data reports

(S)-2-Carboxyethyl L-cysteinyl sulfone

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The title compound {systematic name: (2S)-2-azaniumyl-3-[(2-carboxyethane)-sulfonyl]propanoate}, $C_6H_{11}NO_6S$, forms enantiopure crystals in the monoclinic space group $P2_1$ and exists as a zwitterion, with a protonated α-amino group and a deprotonated α-carboxyl group. Both the carboxyl groups and the amino group are involved in an extensive multicentered intermolecular hydrogen-bonding scheme. In the crystal, the diperiodic network of hydrogen bonds propagates parallel to (101) and involves interconnected heterodromic $R_4^3(10)$ rings. Electrostatic forces are major contributors to the structure energy, which was estimated by DFT calculations as $E_{total} = -333.5$ kJ mol^{-1}.

3D view
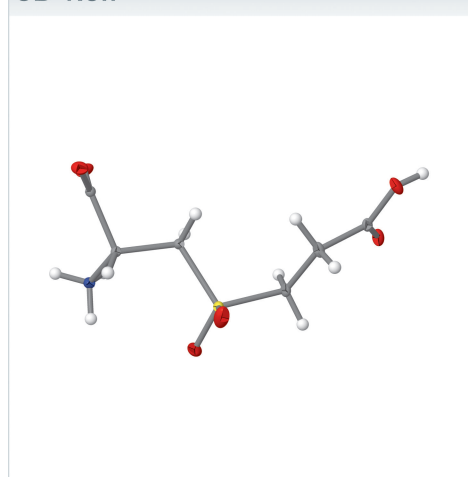
Chemical scheme
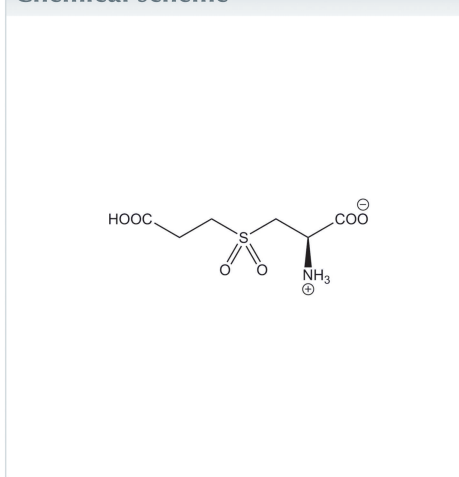
Structure description

S-(2-Carboxyethyl)-L-cysteine (CEC) and its sulfoxide (CECO) are naturally occurring, insecticidal amino acids, most often found in legumes of tropical and subtropical regions (Romeo & Simmonds, 1989; Seneviratne & Fowden, 1968). These non-proteinogenic acids have also been detected in the urine of humans exposed to dietary or occupational acrylamide (Bull *et al.*, 2005), as well as in cystathioninuria patients (Watanabe *et al.*, 1991). Recently, we have described structures and demonstrated the protective effects of both CEC and CECO against hydroxyl free-radical induced DNA degradation (Waters *et al.*, 2022). In addition, these amino acids activated the antioxidant signaling pathway in renal tubular epithelial cells and protected the cells from cytotoxic CuO nanoparticles. In a continuation of our studies on antioxidant amino acids (Waters *et al.*, 2020, 2022; Mawhinney *et al.*, 2020), we have synthesized S-(2-carboxyethyl)-L-cysteine sulfone (CECO2, **I**), an alleged metabolite of CEC, and report here its molecular and crystal structures.

