Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of ethylenedioxytetrathiafulvalene-4,5-bis(thiolbenzoic acid) 0.25-hydrate

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Received 30 June 2017
Accepted 27 July 2017

Edited by H. Ishida, Okayama University, Japan

Keywords: crystal structure; TTF derivative; thiolbenzoate.

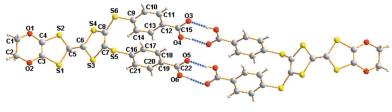
CCDC reference: 1548509

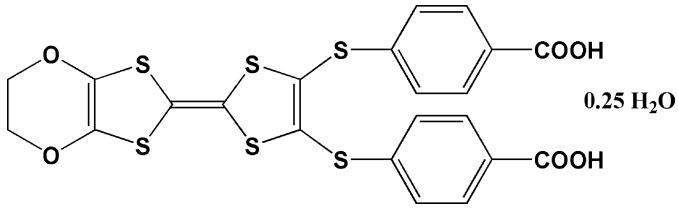
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound (systematic name: 4,4′-{[2-(5,6-dihydro-[1,3]dithiolo-[4,5-*b*][1,4]dioxin-2-ylidene)-1,3-dithiole-4,5-diyl]bis(sulfanediyl)}dibenzoic acid 0.25-hydrate), $C_{22}H_{14}O_6S_6\cdot0.25H_2O$, the tetrathiafulvalene (TTF) core adopts a boat conformation, where the central $S_2C{=}CS_2$ plane makes dihedral angles of 31.34 (4) and 26.83 (6)°, respectively, with the peripheral $S_2C{=}CS_2$ and $S_2C_2O_2$ planes. In the crystal, the benzoic acid molecules are linked *via* O—H···O hydrogen bonds, forming inversion dimers with $R_2^2(8)$ motifs. The dimers are linked through weak C—H···O hydrogen bonds into a chain structure along [$\bar{1}$01]. The chains stack along the *a* axis through S···S and S···C short contacts, forming layers parallel to the *ac* plane.

1. Chemical context

Tetrathiafulvalene (TTF) and its derivatives have received much attention in recent years due to their unique electrical properties and synthetic versatility (Canvert *et al.*, 2009; Xiao *et al.*, 2012). Among them, bis(ethylenedioxy)-TTF (BEDO-TTF) derivatives have afforded two-dimensional stable metallic CT complexes resulting from its self-assembling nature in partially oxidized states (Horiuchi *et al.*, 1996). Ethylenedioxy-TTF (EDO-TTF) is a noted electron-donor molecule, and $(EDO\text{-}TTF)_2PF_6$ shows a metal–insulator thermal transition at near room temperature (Ota *et al.*, 2002). There are also many reports that peripheral arylation of TTF could afford photochemically active organic materials. Recently, Shao's group reported a method to introduce aryls to TTF through the sulfur atom (Sun *et al.*, 2013; Zhang *et al.*, 2015). Our group has also reported a donor molecule, EDO-TTF-pyridine (Xiao *et al.*, 2012). To obtain more insight into this system, we report here the synthesis and crystal structure of the title compound.





2. Structural commentary

The asymmetric unit of the title compound contains one benzoic acid molecule and a quarter molecule of solvent water

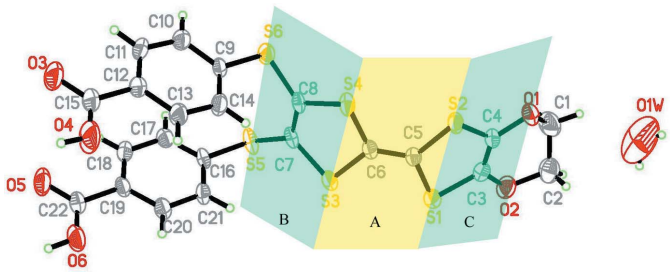


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. *A*, *B* and *C* indicate mean planes defined by six atoms.

