



The crystal structures of two novel polymorphs of bis(oxonium) ethane-1,2-disulfonate

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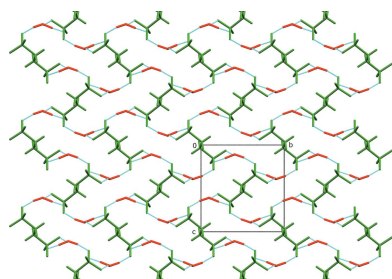
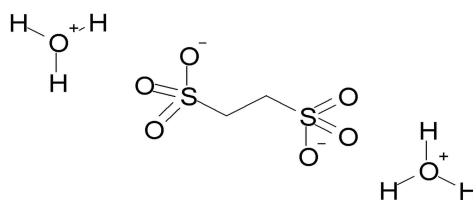
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Keywords: crystal structure; polymorphism; oxonium cation; sulfonate anions.**CCDC references:** 1956689; 1956690**Supporting information:** this article has supporting information at journals.iucr.org/e

Two novel crystal forms of bis(oxonium) ethane-1,2-disulfonate, $2\text{H}_3\text{O}^+ \cdot \text{C}_2\text{H}_4\text{O}_6\text{S}_2^{2-}$, are reported. Polymorph II has monoclinic ($P2_1/n$) symmetry, while the symmetry of form III is triclinic ($P\bar{1}$). Both structures display extensive networks of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. While this network in Form II is similar to that observed for the previously reported Form I [Mootz & Wunderlich (1970). *Acta Cryst. B* **26**, 1820–1825; Sartori *et al.* (1994). *Z. Naturforsch.* **49**, 1467–1472] and extends in all directions, in Form III it differs significantly, forming layers parallel to the *ab* plane. The sulfonate molecule in all three forms adopts a nearly identical geometry. The other observed differences between the forms, apart from the hydrogen-bonding network, are observed in the crystal density and packing index.

1. Chemical context

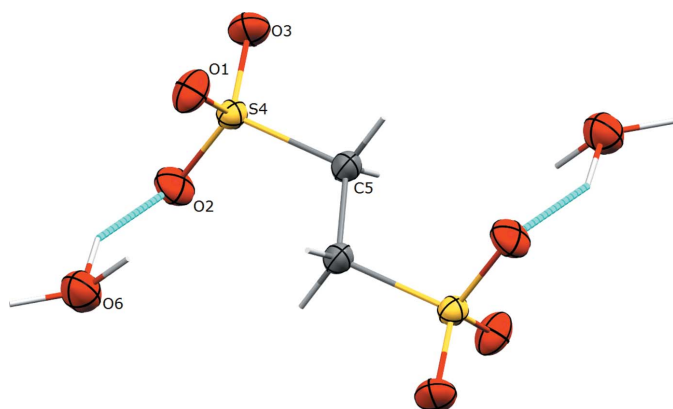
Sulfonic acids are commonly used in salt formation in the pharmaceutical industry, especially for poorly or non soluble in water drugs (Neau & Loka, 2018). Salts of ethane-1,2-disulfonic acid account for 0.38% of all the FDA-approved commercially marketed salts (Steele & Talbir, 2016) and therefore its toxicology, dosage (Saal & Becker, 2013) and various physico-chemical properties are widely studied (Black *et al.*, 2007; Elder *et al.*, 2010). In our laboratory, ethane-1,2-disulfonic acid is commonly used in the salt screening for increasing solubility as well as improving the crystallinity of various researched active pharmaceutical ingredients (APIs).