Searches of SciFinder and the Cambridge Structural Database (Groom *et al.*, 2016) by both structure and chemical names revealed no previous structural description of S-(2-carboxyethyl)-L-cysteine sulfone. The most closely related structures solved by diffrac-

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1$A\cdots$O1^{i}	0.88 (3)	1.95 (3)	2.8113 (17)	168 (2)
N1—H1$A\cdots$O4	0.88 (3)	2.61 (2)	3.0239 (17)	110 (2)
N1—H1$B\cdots$O5^{ii}	0.86 (3)	2.22 (2)	2.8860 (16)	134 (2)
N1—H1$B\cdots$O6^{iii}	0.86 (3)	2.31 (2)	2.9869 (15)	136 (2)
N1—H1$C\cdots$O1^{iv}	0.85 (3)	1.98 (3)	2.8238 (17)	173 (2)
O6—H6$\cdots$O2^{v}	0.83 (3)	1.75 (3)	2.5436 (15)	159 (2)

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

Table 2
Additional $D—H\cdots A$ contacts (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C2—H2$\cdots$O2^{vi}	0.96 (2)	2.55 (2)	3.3104 (18)	136.3 (17)
C3—H3$A\cdots$O4^{vii}	0.95 (2)	2.36 (2)	3.249 (2)	155 (2)
C3—H3$B\cdots$O1^{iv}	0.97 (3)	2.58 (2)	3.3688 (18)	138.3 (18)
C5—H5$A\cdots$O3^{viii}	0.95 (2)	2.58 (2)	2.998 (2)	107.2 (16)

Symmetry codes: (vi) $x + 1, y, z$; (vii) $x - 1, y, z - 1$; (viii) $x - 1, y, z$.

tion methods are S-(2-carboxyethyl)-L-cysteine, S-(2-carboxyethyl)-L-cysteine sulfoxide (Waters *et al.*, 2022), S-carboxymethyl-L-cysteine sulfone (CMCO2; Hubbard *et al.*, 1976), and S-carboxymethyl-L-cysteine sulfoxide (CMCO; Staffa *et al.*, 1976; Waters *et al.*, 2020). The asymmetric unit in crystalline **I** contains one molecule of the amino acid existing as a zwitterion, with a deprotonated α-carboxylic group, and protonated α-amino and ε-carboxylic groups, as shown in Fig.1. The aforementioned related molecules uniformly adopt similar zwitterionic arrangements in their structures. All bond lengths and angles in **I** are within their expected ranges. The conformation of the cysteine moiety in **I** is close to that found in CMCO2 (CCDC #1134461, refcode CXMCYS), triclinic (4R)-CMCO (CCDC #2027234, refcode CMXLCS01), and may be partially stabilized in all three structures by weak intramolecular hydrogen bonds, which exist between the sulfone/sulfoxide oxygen atom O4 and the ammonium group (Fig. 1, Table 1).

The crystal packing in **I** is shown in Fig. 2. The enantiopure crystal of **I** has the symmetry of the monoclinic Sohncke space
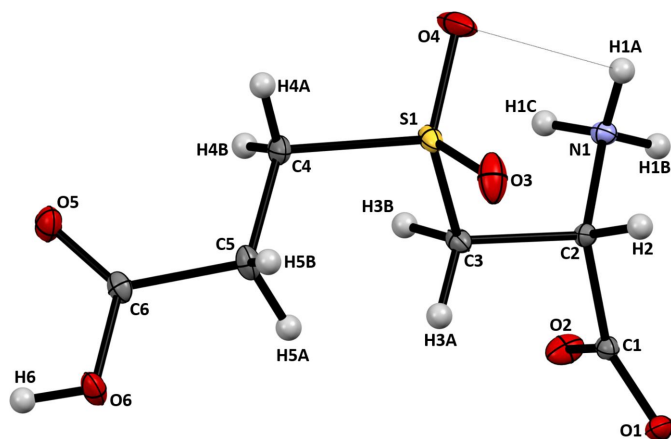
Table 3
Calculated intermolecular interaction energies E (kJ mol^{-1}) in crystalline **I** and related structures.

$E_{total} = 1.057 E_{elstat} + 0.74 E_{polar} + 0.871 E_{energy\text{-}dispersive} + 0.618 E_{repuls}$.