(Fig. 1). The TTF core adopts a boat conformation, as usually observed in neutral TTF derivatives. The central plane *A* (S1/S2/C5/C6/S3/S4) and the adjacent planes *B* (S3/S4/C7/C8/S5/S6) and *C* (S1/S2/C3/C4/O1/O2) are almost planar with r.m.s. deviations of 0.0233, 0.0274 and 0.0105 Å, respectively. The dihedral angles between planes *A* and *B* and *A* and *C* are 31.24 (4) and 26.83 (6)°, respectively. Plane *B* makes dihedral angles of 85.88 (11) and 82.03 (15)°, respectively, with the benzene C9–C14 and C16–C21 rings. These benzene rings are approximately parallel, subtending a dihedral angle of 11.82 (14)°. All bond lengths and angles in the TTF fragment are within the range of the values for a neutral TTF molecule (Zhang *et al.*, 2015).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O5^{i}	0.86 (2)	1.78 (2)	2.629 (3)	165 (5)
O6—H6···O3^{i}	0.84 (2)	1.78 (2)	2.624 (3)	177 (4)
O1*W*—H1*WA*···O5^{ii}	0.85	2.38	3.18 (2)	155
O1*W*—H1*WB*···O3^{ii}	0.85	2.37	3.17 (2)	158
C13—H13*A*···O2^{iii}	0.93	2.67	3.570 (4)	163
C20—H20*A*···O1^{iii}	0.93	2.65	3.552 (4)	164

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

3. Supramolecular features

In the crystal, pairs of inversion-related benzoic acid molecules are linked by O—H···O hydrogen bonds between carboxyl groups (Table 1), forming $R_2^2(8)$ hydrogen-bond motifs (Fig. 2). The water molecule links two carboxyl groups in the benzoic acid molecule through O—H···O hydrogen bonds. The dimers are linked by weak C—H···O hydrogen bonds into a chain structure running along [$\bar{1}$01]. The chains stack along the *a* axis *via* S···S and S···C interactions [S4···S5^{iv} = 3.420 (5) Å and S1···C20^{v} = 3.456 (5) Å; symmetry codes: (iv) $x-1, y, z$; (v) $-x+1, -y, -z+1$], forming a layer parallel to the *ac* plane (Fig. 3).

4. Database survey

The crystal structure of 3′,4′-ethylenedioxotetrathiafulvolenyl-3-carboxylic acid (EDO-TTF-COOH) reported by Mézière *et*

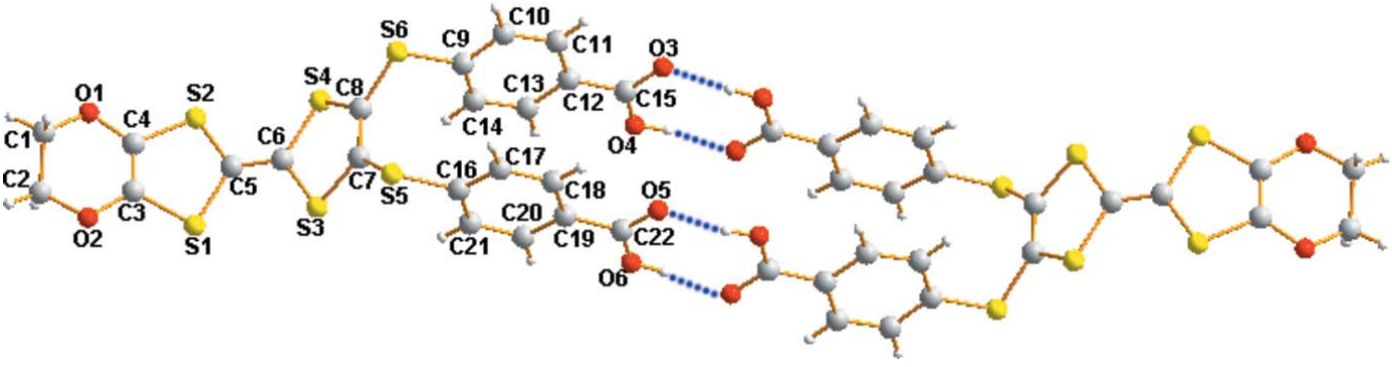


Figure 2
A view of the inversion dimer of the title compound with two $R_2^2(8)$ hydrogen-bond motifs. O—H···O hydrogen bonds are shown as dotted lines.

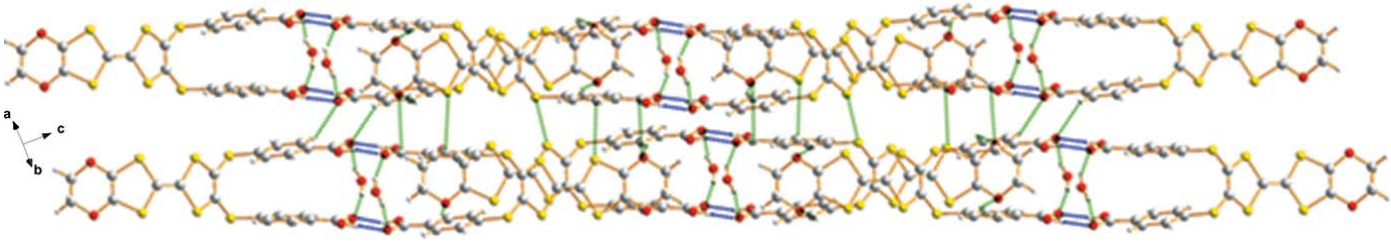


Figure 3
A view of the crystal packing of the title compound, showing O—H···O and C—H···O hydrogen bonds, and S···S and S···C interactions.

