1.163 (6)	0.2922 (11)	0.3217 (18)	0.025*	
H3B	1.253 (5)	0.2090 (17)	0.2961 (16)	0.025*	
N4	0.8734 (5)	0.25101 (15)	0.41903 (15)	0.0221 (5)	
H4	0.897 (6)	0.304 (2)	0.4220 (19)	0.027*	
N5	0.7288 (4)	0.21422 (15)	0.47329 (14)	0.0209 (5)	
C6	0.6012 (5)	0.26348 (17)	0.51479 (17)	0.0207 (6)	
H6	0.611234	0.321565	0.506437	0.025*	
C7	0.4421 (5)	0.23214 (17)	0.57410 (16)	0.0179 (6)	
C8	0.4293 (5)	0.14784 (17)	0.59347 (17)	0.0204 (6)	
C9	0.2738 (5)	0.12280 (18)	0.65151 (18)	0.0239 (6)	
H9	0.265269	0.065663	0.664710	0.029*	
C10	0.1324 (5)	0.17925 (17)	0.69007 (17)	0.0225 (6)	
H10	0.025988	0.161037	0.729373	0.027*	
C11	0.1446 (5)	0.26363 (17)	0.67161 (17)	0.0199 (6)	
C12	0.2983 (5)	0.28879 (17)	0.61429 (16)	0.0209 (6)	
H12	0.306923	0.346085	0.601728	0.025*	
O13	0.5640 (4)	0.08764 (12)	0.55849 (13)	0.0270 (5)	
H13	0.648 (7)	0.106 (2)	0.527 (2)	0.032*	
O14	0.0054 (4)	0.31741 (13)	0.71335 (13)	0.0279 (5)	
H14	0.001 (6)	0.366 (2)	0.697 (2)	0.034*	
S2A	0.8844 (12)	0.5353 (4)	0.6254 (4)	0.0254 (10)	0.501 (6)
O11A	1.081 (3)	0.4743 (10)	0.6620 (9)	0.031 (3)	0.501 (6)
O12A	0.810 (2)	0.5938 (7)	0.6848 (5)	0.030 (2)	0.501 (6)
O13A	0.9688 (11)	0.5797 (2)	0.5572 (3)	0.0297 (14)	0.501 (6)
O14A	0.6216 (9)	0.4839 (3)	0.5891 (3)	0.0302 (13)	0.501 (6)
H14A	0.476218	0.481337	0.608697	0.045*	0.501 (6)
S2B	0.9553 (12)	0.5327 (5)	0.6250 (5)	0.0292 (12)	0.499 (6)
O11B	1.084 (4)	0.4751 (12)	0.6870 (8)	0.038 (3)	0.499 (6)