2. Structural commentary

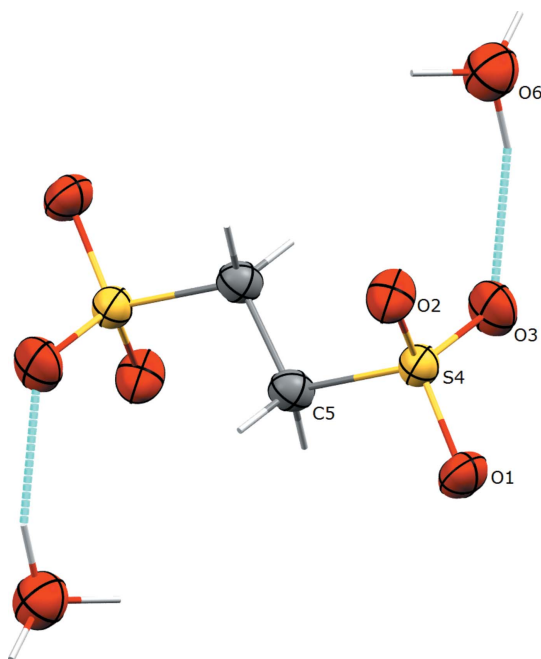
The sulfonate anion in all polymorphs, including the previously determined form (Mootz & Wunderlich, 1970, refcode HOEDSO; Sartori *et al.*, 1994, refcode HOEDSO01) has a nearly identical geometry. In all cases, the center of the C–C bond is located on an inversion center, and the C–S and C–O distances in all cases are within 3σ . The sulfonate group adopts the geometry of an open umbrella with the C–S–O bond angles of 106.51 (6), 105.82 (6), 107.23 (6)° for Form II (Fig. 1) and 106.16 (11), 106.21 (10), 107.20 (12)° for Form III




Figure 1

The molecular structure of an anion-cation pair of Form II, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown in turquoise. Unlabelled atoms are related to labelled ones by the symmetry operator $(-x + 1, -y + 1, -z + 1)$.

(Fig. 2). The values of all O–S–O angles are above 110° [$112.91(7)$, $111.48(7)$, $112.37(7)^\circ$ for Form II and $111.31(11)$, $113.45(11)$, $112.00(12)^\circ$ for Form III]. In this way, the molecular symmetry of the sulfonate group becomes slightly distorted C_{3v} . In all crystals, the oxonium cations have a pyramidal geometry with slightly elongated O–H distances for one H atom. This is most likely an effect of the fast exchange of a proton (H atom) between the sulfonate group and the water molecules.


Figure 2

The molecular structure of anion cation pair of Form III, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown in turquoise. Unlabelled atoms are related to labelled ones by the symmetry operator $(-x + 1, -y + 1, -z + 1)$.

Table 1

 Hydrogen-bond geometry (\AA , $^\circ$) for Form II.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6–H63 \cdots O2	0.99 (2)	2.62 (2)	3.1795 (17)	116 (2)
O6–H61 \cdots O2 ⁱ	1.00 (2)	2.02 (3)	2.9312 (16)	150 (3)
O6–H62 \cdots O3	1.06 (2)	1.92 (3)	2.9141 (16)	154 (3)
O6–H61 \cdots O3 ⁱⁱ	1.00 (2)	2.60 (3)	2.9857 (16)	103 (2)
O6–H63 \cdots O1 ⁱⁱⁱ	0.99 (2)	2.14 (2)	3.0266 (18)	148 (2)

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

Table 2

 Hydrogen-bond geometry (\AA , $^\circ$) for Form III.

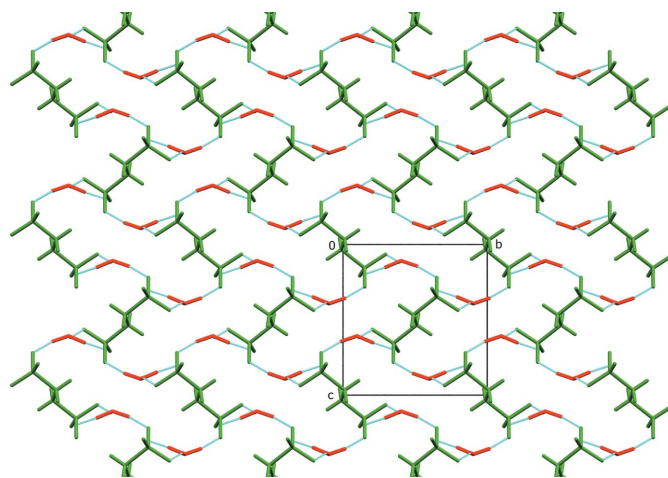
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6–H61 \cdots O1 ⁱ	1.07 (4)	1.93 (4)	2.991 (3)	170 (4)
O6–H62 \cdots O2 ⁱⁱ	1.02 (4)	2.52 (3)	3.002 (3)	108 (2)
O6–H62 \cdots O3	1.02 (4)	1.97 (4)	2.945 (3)	158 (3)
O6–H63 \cdots O1 ⁱⁱⁱ	1.02 (4)	1.89 (4)	2.899 (3)	173 (3)