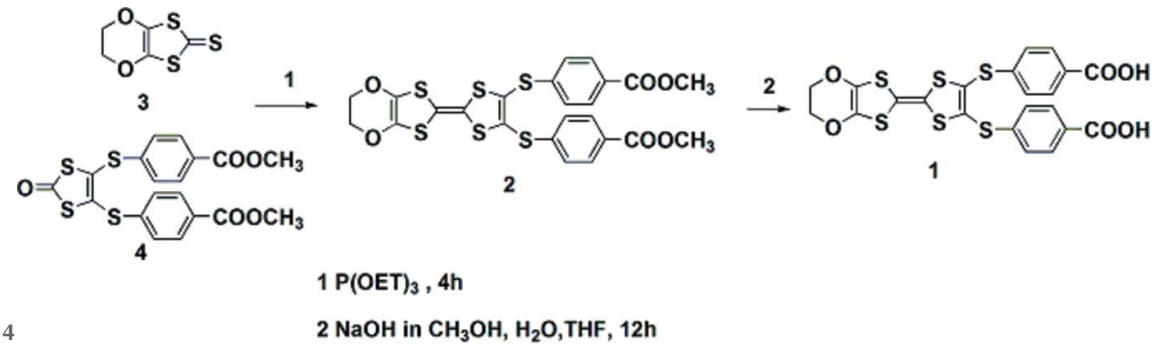


Figure 4
Synthesis of the title compound.

al. (2000) has a similar structure to the title compound. Both structures include O—H···O hydrogen bonds between carboxyl groups with R_2^2 (8) ring motifs.

5. Synthesis and crystallization

The title compound was prepared according to the reaction scheme shown in Fig. 4. 4,5-Ethylenedioy-1,3-dithiole-2-thione, **3**, (systematic name: 5,6-dihydro-[1,3]dithiolo[4,5-*b*]-[1,4]dioxine-2-thione) and 4,5-bis(thiolmethylbenzoate)-1,3-dithiole-2-thion, **4**, [systematic name: dimethyl 4,4′-(2-oxo-1,3-dithiole-4,5-diyl)bis(sufanediyl)dibenzoate] were synthesized by the literature method (Sun *et al.*, 2013). Compound **2** was prepared from compounds **3** and **4** using a standard phosphite-mediated coupling procedure as follows:

Compounds **3** (193 mg 0.1 mmol) and **4** (465 mg 0.1 mmol) were mixed in triethylphosphite (5 ml) and heated at 393 K for 6 h. $P(OEt)_3$ was then removed under reduced pressure and the red residue was purified by column chromatography on silica gel (DCM) to give 310 mg of a red powder of **2** (yield = 53%). ^{1}H NMR [$CDCl_3$, δ (ppm), J (Hz)]: 8.01 (*d*, 4H, J = 8.5), 7.41 (*d*, 4H, J = 8.5), 4.28 (*s*, 4H), 3.94 (*s*, 6H).

Finally, compound **1** was obtained by hydrolysis reaction of compound **2**: A 50 ml flask was charged with compound **2** (260 mg, 0.50 mmol) under an N_2 atmosphere. Degassed methanol (6 ml) and THF (6 ml) were added to generate a suspension. In a separate flask, sodium hydroxide (230 mg, 5.8 mmol) was dissolved in degassed water (4 ml). The sodium hydroxide solution was added to compound **2** and the reaction was heated to reflux for 8 h. The reaction was then cooled to room temperature and the volatiles were removed *in vacuo*. Hydrochloric acid (1 mol l^{-1}, 15 ml) was added to afford a maroon precipitate, which was collected by filtration and washed with water (50 ml). The product was collected and dried under high vacuum for 12 h to afford **1** as a maroon solid (179 mg, 0.35 mmol, 70% yield). ^{1}H NMR [DMSO-d_6, δ (ppm), J (Hz)]: 8.02 (*d*, 4H, J = 8.6),7.43 (*d*, 4H, J = 8.6), 4.28 (*s*, 4H). Elemental analysis calculated for $C_{22}H_{14}O_6S_6$: C 46.62, H 2.49%; found: C 46.67, H 2.51%. Red crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethyl acetate solution of the title compound. Elemental analysis calculated for $C_{22}H_{14}O_6S_6{\cdot}0.25H_2O$: C 46.26, H 2.56%; found: C 46.29, H 2.58%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carboxyl H atoms were located in a difference-Fourier map and refined with O—H = 0.85 (2) Å, and with U_{iso}(H) = 1.2U_{eq}(O). H atoms bonded to C and O(water) atoms were positioned geometrically and included in the refinement in the riding-model approximation (C—H = 0.93 or 0.97 Å, and O—H = 0.85 Å) with U_{iso}(H) = 1.2U_{eq}(C or O). In the refinement, the occupancy of the lattice water molecule was fixed at 0.25, which was estimated from the results of element analysis and gave acceptable displacement parameters for the water O atom.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{14}O_6S_6{\cdot}0.25H_2O$
M_r	571.19
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	7.6995 (6), 9.2634 (8), 17.9198 (14)
α, β, γ (°)	90.970 (4), 92.039 (4), 110.902 (4)
V (Å^3)	1192.64 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.61
Crystal size (mm)	0.32 × 0.22 × 0.16
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.85, 0.91
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40263, 5496, 4411
R_{int}	0.066
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.119, 1.08
No. of reflections	5496
No. of parameters	322
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.27