Molecule	$E_{electrostatic}$	E_{polar}	$E_{dispersion}$	$E_{repulsion}$	E_{total}
CECO2	−289.4	−120.6	−130.1	283	−333.5
(4R)-CECO^{a}	−293.6	−115.5	−130.6	308.6	−319.1
(4S)-CECO^{a}	−168.6	−96.3	−92.9	187.4	−214.7
CMCO2^{b}	−335.7	−142.4	−126	319.7	−372.6
(4R)-CMCO^{c}	−336.8	−148.7	−117.3	350.2	−351.8
(4S)-CMCO^{c}	−323.4	−157.7	−118.7	318.4	−365.6

Notes: (a) Waters *et al.* (2022); (b) Hubbard *et al.* (1976); (c) Waters *et al.* (2020).

group $P2_1$, with two molecules per unit cell. Because this dicarboxylic amino acid is a heteroatom-rich, zwitterionic molecule, there is an extensive intermolecular hydrogen-bonding network, which involves all carboxylic oxygen atoms and all protons in the ammonium group, as listed in Table 1. The ammonium hydrogen atoms H1B and H1A are both involved in bifurcated hydrogen bonds. Among the oxygen atoms, the carboxylic O1 participates in multi-centered hydrogen bonding, while the sulfone O3 is the only oxygen atom not involved in heteroatom contacts. The hydrogen-bonding network topology consists of a system of heterodromic $R_4^3(10)$ rings including both α- and ε-carboxylic groups and the ammonium group. The rings are connected by the N1—H1$C\cdots$O1 and the N1—H1$B\cdots$O6 links, which propagate in the [100] and [001] directions, respectively. In addition, short C—H$\cdots$O contacts are present in the crystal structure of **I** (Table 2).

To account for all interactions involved in the crystal structure of **I**, we have performed DFT calculations, at the B3LYP/6–31 G(d,p) theory level (Thomas *et al.*, 2018; Mackenzie *et al.*, 2017), of the electrostatic, dispersion, polarization, and repulsion energies for the structure. The molecular modeling calculations show that electrostatic forces arising from multiple heteroatom contacts between CECO2 molecules are the main contributors to the crystal packing ener-

Figure 1
Atomic numbering and displacement ellipsoids at the 50% probability level for **I**. The intramolecular hydrogen bond is shown as a dotted line.
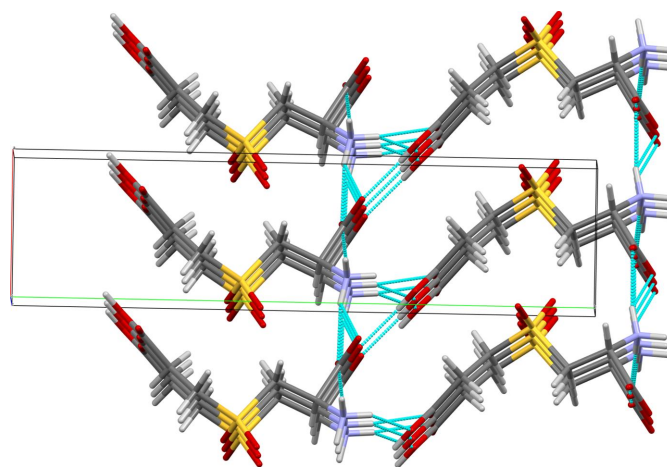