O12B	0.767 (2)	0.5891 (7)	0.6534 (6)	0.038 (2)	0.499 (6)
O13B	1.1639 (10)	0.5733 (3)	0.5857 (3)	0.0294 (13)	0.499 (6)
O14B	0.7723 (10)	0.4819 (4)	0.5562 (3)	0.0506 (17)	0.499 (6)
H14B	0.793868	0.463761	0.509852	0.076*	0.499 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0307 (4)	0.0178 (4)	0.0285 (4)	-0.0005 (3)	0.0136 (3)	0.0018 (3)
C1	0.0313 (14)	0.0220 (15)	0.0354 (18)	0.0012 (12)	0.0162 (13)	0.0003 (13)
C2	0.0205 (11)	0.0207 (14)	0.0172 (14)	-0.0001 (11)	0.0027 (11)	-0.0014 (11)
N3	0.0252 (11)	0.0175 (12)	0.0236 (13)	0.0011 (10)	0.0114 (10)	0.0049 (10)
N4	0.0285 (11)	0.0178 (12)	0.0228 (13)	-0.0013 (10)	0.0121 (10)	0.0013 (10)
N5	0.0226 (10)	0.0229 (12)	0.0188 (12)	-0.0018 (9)	0.0079 (9)	0.0010 (10)
C6	0.0230 (11)	0.0178 (14)	0.0220 (15)	-0.0004 (11)	0.0057 (11)	0.0001 (11)
C7	0.0197 (11)	0.0182 (13)	0.0162 (14)	-0.0007 (10)	0.0040 (10)	-0.0011 (11)
C8	0.0214 (11)	0.0185 (14)	0.0211 (15)	-0.0003 (10)	0.0035 (11)	-0.0024 (11)
C9	0.0285 (13)	0.0185 (14)	0.0252 (15)	-0.0032 (12)	0.0063 (12)	0.0006 (12)
C10	0.0249 (12)	0.0238 (15)	0.0201 (15)	-0.0030 (11)	0.0075 (11)	0.0009 (12)
C11	0.0214 (11)	0.0191 (14)	0.0202 (14)	0.0002 (11)	0.0064 (11)	-0.0040 (11)
C12	0.0244 (12)	0.0172 (14)	0.0213 (15)	-0.0008 (11)	0.0043 (11)	0.0002 (11)
O13	0.0342 (11)	0.0182 (10)	0.0329 (13)	0.0024 (9)	0.0175 (9)	-0.0009 (9)
O14	0.0363 (10)	0.0186 (10)	0.0336 (12)	0.0014 (9)	0.0186 (9)	-0.0015 (9)
S2A	0.038 (3)	0.0164 (14)	0.0231 (13)	-0.0028 (16)	0.0076 (16)	0.0061 (9)
O11A	0.028 (3)	0.020 (3)	0.043 (8)	0.003 (3)	0.007 (5)	0.010 (5)
O12A	0.040 (4)	0.026 (3)	0.026 (4)	-0.010 (3)	0.009 (3)	-0.005 (3)
O13A	0.050 (3)	0.018 (2)	0.026 (3)	-0.004 (2)	0.021 (2)	0.0035 (18)
O14A	0.031 (2)	0.025 (2)	0.038 (3)	-0.0049 (18)	0.016 (2)	-0.0021 (19)
S2B	0.037 (3)	0.0182 (14)	0.0338 (15)	-0.0054 (16)	0.0117 (17)	-0.0075 (10)
O11B	0.051 (4)	0.030 (4)	0.035 (7)	-0.001 (3)	0.014 (5)	0.007 (5)
O12B	0.038 (4)	0.017 (3)	0.062 (7)	0.005 (3)	0.021 (5)	-0.011 (5)
O13B	0.030 (3)	0.025 (2)	0.036 (3)	0.0028 (19)	0.014 (2)	0.008 (2)
O14B	0.042 (3)	0.068 (4)	0.044 (3)	-0.018 (3)	0.012 (3)	-0.029 (3)

Geometric parameters (Å, °)

S1—C2	1.728 (3)	C9—H9	0.9500
S1—C1	1.794 (3)	C10—C11	1.399 (4)
C1—H1A	0.9800	C10—H10	0.9500
C1—H1B	0.9800	C11—O14	1.367 (3)
C1—H1C	0.9800	C11—C12	1.374 (3)
C2—N3	1.305 (3)	C12—H12	0.9500
C2—N4	1.332 (3)	O13—H13	0.78 (3)
N3—H3A	0.890 (18)	O14—H14	0.83 (4)
N3—H3B	0.861 (17)	S2A—O11A	1.435 (8)
N4—N5	1.374 (3)	S2A—O12A	1.452 (7)
N4—H4	0.86 (3)	S2A—O13A	1.453 (6)
N5—C6	1.285 (3)	S2A—O14A	1.564 (8)

