Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

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]

[a]Laboratoire de Chimie Inorganique et Environnement, Université de Tlemcen, BP 119, 13000 Tlemcen, Algeria, and [b]Centre de Diffractometrie X, UMR 6226 CNRS, Unit Sciences Chimiques de Rennes, Universite de Rennes I, 263 Avenue du General Leclerc, 35042 Rennes, France. *Correspondence e-mail: oussamanehar@gmail.com

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.

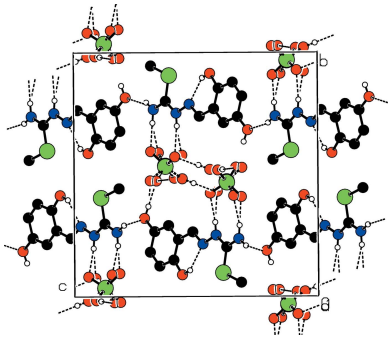
CCDC reference: 1960006

Supporting information: this article has supporting information at journals.iucr.org/e

The title molecular salt, $C_9H_{12}N_3O_2S^+\cdot HSO_4^-$, 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; Küçükgüzel *et al.*, 2006), anti-inflammatory (Palaska *et al.*, 2002) and antiumoural (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 $^+NH_2$ 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

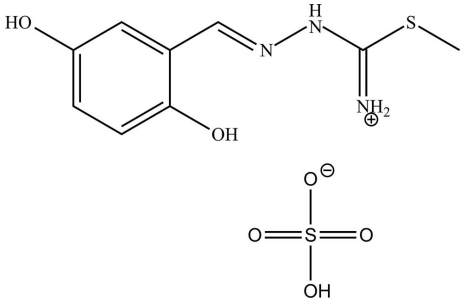
The molecular structure of the title molecular salt is illustrated in Fig. 1. It comprises two entities, *i.e.* a thiosemicarbazone cation and a hydrogen sulfate anion. The cation is essentially planar and shows an *E* conformation with regard to the C6—N5 bond, the maximum deviation from the mean plane 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···A	D—H	H···A	D···A	D—H···A
C10—H10···O12A^{i}	0.95	2.60	3.541 (10)	170
N3—H3A···O12A^{ii}	0.89 (2)	1.85 (2)	2.738 (12)	178 (3)
N3—H3A···O12B^{ii}	0.89 (2)	1.98 (2)	2.841 (11)	163 (3)
N3—H3B···O14^{iii}	0.86 (2)	2.05 (2)	2.874 (3)	160 (3)
N4—H4···O13A^{ii}	0.86 (3)	2.00 (3)	2.849 (5)	167 (3)
N4—H4···O13B^{ii}	0.86 (3)	2.00 (3)	2.841 (5)	164 (3)
O13—H13···N5	0.78 (3)	2.03 (3)	2.685 (3)	142 (3)
O14—H14···O11A^{iv}	0.83 (4)	1.90 (4)	2.716 (16)	167 (3)
O14—H14···O11B^{iv}	0.83 (4)	1.82 (4)	2.62 (2)	162 (3)
O14A—H14A···O11A^{iv}	0.84	2.28	3.123 (17)	180
O14B—H14B···S2B^{ii}	0.84	2.73	3.490 (9)	152
O14B—H14B···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···O and N—H···O hydrogen bonds. Also within this network exists a weak C—H···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; Boto-shansky *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 bond lengths and angles are similar to those of the title molecular salt.