Figure 2
Molecular packing of **I**. Intermolecular hydrogen bonds are shown as cyan dotted lines. Crystallographic axes color codes: a – red; b – green; c – blue.
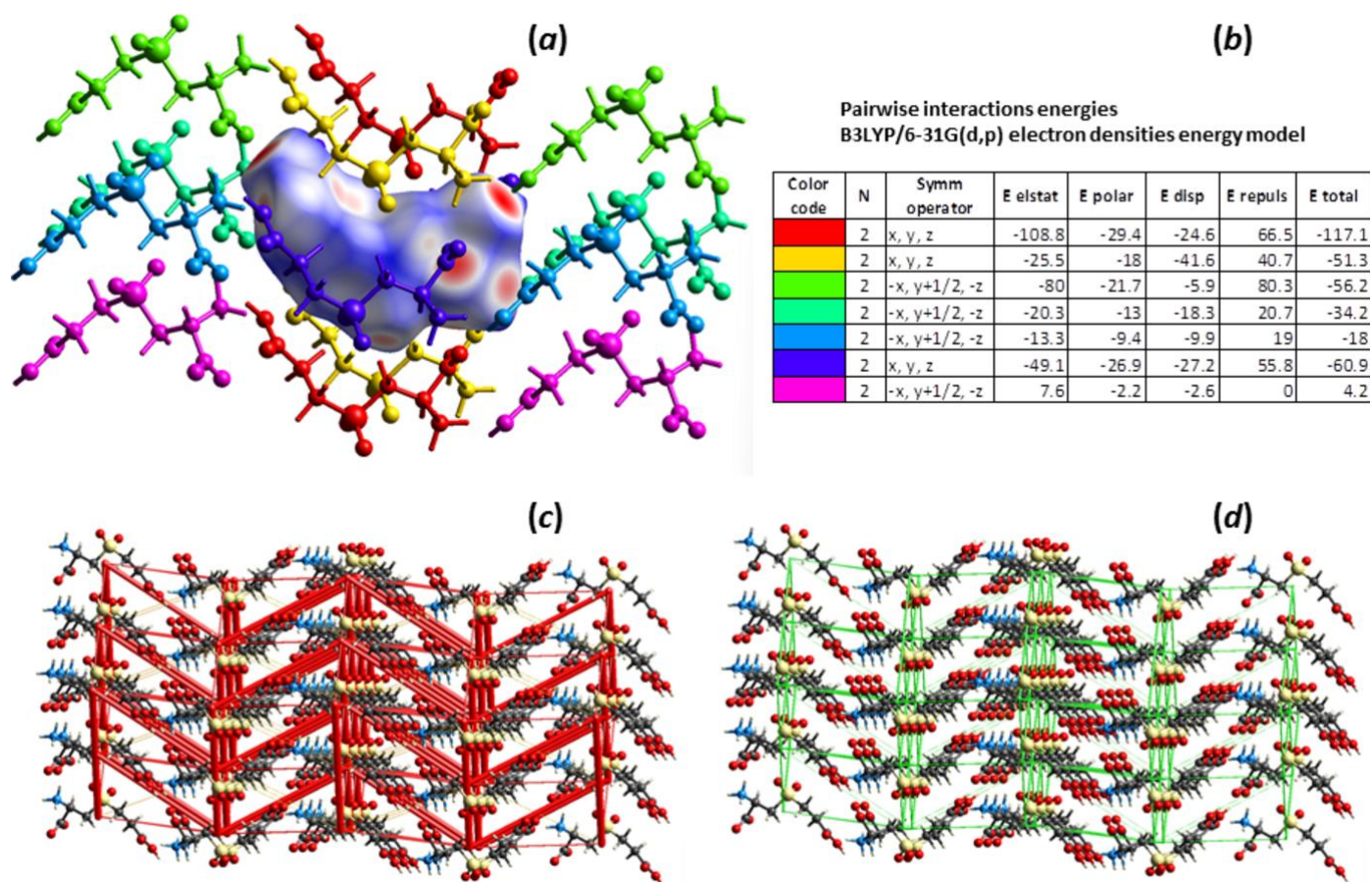
Figure 3
Interaction energies in crystal structure of **I**. (*a*) A view of interactions between a central molecule of CECO2 in crystalline **I**, shown as its Hirshfeld surface, and 14 molecules that share the interaction surfaces with the central molecule. (*b*) Calculated energies (electrostatic, polarization, dispersion, repulsion, and total) of pairwise interactions in **I** between the central molecule and those indicated by respective colors. (*c*) Energy framework for pairwise electrostatic interaction energies in **I**. The cylinders link molecular centroids, and the cylinder thickness is proportional to the magnitude of the energies, such as those shown in (*b*). For clarity, the cylinders corresponding to energies <5 kJ mol^{-1} are not shown. (*d*) The pairwise dispersion energy framework in **I**.