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

The biggest differences between forms are observed in the density of the crystal, as well as in the packing coefficient (Kitajgorodskij, 1973). The lowest values of both parameters are attributed to Form III (1.60 g cm^{-3} and 0.67, respectively), which suggests that this polymorph is the least stable. Form II presented here has a slightly better packing index than previously reported for Form I (Mootz & Wunderlich, 1970; Sartori *et al.*, 1994) 0.75 *versus* 0.73. On the other hand, the density is lower: 1.78 *versus* 1.82 g cm^{-3} , respectively.

3. Supramolecular features

The hydrogen bonds between the oxonium cations and sulfonate anions in the crystal of Form II (Table 1, Fig. 3) extend in all directions forming a three-dimensional network similar to that observed for Form I (Mootz & Wunderlich, 1970; Sartori *et al.*, 1994). However, contrary to the previously


Figure 3

The crystal packing of Form II, viewed along the a axis. The ethane-1,2-disulfonate dianions are coloured in green, while oxonium cations are red and hydrogen bonds are shown in turquoise.

Table 3
Experimental details.

	Form II	Form III
Crystal data		
Chemical formula	$2\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_4\text{O}_6\text{S}_2^{2-}$	$2\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_4\text{O}_6\text{S}_2^{2-}$
M_r	226.22	226.22
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Temperature (K)	296	296
a, b, c (Å)	5.8050 (3), 8.3566 (6), 8.7433 (6)	5.0371 (3), 5.5424 (2), 8.8188 (4)
α, β, γ (°)	90, 95.148 (4), 90	98.426 (5), 104.511 (3), 91.663 (4)
V (Å ³)	422.43 (5)	235.22 (2)
Z	2	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.64	0.58
Crystal size (mm)	0.45 × 0.32 × 0.23	0.30 × 0.12 × 0.11
Data collection		
Diffractometer	Bruker KappaCCD	Bruker KappaCCD
Absorption correction	Gaussian integration (Coppens, 1970)	Gaussian integration (Coppens, 1970)
T_{\min}, T_{\max}	0.748, 0.907	0.813, 0.947
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17906, 1848, 1768	7504, 1708, 1192
R_{int}	0.075	0.131
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.806	0.758
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.121, 1.04	0.058, 0.163, 1.04
No. of reflections	1848	1708
No. of parameters	76	76
No. of restraints	3	0
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.62, -0.93	0.66, -0.67

Computer programs: COLLECT (Hooft, 1998), HKL SCALEPACK and DENZO (Otwinowski & Minor, 1997), SHELXT (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b), Mercury (Macrae *et al.*, 2008) and enCIFer (Allen *et al.*, 2004).

reported form, where the hydrogen-bond network is built from alternate anion–cations layers, in Form II such layers could not be distinguished. The supramolecular behaviour of Form III is significantly different. In this case (Table 2 and Fig. 4), the anion–cation hydrogen-bond network forms separate layers parallel to the ab plane built from sulfonate anions surrounded by oxonium cations with no interactions between the planes.

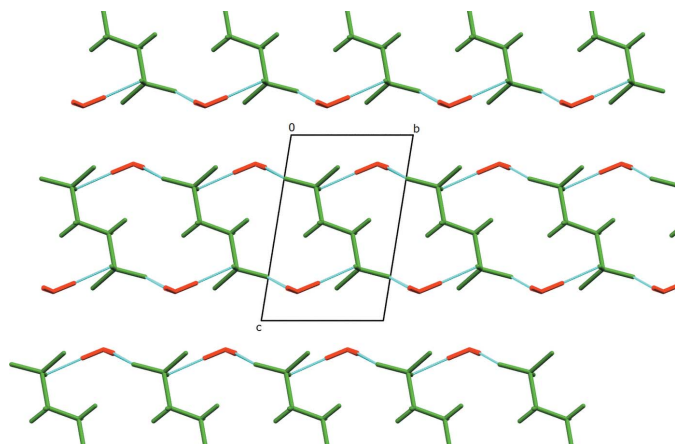


Figure 4
The crystal packing of Form III, viewed along the a axis. The ethane-1,2-disulfonate dianions are coloured in green, while oxonium cations are red and hydrogen bonds are shown in turquoise.