C6—C7	1.449 (3)	O14A—H14A	0.8399
C6—H6	0.9500	S2B—O12B	1.437 (7)
C7—C12	1.395 (4)	S2B—O11B	1.439 (8)
C7—C8	1.401 (4)	S2B—O13B	1.467 (6)
C8—O13	1.362 (3)	S2B—O14B	1.549 (9)
C8—C9	1.388 (4)	O14B—H14B	0.8401
C9—C10	1.371 (4)		
C2—S1—C1	101.32 (13)	C10—C9—H9	119.5
S1—C1—H1A	109.5	C8—C9—H9	119.5
S1—C1—H1B	109.5	C9—C10—C11	120.1 (2)
H1A—C1—H1B	109.5	C9—C10—H10	120.0
S1—C1—H1C	109.5	C11—C10—H10	120.0
H1A—C1—H1C	109.5	O14—C11—C12	123.2 (3)
H1B—C1—H1C	109.5	O14—C11—C10	117.6 (2)
N3—C2—N4	119.2 (3)	C12—C11—C10	119.2 (2)
N3—C2—S1	124.2 (2)	C11—C12—C7	121.5 (3)
N4—C2—S1	116.7 (2)	C11—C12—H12	119.2
C2—N3—H3A	119.5 (19)	C7—C12—H12	119.2
C2—N3—H3B	123 (2)	C8—O13—H13	112 (2)
H3A—N3—H3B	118 (3)	C11—O14—H14	115 (2)
C2—N4—N5	118.6 (2)	O11A—S2A—O12A	113.5 (9)
C2—N4—H4	122 (2)	O11A—S2A—O13A	113.2 (7)
N5—N4—H4	118 (2)	O12A—S2A—O13A	109.8 (7)
C6—N5—N4	116.1 (2)	O11A—S2A—O14A	104.4 (10)
N5—C6—C7	121.3 (3)	O12A—S2A—O14A	107.9 (5)
N5—C6—H6	119.4	O13A—S2A—O14A	107.6 (5)
C7—C6—H6	119.4	S2A—O14A—H14A	126.1
C12—C7—C8	118.7 (2)	O12B—S2B—O11B	114.1 (9)
C12—C7—C6	118.3 (2)	O12B—S2B—O13B	114.0 (7)
C8—C7—C6	123.0 (2)	O11B—S2B—O13B	110.1 (9)
O13—C8—C9	117.1 (2)	O12B—S2B—O14B	104.2 (6)
O13—C8—C7	123.4 (2)	O11B—S2B—O14B	107.4 (11)
C9—C8—C7	119.5 (2)	O13B—S2B—O14B	106.2 (5)
C10—C9—C8	121.0 (3)	S2B—O14B—H14B	133.8
C1—S1—C2—N3	-4.6 (3)	C6—C7—C8—C9	179.5 (2)
C1—S1—C2—N4	175.8 (2)	O13—C8—C9—C10	179.7 (2)
N3—C2—N4—N5	-178.0 (2)	C7—C8—C9—C10	0.1 (4)
S1—C2—N4—N5	1.6 (3)	C8—C9—C10—C11	-0.4 (4)
C2—N4—N5—C6	178.8 (2)	C9—C10—C11—O14	-178.4 (2)
N4—N5—C6—C7	-179.8 (2)	C9—C10—C11—C12	0.3 (4)
N5—C6—C7—C12	-177.1 (2)	O14—C11—C12—C7	178.7 (2)
N5—C6—C7—C8	3.7 (4)	C10—C11—C12—C7	0.1 (4)
C12—C7—C8—O13	-179.3 (2)	C8—C7—C12—C11	-0.4 (4)
C6—C7—C8—O13	-0.1 (4)	C6—C7—C12—C11	-179.6 (2)
C12—C7—C8—C9	0.3 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C10—H10 \cdots O12 <i>A</i> ⁱ	0.95	2.60	3.541 (10)	170
N3—H3 <i>A</i> \cdots O12 <i>A</i> ⁱⁱ	0.89 (2)	1.85 (2)	2.738 (12)	178 (3)
N3—H3 <i>A</i> \cdots O12 <i>B</i> ⁱⁱ	0.89 (2)	1.98 (2)	2.841 (11)	163 (3)
N3—H3 <i>B</i> \cdots O14 ⁱⁱⁱ	0.86 (2)	2.05 (2)	2.874 (3)	160 (3)
N4—H4 \cdots O13 <i>A</i> ⁱⁱ	0.86 (3)	2.00 (3)	2.849 (5)	167 (3)
N4—H4 \cdots O13 <i>B</i> ⁱⁱ	0.86 (3)	2.00 (3)	2.841 (5)	164 (3)
O13—H13 \cdots N5	0.78 (3)	2.03 (3)	2.685 (3)	142 (3)
O14—H14 \cdots O11 <i>A</i> ^{iv}	0.83 (4)	1.90 (4)	2.716 (16)	167 (3)
O14—H14 \cdots O11 <i>B</i> ^{iv}	0.83 (4)	1.82 (4)	2.62 (2)	162 (3)
O14 <i>A</i> —H14 <i>A</i> \cdots O11 <i>A</i> ^{iv}	0.84	2.28	3.123 (17)	180
O14 <i>B</i> —H14 <i>B</i> \cdots S2 <i>B</i> ⁱⁱ	0.84	2.73	3.490 (9)	152
O14 <i>B</i> —H14 <i>B</i> \cdots O13 <i>B</i> ⁱⁱ	0.84	1.73	2.567 (7)	180

Symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $-x+2, -y+1, -z+1$; (iii) $x+3/2, -y+1/2, z-1/2$; (iv) $x-1, y, z$.