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

Funding information

This work was supported by Zhejiang Province Planted Talent Plan, Ningbo Natural Science Foundation 2017 A610013.

References

Bruker (2014). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Canvert, D., Sallé, M., Zhang, G. & Zhang, D. (2009). *Chem. Commun.* pp. 2245–2269.
Horiuchi, S., Yamochi, H., Saito, G., Sakaguchi, K. & Kusunoki, M. (1996). *J. Am. Chem. Soc.* **118**, 8604–8622.
Mézière, C., Fourmigué, M. & Fabre, J.-M. (2000). *C. R. Acad. Sci. Ser. IIc Chim.* **3**, 387–395.
Ota, A., Yamochi, H. & Saito, G. (2002). *J. Mater. Chem.* **12**, 2600–2602.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Sun, J., Lu, X., Shao, J., Cui, Z., Shao, Y., Jiang, G., Yu, W. & Shao, X. (2013). *RSC Adv.* **3**, 10193–10196.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Xiao, X., Wang, G., Shen, L., Fang, J. & Gao, H. (2012). *Synth. Met.* **162**, 900–903.
Zhang, X., Lu, X., Sun, J., Zhao, Y. & Shao, X. (2015). *CrystEngComm*, **17**, 4110–4116.

supporting information

Acta Cryst. (2017). E**73**, 1275-1278 [https://doi.org/10.1107/S2056989017011070]

Crystal structure of ethylenedioxytetrathiafulvalene-4,5-bis(thiolbenzoic acid) 0.25-hydrate

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT-Plus* (Bruker, 2014); data reduction: *SAINT-Plus* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

4,4′-{[2-(5,6-Dihydro-[1,3]dithiolo[4,5-*b*][1,4]dioxin-2-ylidene)-1,3-dithiole-4,5-diyl]bis(sulfanediyl)}dibenzoic acid 0.25-hydrate