4. Database survey

As mentioned above, the crystal structure of a different polymorphic form of oxonium ethane-1,2-disulfonate has been previously reported (Mootz, & Wunderlich, 1970, refcode HOEDSO; Sartori *et al.*, 1994, refcode HOEDSO01). Apart from these structures, there are 12 hits for ethane-1,2-disulfonate salts in the Cambridge Structural Database (CSD, Version 5.40; ConQuest 2.02; Groom *et al.*, 2016), one of which is disordered. The geometry of the sulfonate group in all of the anions is nearly the same, with slightly distorted C_{3v} molecular symmetry for the open-umbrella geometry. The average values of the C–S–O and O–S–O bond angles are very close to those reported in this paper: 105.9 ± 0.8 and $112.8\pm 0.9^\circ$, respectively.

5. Synthesis and crystallization

Both crystals were obtained from an aqueous solution during unsuccessful salt formation with an unnamed free base (API) in water. Firstly, columnar crystals of Form III that appeared to be unstable were grown from the thick oil and within time transformed into prismatic crystals of Form II.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were found in

difference-Fourier maps and refined with isotropic displacement parameters. The DFIX 0.98 0.03 O6 H61, O6 H62 and O6 H63 instruction in *SHELXL2014/7* (Sheldrick, 2015b) was used to restrain the oxonium O—H distance in Form II. All of the oxonium H atoms in Form III were refined independently without any restraints.

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supporting information

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Computing details

For both structures, data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Bis(oxonium) ethane-1,2-disulfonate (I)

Crystal data



$$M_r = 226.22$$

Monoclinic, $P2_1/n$

$$a = 5.8050 (3) \text{ \AA}$$

$$b = 8.3566 (6) \text{ \AA}$$

$$c = 8.7433 (6) \text{ \AA}$$

$$\beta = 95.148 (4)^\circ$$

$$V = 422.43 (5) \text{ \AA}^3$$

$$Z = 2$$

$$F(000) = 236$$

$$D_x = 1.778 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 11538 reflections

$$\theta = 1.0\text{--}35.0^\circ$$

$$\mu = 0.64 \text{ mm}^{-1}$$

$$T = 296 \text{ K}$$

Prism, pale yellow

$$0.45 \times 0.32 \times 0.23 \text{ mm}$$

Data collection

Bruker KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal
monochromator

Detector resolution: 9 pixels mm^{-1}

CCD scans

Absorption correction: integration

Gaussian integration (Coppens, 1970)

$$T_{\min} = 0.748, T_{\max} = 0.907$$

17906 measured reflections

1848 independent reflections

1768 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.075$$

$$\theta_{\max} = 34.9^\circ, \theta_{\min} = 3.4^\circ$$

$$h = -9 \rightarrow 9$$

$$k = -13 \rightarrow 13$$

$$l = -14 \rightarrow 14$$

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.041$$

$$wR(F^2) = 0.121$$

$$S = 1.04$$

1848 reflections

76 parameters

3 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.1864P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.026$$