gies (Fig. 3, Table 3). The spatial distribution of the energetically most significant interactions is also illustrated in Fig. 3. As was previously noted (Waters *et al.*, 2022), there is a relatively large difference in total structural energy estimated for CECO epimers, due to a more extensive hydrogen-bonding network found in the crystal structure of the (4*R*)-epimer, as compared to that of the (4*S*)-epimer (Table 3). Both electrostatic and total energies estimated for **I** are close to those calculated for both (4*R*)-CECO and more compact molecules CMCO and CMCO2.

Synthesis and crystallization

Compound **I** was synthesized by performic acid oxidation of *S*-(2-carboxyethyl)-L-cysteine. CEC was prepared as reported earlier (Waters *et al.*, 2022). Performic acid was made fresh by adding 10 ml of 30% hydrogen peroxide to 90 ml of 98% formic acid. Then 20 g (0.104 moles) of CEC were dissolved in 100 ml of cold performic acid and left overnight in an ice bath. The reaction was monitored using an amino acid analyser (Hitachi L8900). Upon reaction completeness, the performic acid solution was left at room temperature for 1 h, cooled down to −80°C, and then the excess of performic acid was removed by vacuum freeze drying at −50°C. The residue was recrystallized from water to afford chromatographically pure **I** as colorless plates. $[\alpha]_D^{23}$ +10.9° (*c* 1, 0.2 N HCl). Elemental analysis: calculated for $C_6H_{11}NO_6S$: N, 6.22%. Found: N, 6.17%. Exact mass of the $[M+H]^+$ ion. Calculated for $C_6H_{12}NO_4S$: *m/z* 226.02. Found: *m/z* 226.00.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Enantiopurity of the crystal was established on the basis of Flack absolute structure parameter determined [−0.001 (11) for 1277 quotients (Parsons *et al.*, 2013)].

Funding information

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Table 4
Experimental details.

Crystal data	
Chemical formula	$C_6H_{11}NO_6S$
M_r	225.22
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	4.8838 (2), 18.3867 (7), 5.1522 (2)
β (°)	110.3246 (16)
V (Å^3)	433.85 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.38
Crystal size (mm)	$0.45 \times 0.28 \times 0.02$
Data collection	
Diffractometer	Bruker APEXII area detector
Absorption correction	Multi-scan (*AXScale*; Bruker, 2014)
T_{min}, T_{max}	0.705, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15133, 2656, 2644
R_{int}	0.017
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.051, 1.10
No. of reflections	2656
No. of parameters	160
No. of restraints	1
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.18
Absolute structure	Flack x determined using 1277 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons *et al.*, 2013)
Absolute structure parameter	−0.001 (11)

Computer programs: *APEX3* and *SAINT* (Bruker, 2014), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *CrystalExplorer 17.5* (Mackenzie *et al.*, 2017), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

full crystallographic data

(*S*)-2-Carboxyethyl ʟ-cysteinyl sulfone

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(2*S*)-2-Azaniumyl-3-[(2-carboxyethane)sulfonyl]propanoate

Crystal data

$C_6H_{11}NO_6S$	$F(000) = 236$
$M_r = 225.22$	$D_x = 1.724$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.8838$ (2) Å	Cell parameters from 9939 reflections
$b = 18.3867$ (7) Å	$\theta = 3.3$–30.6°
$c = 5.1522$ (2) Å	$\mu = 0.38$ mm^{-1}
$\beta = 110.3246$ (16)°	$T = 100$ K
$V = 433.85$ (3) Å^3	Plate, colourless
$Z = 2$	$0.45 \times 0.28 \times 0.02$ mm