Crystal data

$C_{22}H_{14}O_6S_6 \cdot 0.25H_2O$
$M_r = 571.19$
Triclinic, $P\overline{1}$
$a = 7.6995$ (6) Å
$b = 9.2634$ (8) Å
$c = 17.9198$ (14) Å
$\alpha = 90.970$ (4)°
$\beta = 92.039$ (4)°
$\gamma = 110.902$ (4)°
$V = 1192.64$ (17) Å^3
$Z = 2$
$F(000) = 585$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9956 reflections
$\theta = 2.6$–27.6°
$\mu = 0.61$ mm^{-1}
$T = 296$ K
Block, red
0.32 × 0.22 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.85$, $T_{max} = 0.91$
40263 measured reflections
5496 independent reflections
4411 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.6°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.08$
5496 reflections
322 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.3142P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ 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}	Occ. (<1)
S1	0.11044 (11)	0.09238 (9)	0.66738 (4)	0.04393 (19)	
S2	−0.09625 (9)	0.29064 (8)	0.61324 (4)	0.03501 (16)	
S3	0.32187 (10)	0.13385 (8)	0.51255 (4)	0.03623 (17)	
S4	0.12080 (9)	0.32989 (8)	0.45679 (4)	0.03457 (16)	
S5	0.66618 (9)	0.29700 (9)	0.42971 (4)	0.04079 (19)	
S6	0.42943 (10)	0.51964 (8)	0.36264 (4)	0.03834 (17)	
O1	−0.1244 (3)	0.3703 (2)	0.75549 (11)	0.0433 (5)	
O1W	−0.114 (3)	0.387 (2)	1.0200 (8)	0.189 (11)	0.25
H1WA	−0.1141	0.2992	1.0328	0.227*	0.25
H1WB	−0.2242	0.3865	1.0236	0.227*	0.25
O2	0.0741 (3)	0.1748 (3)	0.80773 (11)	0.0470 (5)	
O3	0.4480 (5)	0.2974 (3)	0.00584 (14)	0.0900 (11)	
O4	0.2328 (5)	0.0854 (3)	0.04444 (14)	0.0863 (10)	
H4	0.222 (7)	0.048 (5)	−0.0006 (14)	0.104*	
O5	0.7607 (4)	0.0500 (3)	0.08500 (12)	0.0664 (7)	
O6	0.5255 (4)	−0.1560 (3)	0.11897 (12)	0.0575 (6)	
H6	0.539 (5)	−0.200 (4)	0.0790 (14)	0.069*	
C1	−0.0452 (6)	0.3816 (4)	0.83013 (18)	0.0591 (9)	
H1A	−0.1185	0.4167	0.8640	0.071*	
H1B	0.0800	0.4579	0.8322	0.071*	
C2	−0.0387 (6)	0.2316 (4)	0.85521 (18)	0.0599 (9)	
H2A	0.0124	0.2441	0.9062	0.072*	
H2B	−0.1642	0.1559	0.8547	0.072*	
C3	0.0365 (4)	0.1960 (3)	0.73426 (15)	0.0362 (6)	
C4	−0.0543 (4)	0.2847 (3)	0.71027 (14)	0.0335 (6)	
C5	0.0641 (3)	0.1999 (3)	0.59408 (14)	0.0318 (5)	
C6	0.1508 (3)	0.2153 (3)	0.52984 (14)	0.0291 (5)	
C7	0.4361 (3)	0.2753 (3)	0.44870 (13)	0.0295 (5)	
C8	0.3442 (3)	0.3653 (3)	0.42336 (13)	0.0291 (5)	
C9	0.3906 (3)	0.4271 (3)	0.27335 (13)	0.0290 (5)	
C10	0.4906 (4)	0.5139 (3)	0.21609 (15)	0.0415 (7)	
H10A	0.5698	0.6155	0.2256	0.050*	
C11	0.4719 (5)	0.4482 (3)	0.14444 (16)	0.0472 (7)	
H11A	0.5394	0.5058	0.1062	0.057*	
C12	0.3526 (4)	0.2970 (3)	0.13006 (15)	0.0394 (6)	
C13	0.2478 (4)	0.2132 (3)	0.18680 (15)	0.0412 (7)	
H13A	0.1639	0.1134	0.1767	0.049*	
C14	0.2677 (4)	0.2776 (3)	0.25845 (14)	0.0375 (6)	
H14A	0.1986	0.2204	0.2965	0.045*	