$$\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.93 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2014/7
(Sheldrick 2015b),
 $Fc^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.20 (2)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.03777 (17)	0.61584 (15)	0.29236 (14)	0.0319 (2)
O2	0.4298 (2)	0.65073 (13)	0.21941 (13)	0.0302 (2)
O3	0.30307 (19)	0.79554 (12)	0.43552 (13)	0.0308 (2)
S4	0.27802 (4)	0.64978 (3)	0.34467 (3)	0.01890 (13)
C5	0.3753 (2)	0.48838 (15)	0.46678 (14)	0.0231 (2)
H5A	0.270 (5)	0.476 (3)	0.541 (3)	0.043 (6)*
H5B	0.360 (4)	0.393 (3)	0.404 (2)	0.025 (5)*
O6	0.7708 (2)	0.90258 (15)	0.39286 (16)	0.0363 (3)
H61	0.822 (6)	1.009 (3)	0.357 (4)	0.066 (9)*
H62	0.588 (4)	0.889 (4)	0.383 (4)	0.067 (9)*
H63	0.797 (4)	0.795 (3)	0.350 (3)	0.041 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0219 (4)	0.0345 (5)	0.0373 (5)	-0.0002 (3)	-0.0079 (4)	0.0012 (4)
O2	0.0341 (5)	0.0339 (5)	0.0238 (4)	0.0083 (4)	0.0096 (4)	0.0055 (3)
O3	0.0333 (5)	0.0227 (4)	0.0362 (5)	0.0020 (3)	0.0025 (4)	-0.0081 (4)
S4	0.01863 (17)	0.01917 (17)	0.01865 (17)	0.00184 (7)	0.00025 (10)	0.00054 (7)
C5	0.0218 (4)	0.0231 (5)	0.0234 (5)	-0.0027 (3)	-0.0032 (3)	0.0061 (4)
O6	0.0307 (5)	0.0320 (5)	0.0452 (6)	-0.0022 (4)	-0.0012 (4)	0.0000 (5)

Geometric parameters (\AA , $^\circ$)

O1—S4	1.4561 (10)	C5—H5A	0.94 (3)
O2—S4	1.4658 (11)	C5—H5B	0.97 (2)
O3—S4	1.4544 (10)	O6—H61	1.00 (2)
S4—C5	1.7804 (11)	O6—H62	1.06 (2)
C5—C5 ⁱ	1.523 (2)	O6—H63	0.99 (2)
O3—S4—O1	112.37 (7)	S4—C5—H5A	108.0 (16)
O3—S4—O2	111.48 (7)	C5 ⁱ —C5—H5B	110.7 (12)
O1—S4—O2	112.91 (7)	S4—C5—H5B	106.3 (12)
O3—S4—C5	107.23 (6)	H5A—C5—H5B	105 (2)
O1—S4—C5	106.51 (6)	H61—O6—H62	113 (3)

O2—S4—C5	105.82 (6)	H61—O6—H63	129 (2)
C5 ⁱ —C5—S4	111.82 (11)	H62—O6—H63	93 (2)
C5 ⁱ —C5—H5A	114.1 (17)		
O3—S4—C5—C5 ⁱ	−57.98 (14)	O2—S4—C5—C5 ⁱ	61.12 (14)
O1—S4—C5—C5 ⁱ	−178.48 (12)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

<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>
O6—H63 \cdots O2	0.99 (2)	2.62 (2)	3.1795 (17)	116 (2)
O6—H61 \cdots O2 ⁱⁱ	1.00 (2)	2.02 (3)	2.9312 (16)	150 (3)
O6—H62 \cdots O3	1.06 (2)	1.92 (3)	2.9141 (16)	154 (3)
O6—H61 \cdots O3 ⁱⁱⁱ	1.00 (2)	2.60 (3)	2.9857 (16)	103 (2)
O6—H63 \cdots O1 ^{iv}	0.99 (2)	2.14 (2)	3.0266 (18)	148 (2)

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

Bis(oxonium) ethane-1,2-disulfonate (II)

Crystal data



$M_r = 226.22$

Triclinic, $P\bar{1}$

$a = 5.0371$ (3) \AA

$b = 5.5424$ (2) \AA

$c = 8.8188$ (4) \AA

$\alpha = 98.426$ (5) $^\circ$

$\beta = 104.511$ (3) $^\circ$

$\gamma = 91.663$ (4) $^\circ$

$V = 235.22$ (2) \AA^3

$Z = 1$

$F(000) = 118$

$D_x = 1.597$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 4728 reflections

$\theta = 1.0\text{--}32.6^\circ$

$\mu = 0.57$ mm^{-1}

$T = 296$ K

Columnar, colorless

$0.30 \times 0.12 \times 0.11$ mm

Data collection

Bruker KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal

monochromator

Detector resolution: 9 pixels mm^{-1}

CCD scans

Absorption correction: integration

Gaussian integration (Coppens, 1970)