Data collection

Bruker APEXII area detector diffractometer	15133 measured reflections
Radiation source: Sealed Source Mo with TRIUMPH optics	2656 independent reflections
	2644 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.017$
ω and phi scans	$\theta_{max} = 30.6°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*AXScale*; Bruker, 2014)	$h = -6 \rightarrow 6$
	$k = -26 \rightarrow 26$
$T_{min} = 0.705$, $T_{max} = 0.746$	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	Only H-atom coordinates refined
$R[F^2 > 2\sigma(F^2)] = 0.019$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.0609P]$
$wR(F^2) = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2656 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
1 restraint	Absolute structure: Flack x determined using 1277 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	Absolute structure parameter: -0.001 (11)

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. Data were corrected for Lorentz, polarization, and absorption effects. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydroxyl and ammonium hydrogen atoms were located in difference Fourier maps and were allowed to refine freely. The remaining H atoms were placed at calculated positions and included in the refinement using a riding model. All hydrogen atom thermal parameters were constrained to ride on the carrier atoms (U_{iso}(methine, methylene H) = $1.2U_{eq}$ and U_{iso}(hydroxyl, ammonium H) = $1.5U_{eq}$).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.85411 (6)	0.89496 (2)	0.84809 (6)	0.01103 (8)
O6	0.1220 (2)	0.69175 (6)	0.5230 (2)	0.01356 (19)
H6	0.006 (6)	0.6645 (14)	0.561 (5)	0.020*
O4	1.0462 (3)	0.92863 (7)	1.0965 (3)	0.0239 (3)
O5	0.2537 (2)	0.72208 (6)	0.9711 (2)	0.0144 (2)
C1	0.4393 (3)	1.06770 (7)	0.3928 (3)	0.0085 (2)
C6	0.2813 (3)	0.72813 (7)	0.7474 (3)	0.0100 (2)
O2	0.2657 (2)	1.09831 (6)	0.4873 (2)	0.0141 (2)
N1	0.8143 (3)	1.07575 (6)	0.8579 (2)	0.0091 (2)
H1A	0.998 (5)	1.0653 (13)	0.951 (5)	0.014*
H1B	0.801 (5)	1.1210 (14)	0.816 (4)	0.014*
H1C	0.707 (5)	1.0726 (13)	0.957 (5)	0.014*
O1	0.4180 (2)	1.06328 (6)	0.14494 (19)	0.01234 (18)
C4	0.6697 (3)	0.82185 (7)	0.9387 (3)	0.0115 (2)
H4A	0.818 (5)	0.7954 (13)	1.063 (4)	0.014*
H4B	0.548 (5)	0.8430 (13)	1.023 (4)	0.014*
C3	0.5730 (3)	0.95792 (7)	0.6791 (3)	0.0095 (2)
C2	0.6965 (3)	1.02859 (7)	0.6080 (2)	0.0076 (2)
H2	0.854 (5)	1.0212 (12)	0.541 (4)	0.009*
O3	0.9803 (3)	0.87027 (6)	0.6484 (3)	0.0207 (2)
C5	0.4975 (3)	0.77739 (7)	0.6867 (3)	0.0117 (2)
H5A	0.395 (5)	0.8068 (13)	0.533 (4)	0.014*
H5B	0.618 (5)	0.7471 (14)	0.621 (4)	0.014*
H3A	0.445 (5)	0.9346 (13)	0.517 (5)	0.014*
H3B	0.459 (5)	0.9664 (12)	0.797 (5)	0.014*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.00737 (13)	0.00812 (13)	0.01511 (13)	−0.00088 (11)	0.00073 (9)	0.00364 (11)
O6	0.0136 (4)	0.0127 (4)	0.0158 (4)	−0.0061 (4)	0.0068 (4)	−0.0039 (3)
O4	0.0206 (6)	0.0166 (5)	0.0208 (5)	−0.0083 (4)	−0.0100 (4)	0.0045 (4)
O5	0.0184 (5)	0.0110 (5)	0.0152 (4)	−0.0032 (4)	0.0075 (4)	0.0006 (3)
C1	0.0077 (5)	0.0071 (5)	0.0096 (5)	−0.0006 (4)	0.0017 (4)	0.0009 (4)
C6	0.0097 (5)	0.0064 (5)	0.0143 (5)	0.0000 (4)	0.0047 (4)	−0.0005 (4)