C15	0.3430 (5)	0.2226 (4)	0.05515 (16)	0.0514 (8)
C16	0.6443 (3)	0.2013 (3)	0.34120 (13)	0.0296 (5)
C17	0.7745 (4)	0.2746 (3)	0.28949 (15)	0.0387 (6)
H17A	0.8628	0.3721	0.3008	0.046*
C18	0.7729 (4)	0.2022 (3)	0.22095 (16)	0.0419 (7)
H18A	0.8597	0.2515	0.1862	0.050*
C19	0.6421 (4)	0.0565 (3)	0.20418 (14)	0.0330 (5)
C20	0.5125 (4)	−0.0176 (3)	0.25668 (15)	0.0354 (6)
H20A	0.4252	−0.1158	0.2458	0.042*
C21	0.5142 (3)	0.0553 (3)	0.32484 (14)	0.0340 (6)
H21A	0.4278	0.0061	0.3598	0.041*
C22	0.6426 (4)	−0.0211 (3)	0.13115 (15)	0.0407 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0568 (4)	0.0448 (4)	0.0426 (4)	0.0312 (4)	0.0196 (3)	0.0122 (3)
S2	0.0351 (3)	0.0449 (4)	0.0316 (3)	0.0212 (3)	0.0112 (3)	0.0041 (3)
S3	0.0419 (4)	0.0402 (4)	0.0346 (3)	0.0238 (3)	0.0106 (3)	−0.0010 (3)
S4	0.0305 (3)	0.0527 (4)	0.0268 (3)	0.0221 (3)	0.0060 (2)	0.0005 (3)
S5	0.0269 (3)	0.0621 (5)	0.0336 (4)	0.0172 (3)	0.0012 (3)	−0.0215 (3)
S6	0.0484 (4)	0.0341 (3)	0.0279 (3)	0.0087 (3)	0.0086 (3)	−0.0067 (3)
O1	0.0529 (12)	0.0482 (12)	0.0359 (10)	0.0260 (10)	0.0124 (9)	−0.0025 (9)
O1W	0.25 (2)	0.169 (18)	0.059 (9)	−0.035 (16)	0.038 (12)	−0.041 (10)
O2	0.0530 (12)	0.0575 (13)	0.0358 (11)	0.0253 (10)	0.0093 (9)	0.0118 (9)
O3	0.165 (3)	0.0509 (15)	0.0402 (13)	0.0183 (17)	0.0469 (17)	−0.0017 (11)
O4	0.134 (3)	0.0605 (16)	0.0378 (14)	0.0012 (16)	0.0300 (15)	−0.0190 (12)
O5	0.0908 (18)	0.0584 (14)	0.0373 (12)	0.0089 (13)	0.0296 (12)	−0.0078 (10)
O6	0.0739 (16)	0.0509 (13)	0.0378 (12)	0.0099 (12)	0.0164 (11)	−0.0167 (10)
C1	0.079 (2)	0.062 (2)	0.0426 (18)	0.0330 (19)	0.0057 (16)	−0.0096 (15)
C2	0.080 (2)	0.070 (2)	0.0342 (16)	0.031 (2)	0.0124 (16)	0.0041 (15)
C3	0.0368 (14)	0.0379 (14)	0.0349 (14)	0.0133 (11)	0.0098 (11)	0.0064 (11)
C4	0.0340 (13)	0.0358 (13)	0.0325 (13)	0.0136 (11)	0.0119 (10)	0.0013 (11)
C5	0.0299 (12)	0.0326 (13)	0.0347 (13)	0.0126 (10)	0.0096 (10)	0.0013 (10)
C6	0.0269 (11)	0.0324 (13)	0.0293 (12)	0.0119 (10)	0.0048 (9)	−0.0027 (10)
C7	0.0245 (11)	0.0384 (13)	0.0262 (12)	0.0125 (10)	0.0030 (9)	−0.0115 (10)
C8	0.0293 (12)	0.0380 (13)	0.0196 (11)	0.0118 (10)	0.0043 (9)	−0.0084 (9)
C9	0.0338 (12)	0.0339 (13)	0.0230 (12)	0.0159 (10)	0.0078 (9)	−0.0014 (9)
C10	0.0545 (17)	0.0317 (14)	0.0334 (14)	0.0084 (12)	0.0131 (12)	−0.0012 (11)
C11	0.073 (2)	0.0389 (15)	0.0278 (14)	0.0164 (14)	0.0216 (14)	0.0056 (11)
C12	0.0598 (18)	0.0361 (14)	0.0244 (13)	0.0191 (13)	0.0090 (12)	−0.0002 (10)
C13	0.0513 (16)	0.0346 (14)	0.0305 (14)	0.0062 (12)	0.0087 (12)	−0.0059 (11)
C14	0.0418 (14)	0.0380 (14)	0.0272 (13)	0.0064 (12)	0.0120 (11)	−0.0017 (11)
C15	0.084 (2)	0.0416 (17)	0.0279 (14)	0.0212 (16)	0.0164 (15)	−0.0029 (12)
C16	0.0273 (11)	0.0394 (14)	0.0265 (12)	0.0173 (10)	0.0042 (9)	−0.0063 (10)
C17	0.0450 (15)	0.0324 (13)	0.0359 (14)	0.0097 (12)	0.0112 (12)	−0.0042 (11)
C18	0.0517 (17)	0.0382 (15)	0.0339 (14)	0.0122 (13)	0.0184 (12)	0.0015 (11)
C19	0.0401 (14)	0.0378 (14)	0.0255 (12)	0.0190 (11)	0.0065 (10)	−0.0040 (10)

C20	0.0331 (13)	0.0381 (14)	0.0329 (14)	0.0104 (11)	0.0047 (10)	−0.0073 (11)
C21	0.0302 (12)	0.0428 (15)	0.0289 (13)	0.0124 (11)	0.0103 (10)	−0.0042 (11)
C22	0.0544 (17)	0.0431 (16)	0.0271 (13)	0.0200 (13)	0.0090 (12)	−0.0040 (11)

Geometric parameters (Å, º)