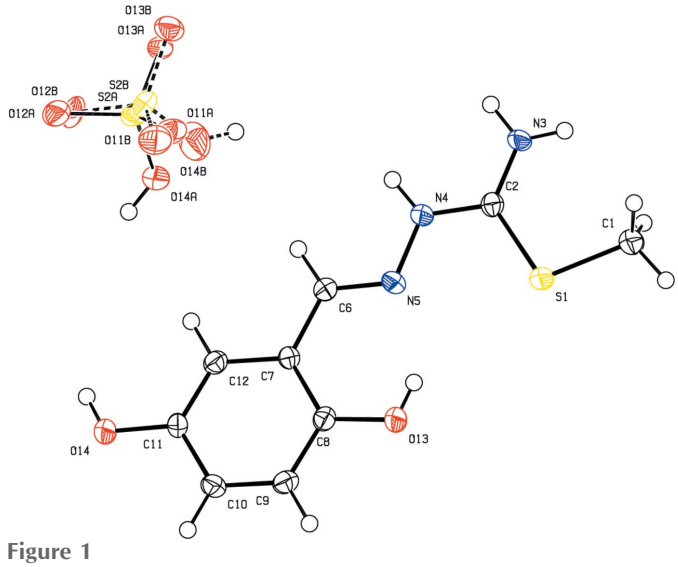


Figure 1
The molecular structure of the title molecular salt, showing the labelling and with displacement ellipsoids drawn at the 50% probability level. The disordered hydrogen sulfate anion is shown.

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.

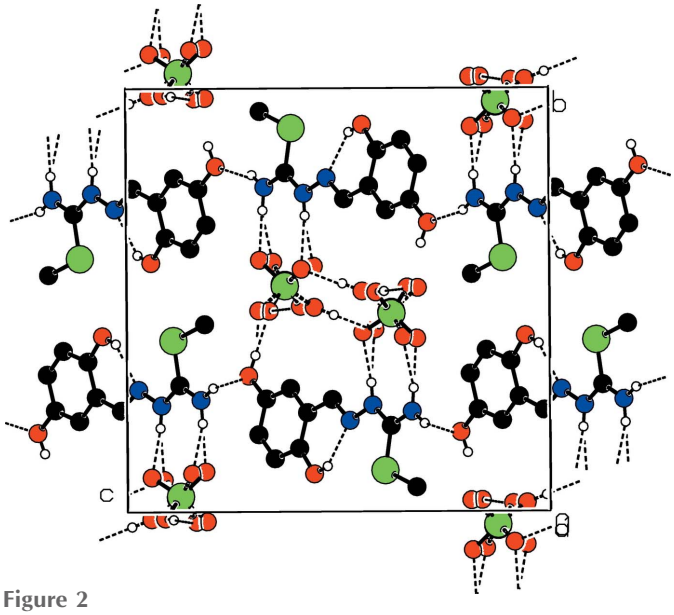


Figure 2
Projection along the *a* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines.

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_{iso}(H) = 1.5U_{eq}(C) and C—H = 0.98 Å for methyl H atoms, and U_{iso}(H) = 1.2U_{eq}(C,N) and C—H = 0.95 Å or N—H = 0.88 Å otherwise.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}N_3O_2S^+\cdot HSO_4^-$
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 (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.838, 0.948
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7962, 2846, 2014
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.46

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

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., Gerbeleu, 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.* E**71**, 305–308.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 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.* E**69**, o1469.
Joseph, M., Suni, V., Nayar, C. R., Kurup, M. R. P. & Fun, H.-K. (2004). *J. Mol. Struct.* **705**, 63–70.
Küçükgüzel, 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.* E**72**, 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, 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. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 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). E**75**, 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

$C_9H_{12}N_3O_2S^+\cdot HSO_4^-$
M_r = 323.34
Monoclinic, $P2_1/n$
a = 4.9411 (8) Å
b = 16.139 (2) Å
c = 16.426 (3) Å
β = 100.440 (7)°
V = 1288.2 (3) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.667 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2859 reflections
θ = 2.5–27.0°
μ = 0.44 mm^{-1}
T = 150 K
Prism, colourless
0.38 × 0.15 × 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_{int} = 0.045
θ_{max} = 27.3°, θ_{min} = 3.6°
h = −6→4
k = −19→20
l = −21→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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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, º)

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, º)

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