O2	0.0130 (5)	0.0164 (5)	0.0130 (4)	0.0072 (4)	0.0046 (4)	0.0016 (4)
N1	0.0088 (5)	0.0086 (5)	0.0088 (4)	−0.0004 (4)	0.0015 (4)	−0.0006 (3)
O1	0.0106 (4)	0.0180 (5)	0.0079 (4)	−0.0008 (4)	0.0025 (3)	0.0012 (4)
C4	0.0118 (6)	0.0088 (5)	0.0129 (5)	−0.0024 (4)	0.0028 (4)	0.0025 (4)
C3	0.0074 (5)	0.0071 (5)	0.0122 (5)	−0.0001 (4)	0.0011 (4)	0.0008 (4)
C2	0.0079 (5)	0.0066 (5)	0.0077 (4)	0.0002 (4)	0.0019 (4)	0.0000 (4)
O3	0.0186 (5)	0.0143 (5)	0.0356 (6)	0.0035 (4)	0.0177 (5)	0.0059 (4)
C5	0.0119 (5)	0.0093 (5)	0.0157 (5)	−0.0025 (5)	0.0072 (4)	−0.0016 (4)

Geometric parameters (Å, °)

S1—O4	1.4380 (12)	C3—C2	1.5293 (18)
S1—C4	1.7686 (13)	O6—H6	0.83 (3)
S1—C3	1.7756 (13)	N1—H1A	0.88 (3)
S1—O3	1.4440 (12)	N1—H1B	0.86 (3)
O6—C6	1.3285 (16)	N1—H1C	0.85 (3)
O5—C6	1.2107 (16)	C2—H2	0.96 (2)
C1—O2	1.2489 (16)	C3—H3A	0.95 (2)
C1—O1	1.2471 (15)	C3—H3B	0.97 (3)
C1—C2	1.5353 (18)	C4—H4A	0.92 (2)
C6—C5	1.5038 (19)	C4—H4B	0.93 (2)
N1—C2	1.4919 (16)	C5—H5A	0.95 (2)
C4—C5	1.5174 (19)	C5—H5B	0.95 (2)
O4—S1—C4	109.09 (7)	H1A—N1—H1B	109 (2)
O4—S1—C3	108.07 (7)	H1A—N1—H1C	113 (2)
O4—S1—O3	117.48 (9)	H1B—N1—H1C	102 (2)
C4—S1—C3	104.31 (6)	N1—C2—H2	106.1 (13)
O3—S1—C4	109.37 (7)	C1—C2—H2	111.4 (12)
O3—S1—C3	107.71 (7)	C3—C2—H2	113.5 (13)
O2—C1—C2	115.16 (11)	S1—C3—H3A	107.2 (15)
O1—C1—O2	127.01 (13)	S1—C3—H3B	108.2 (14)
O1—C1—C2	117.75 (12)	C2—C3—H3A	111.4 (15)
O6—C6—C5	111.32 (11)	C2—C3—H3B	112.0 (13)
O5—C6—O6	123.82 (13)	H3A—C3—H3B	106 (2)
O5—C6—C5	124.85 (12)	S1—C4—H4A	103.6 (15)
C5—C4—S1	111.44 (9)	S1—C4—H4B	105.7 (15)
C2—C3—S1	111.67 (9)	C5—C4—H4A	112.3 (14)
N1—C2—C1	108.94 (10)	C5—C4—H4B	111.7 (14)
N1—C2—C3	110.69 (10)	H4A—C4—H4B	111.7 (19)
C3—C2—C1	106.21 (10)	C4—C5—H5A	112.5 (14)
C6—C5—C4	111.54 (11)	C4—C5—H5B	113.0 (14)
C6—O6—H6	109.9 (17)	C6—C5—H5A	108.2 (15)
C2—N1—H1A	111.0 (16)	C6—C5—H5B	106.7 (15)
C2—N1—H1B	112.0 (13)	H5A—C5—H5B	104.4 (19)
C2—N1—H1C	110.2 (16)		
O3—S1—C3—C2	−69.00 (11)	O2—C1—C2—H2	−159.7 (14)