S1—C3	1.755 (3)	C2—H2A	0.9700
S1—C5	1.763 (3)	C2—H2B	0.9700
S2—C4	1.762 (3)	C3—C4	1.323 (4)
S2—C5	1.763 (3)	C5—C6	1.336 (3)
S3—C7	1.761 (3)	C7—C8	1.346 (4)
S3—C6	1.769 (2)	C9—C14	1.386 (4)
S4—C6	1.759 (3)	C9—C10	1.391 (3)
S4—C8	1.762 (2)	C10—C11	1.392 (4)
S5—C7	1.757 (2)	C10—H10A	0.9300
S5—C16	1.777 (2)	C11—C12	1.387 (4)
S6—C8	1.759 (3)	C11—H11A	0.9300
S6—C9	1.767 (2)	C12—C13	1.388 (4)
O1—C4	1.375 (3)	C12—C15	1.486 (4)
O1—C1	1.436 (4)	C13—C14	1.387 (4)
O1W—H1WA	0.8522	C13—H13A	0.9300
O1W—H1WB	0.8483	C14—H14A	0.9300
O2—C3	1.371 (3)	C16—C21	1.385 (4)
O2—C2	1.455 (4)	C16—C17	1.388 (4)
O3—C15	1.260 (4)	C17—C18	1.387 (4)
O4—C15	1.258 (4)	C17—H17A	0.9300
O4—H4	0.863 (19)	C18—C19	1.387 (4)
O5—C22	1.261 (3)	C18—H18A	0.9300
O6—C22	1.263 (4)	C19—C20	1.397 (4)
O6—H6	0.843 (18)	C19—C22	1.483 (3)
C1—C2	1.485 (5)	C20—C21	1.383 (3)
C1—H1A	0.9700	C20—H20A	0.9300
C1—H1B	0.9700	C21—H21A	0.9300
C3—S1—C5	91.86 (12)	C14—C9—S6	123.81 (19)
C4—S2—C5	91.46 (12)	C10—C9—S6	116.2 (2)
C7—S3—C6	93.69 (12)	C9—C10—C11	119.9 (3)
C6—S4—C8	93.76 (12)	C9—C10—H10A	120.1
C7—S5—C16	103.60 (11)	C11—C10—H10A	120.1
C8—S6—C9	103.42 (11)	C12—C11—C10	120.1 (2)
C4—O1—C1	110.0 (2)	C12—C11—H11A	120.0
H1WA—O1W—H1WB	107.7	C10—C11—H11A	120.0
C3—O2—C2	109.7 (2)	C11—C12—C13	119.8 (2)
C15—O4—H4	116 (3)	C11—C12—C15	120.2 (3)
C22—O6—H6	115 (3)	C13—C12—C15	120.0 (3)
O1—C1—C2	112.2 (3)	C14—C13—C12	120.3 (3)
O1—C1—H1A	109.2	C14—C13—H13A	119.8
C2—C1—H1A	109.2	C12—C13—H13A	119.8

O1—C1—H1B	109.2	C9—C14—C13	119.9 (2)
C2—C1—H1B	109.2	C9—C14—H14A	120.0
H1A—C1—H1B	107.9	C13—C14—H14A	120.0
O2—C2—C1	111.8 (3)	O4—C15—O3	122.8 (3)
O2—C2—H2A	109.2	O4—C15—C12	118.2 (3)
C1—C2—H2A	109.2	O3—C15—C12	119.0 (3)
O2—C2—H2B	109.2	C21—C16—C17	120.1 (2)
C1—C2—H2B	109.2	C21—C16—S5	122.88 (19)
H2A—C2—H2B	107.9	C17—C16—S5	116.8 (2)
C4—C3—O2	125.3 (3)	C18—C17—C16	119.9 (2)
C4—C3—S1	118.0 (2)	C18—C17—H17A	120.0
O2—C3—S1	116.7 (2)	C16—C17—H17A	120.0
C3—C4—O1	125.0 (2)	C19—C18—C17	120.1 (2)
C3—C4—S2	118.2 (2)	C19—C18—H18A	120.0
O1—C4—S2	116.75 (19)	C17—C18—H18A	120.0
C6—C5—S2	123.0 (2)	C18—C19—C20	119.8 (2)
C6—C5—S1	121.6 (2)	C18—C19—C22	119.8 (2)
S2—C5—S1	115.37 (14)	C20—C19—C22	120.4 (2)
C5—C6—S4	123.8 (2)	C21—C20—C19	119.9 (2)
C5—C6—S3	123.1 (2)	C21—C20—H20A	120.1
S4—C6—S3	112.94 (13)	C19—C20—H20A	120.1
C8—C7—S5	125.7 (2)	C20—C21—C16	120.2 (2)
C8—C7—S3	116.87 (18)	C20—C21—H21A	119.9
S5—C7—S3	117.18 (15)	C16—C21—H21A	119.9
C7—C8—S6	126.18 (19)	O5—C22—O6	123.6 (3)
C7—C8—S4	117.00 (19)	O5—C22—C19	118.5 (3)
S6—C8—S4	116.78 (15)	O6—C22—C19	118.0 (2)
C14—C9—C10	120.0 (2)		