$T_{\min} = 0.813$, $T_{\max} = 0.947$

7504 measured reflections

1708 independent reflections

1192 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.131$

$\theta_{\max} = 32.6^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -7 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -11 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.163$

$S = 1.04$

1708 reflections

76 parameters

0 restraints

Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 0.0186P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.016$$

$$\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2014/7
(Sheldrick 2015b),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.19 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.6030 (4)	0.9888 (3)	0.7642 (2)	0.0387 (4)
O2	0.6622 (4)	0.5760 (3)	0.8252 (2)	0.0378 (4)
O3	0.2119 (4)	0.6995 (4)	0.7086 (3)	0.0417 (5)
S4	0.50463 (11)	0.73087 (9)	0.72171 (6)	0.0267 (2)
C5	0.5533 (5)	0.6324 (4)	0.5302 (3)	0.0290 (5)
H5A	0.473 (7)	0.750 (6)	0.459 (4)	0.043 (8)*
H5B	0.737 (7)	0.654 (6)	0.526 (4)	0.054 (9)*
O6	0.1360 (5)	0.2554 (4)	0.8443 (3)	0.0477 (5)
H61	0.318 (10)	0.173 (8)	0.827 (5)	0.083 (13)*
H62	0.113 (7)	0.415 (6)	0.798 (5)	0.049 (9)*
H63	-0.056 (8)	0.173 (6)	0.822 (5)	0.057 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0405 (11)	0.0264 (8)	0.0464 (10)	-0.0019 (7)	0.0115 (8)	-0.0030 (7)
O2	0.0425 (11)	0.0396 (9)	0.0301 (8)	0.0109 (8)	0.0059 (7)	0.0062 (7)
O3	0.0235 (9)	0.0476 (10)	0.0538 (11)	0.0009 (7)	0.0125 (8)	0.0028 (8)
S4	0.0229 (3)	0.0261 (3)	0.0297 (3)	0.0012 (2)	0.0060 (2)	0.0014 (2)
C5	0.0289 (12)	0.0297 (11)	0.0271 (10)	-0.0025 (9)	0.0059 (9)	0.0034 (8)
O6	0.0415 (13)	0.0454 (11)	0.0535 (12)	0.0046 (9)	0.0092 (10)	0.0046 (9)

Geometric parameters (\AA , $^\circ$)

O1—S4	1.4625 (17)	C5—H5A	0.99 (3)
O2—S4	1.4509 (18)	C5—H5B	0.94 (4)
O3—S4	1.4532 (19)	O6—H61	1.07 (4)
S4—C5	1.777 (2)	O6—H62	1.02 (4)
C5—C5 ⁱ	1.519 (4)	O6—H63	1.02 (4)
O2—S4—O3	112.00 (12)	S4—C5—H5A	109.0 (18)
O2—S4—O1	113.45 (11)	C5 ⁱ —C5—H5B	110 (2)
O3—S4—O1	111.31 (11)	S4—C5—H5B	113 (2)
O2—S4—C5	106.21 (10)	H5A—C5—H5B	98 (3)
O3—S4—C5	107.20 (12)	H61—O6—H62	111 (3)

O1—S4—C5	106.16 (11)	H61—O6—H63	127 (3)
C5 ⁱ —C5—S4	111.0 (2)	H62—O6—H63	107 (3)
C5 ⁱ —C5—H5A	114.8 (19)		
O2—S4—C5—C5 ⁱ	61.3 (3)	O1—S4—C5—C5 ⁱ	-177.6 (2)
O3—S4—C5—C5 ⁱ	-58.6 (3)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O6—H61...O1 ⁱⁱ	1.07 (4)	1.93 (4)	2.991 (3)	170 (4)
O6—H62...O2 ⁱⁱⁱ	1.02 (4)	2.52 (3)	3.002 (3)	108 (2)
O6—H62...O3	1.02 (4)	1.97 (4)	2.945 (3)	158 (3)
O6—H63...O1 ^{iv}	1.02 (4)	1.89 (4)	2.899 (3)	173 (3)

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