O4—S1—C3—C2	58.88 (12)	C1—C2—N1—H1A	−155.6 (17)
C4—S1—C3—C2	174.85 (9)	C1—C2—N1—H1B	−33.7 (18)
O3—S1—C4—C5	−41.94 (13)	C1—C2—N1—H1C	79.2 (18)
O4—S1—C4—C5	−171.68 (11)	C3—C2—N1—H1A	88.0 (17)
C3—S1—C4—C5	73.05 (11)	C3—C2—N1—H1B	−150.1 (18)
O1—C1—C2—N1	139.90 (13)	C3—C2—N1—H1C	−37.2 (18)
O1—C1—C2—C3	−100.88 (14)	H2—C2—N1—H1A	−36 (2)
O2—C1—C2—N1	−43.00 (16)	H2—C2—N1—H1B	86 (2)
O2—C1—C2—C3	76.23 (14)	H2—C2—N1—H1C	−161 (2)
N1—C2—C3—S1	−78.37 (13)	N1—C2—C3—H3A	161.7 (17)
C1—C2—C3—S1	163.54 (9)	N1—C2—C3—H3B	43.1 (16)
S1—C4—C5—C6	−165.17 (10)	C1—C2—C3—H3A	43.7 (17)
C4—C5—C6—O5	−2.7 (2)	C1—C2—C3—H3B	−75.0 (16)
C4—C5—C6—O6	177.18 (12)	H2—C2—C3—S1	40.8 (13)
O3—S1—C3—H3A	53.3 (16)	H2—C2—C3—H3A	−79 (2)
O3—S1—C3—H3B	167.4 (15)	H2—C2—C3—H3B	162 (2)
O4—S1—C3—H3A	−178.8 (16)	S1—C4—C5—H5A	−43.3 (17)
O4—S1—C3—H3B	−64.8 (15)	S1—C4—C5—H5B	74.7 (16)
C4—S1—C3—H3A	−62.8 (16)	H4A—C4—C5—C6	79.1 (16)
C4—S1—C3—H3B	51.2 (15)	H4A—C4—C5—H5A	−159 (2)
O3—S1—C4—H4A	79.0 (14)	H4A—C4—C5—H5B	−41 (2)
O3—S1—C4—H4B	−163.4 (13)	H4B—C4—C5—C6	−47.2 (15)
O4—S1—C4—H4A	−50.8 (14)	H4B—C4—C5—H5A	75 (2)
O4—S1—C4—H4B	66.8 (13)	H4B—C4—C5—H5B	−167 (2)
C3—S1—C4—H4A	−166.1 (14)	H5A—C5—C6—O5	−127.0 (14)
C3—S1—C4—H4B	−48.4 (13)	H5A—C5—C6—O6	52.9 (14)
H6—O6—C6—O5	−1 (2)	H5B—C5—C6—O5	121.2 (13)
H6—O6—C6—C5	179 (2)	H5B—C5—C6—O6	−59.0 (13)
O1—C1—C2—H2	23.2 (14)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1[i]	0.88 (3)	1.95 (3)	2.8113 (17)	168 (2)
N1—H1A···O4	0.88 (3)	2.61 (2)	3.0239 (17)	110 (2)
N1—H1B···O5[ii]	0.86 (3)	2.22 (2)	2.8860 (16)	134 (2)
N1—H1B···O6[iii]	0.86 (3)	2.31 (2)	2.9869 (15)	136 (2)
N1—H1C···O1[iv]	0.85 (3)	1.98 (3)	2.8238 (17)	173 (2)
O6—H6···O2[v]	0.83 (3)	1.75 (3)	2.5436 (15)	159 (2)

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