C4—O1—C1—C2	−43.5 (4)	C9—S6—C8—S4	−100.45 (15)
C3—O2—C2—C1	−42.7 (4)	C6—S4—C8—C7	14.3 (2)
O1—C1—C2—O2	60.5 (4)	C6—S4—C8—S6	−163.43 (14)
C2—O2—C3—C4	14.2 (4)	C8—S6—C9—C14	18.4 (3)
C2—O2—C3—S1	−164.1 (2)	C8—S6—C9—C10	−162.2 (2)
C5—S1—C3—C4	12.6 (2)	C14—C9—C10—C11	−2.3 (4)
C5—S1—C3—O2	−169.0 (2)	S6—C9—C10—C11	178.3 (2)
O2—C3—C4—O1	0.4 (4)	C9—C10—C11—C12	0.5 (5)
S1—C3—C4—O1	178.6 (2)	C10—C11—C12—C13	2.0 (5)
O2—C3—C4—S2	−177.6 (2)	C10—C11—C12—C15	−175.3 (3)
S1—C3—C4—S2	0.7 (3)	C11—C12—C13—C14	−2.8 (5)
C1—O1—C4—C3	14.8 (4)	C15—C12—C13—C14	174.6 (3)
C1—O1—C4—S2	−167.3 (2)	C10—C9—C14—C13	1.5 (4)
C5—S2—C4—C3	−13.6 (2)	S6—C9—C14—C13	−179.1 (2)
C5—S2—C4—O1	168.3 (2)	C12—C13—C14—C9	1.0 (5)
C4—S2—C5—C6	−155.6 (2)	C11—C12—C15—O4	−179.9 (4)
C4—S2—C5—S1	22.02 (16)	C13—C12—C15—O4	2.7 (5)
C3—S1—C5—C6	155.8 (2)	C11—C12—C15—O3	1.9 (5)
C3—S1—C5—S2	−21.84 (17)	C13—C12—C15—O3	−175.5 (3)

S2—C5—C6—S4	1.2 (3)	C7—S5—C16—C21	−47.9 (2)
S1—C5—C6—S4	−176.19 (14)	C7—S5—C16—C17	137.0 (2)
S2—C5—C6—S3	176.14 (14)	C21—C16—C17—C18	0.8 (4)
S1—C5—C6—S3	−1.3 (3)	S5—C16—C17—C18	176.0 (2)
C8—S4—C6—C5	152.2 (2)	C16—C17—C18—C19	−0.3 (5)
C8—S4—C6—S3	−23.12 (15)	C17—C18—C19—C20	−0.3 (4)
C7—S3—C6—C5	−152.4 (2)	C17—C18—C19—C22	−179.2 (3)
C7—S3—C6—S4	23.01 (15)	C18—C19—C20—C21	0.5 (4)
C16—S5—C7—C8	−83.1 (2)	C22—C19—C20—C21	179.5 (3)
C16—S5—C7—S3	102.52 (15)	C19—C20—C21—C16	−0.1 (4)
C6—S3—C7—C8	−13.8 (2)	C17—C16—C21—C20	−0.6 (4)
C6—S3—C7—S5	161.13 (14)	S5—C16—C21—C20	−175.5 (2)
S5—C7—C8—S6	2.8 (3)	C18—C19—C22—O5	−1.7 (4)
S3—C7—C8—S6	177.20 (13)	C20—C19—C22—O5	179.4 (3)
S5—C7—C8—S4	−174.74 (13)	C18—C19—C22—O6	177.6 (3)
S3—C7—C8—S4	−0.3 (3)	C20—C19—C22—O6	−1.4 (4)
C9—S6—C8—C7	82.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O5^{i}	0.86 (2)	1.78 (2)	2.629 (3)	165 (5)
O6—H6···O3^{i}	0.84 (2)	1.78 (2)	2.624 (3)	177 (4)
O1*W*—H1*WA*···O5^{ii}	0.85	2.38	3.18 (2)	155
O1*W*—H1*WB*···O3^{ii}	0.85	2.37	3.17 (2)	158
C13—H13*A*···O2^{iii}	0.93	2.67	3.570 (4)	163
C20—H20*A*···O1^{iii}	0.93	2.65	3.552 (4)	164

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) *x*−1, *y*, *z*+1; (iii) −*x*, −*y*, −*z*+1.