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Crystal structure of a new europium(III) compound based on thiopheneacrylic acid

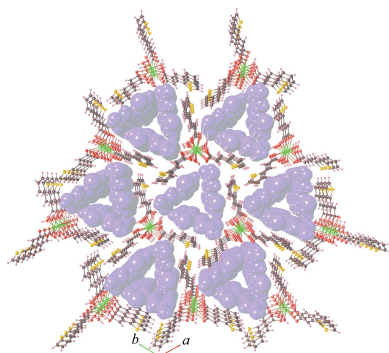
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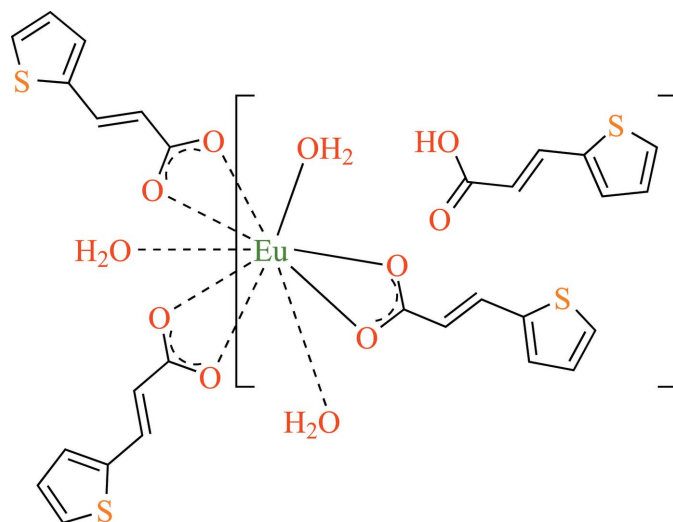
A europium(III) coordination compound based on thiopheneacrylic acid (Htpa), triaquatris[3-(thiophen-2-yl)prop-2-enoato- $\kappa^2 O, O'$]europium(III)–3-(thiophen-2-yl)prop-2-enoic acid (1/3), $[\text{Eu}(\text{C}_7\text{H}_5\text{O}_2\text{S})_3(\text{H}_2\text{O})_3] \cdot 3\text{C}_7\text{H}_6\text{O}_2\text{S}$ or $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3] \cdot 3(\text{Htpa})$ (**1**), where tpa is the conjugate base of Htpa, has been synthesized and structurally characterized. Compound **1** crystallizes in the trigonal space group $R\bar{3}$. The structure of **1** consists of a discrete molecular complex $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3]$ species and the Htpa molecule. In the crystal, the two components are involved in $\text{O}–\text{H} \cdots \text{O}$ [ring motif $R_2^2(8)$] and $\text{C}–\text{H} \cdots \pi$ hydrogen-bonding interactions. These interactions were further investigated by Hirshfeld surface analysis, which showed high contributions of $\text{H} \cdots \text{H}$, $\text{H} \cdots \text{C}/\text{C} \cdots \text{H}$ and $\text{H} \cdots \text{O}/\text{O} \cdots \text{H}$ contacts to the total Hirshfeld surfaces.

1. Chemical context

In crystal engineering, non-covalent interactions are used as a tool in the design and synthesis of functional crystalline materials with predictable structures and desirable physical properties (Desiraju, 2013; Mirzaei *et al.*, 2014). Despite the significant number of structures known, this still remains a challenging task, and more especially for the lanthanide-based systems. This is due to the high and variable coordination number exhibited by the $4f$ metals and their small energy difference among various coordination geometries, which can give rise to the appearance of multiple-connected framework structures with a variety of topologies (Sairenji *et al.*, 2016). In recent years, the design and synthesis of porous materials combining crystal engineering and coordination chemistry have attracted great attention because of their appealing structures and their potential applications in catalysis, ion-exchange, molecular adsorption and chemical sensing (Cawthray *et al.*, 2015; Pan *et al.*, 2021; Theppitak *et al.*, 2021; Jiajaroen *et al.*, 2022). However, the successful construction of such materials comes only from understanding and controlling the relationship between the geometry frameworks and the involved intermolecular interactions. In this work, we report the synthesis and supramolecular structure of a new europium(III) compound based on thiopheneacrylate (tpa), $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3] \cdot 3(\text{Htpa})$ (**1**). The intermolecular interactions involved in the formation of the supramolecular structure of the title compound **1** are discussed in detail. In addition, a Hirshfeld surface analysis was performed to investigate the intermolecular interactions.



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2. Structural commentary

Single crystal X-ray structural analysis reveals that the title compound **1** crystallizes in the trigonal system with space group $R\bar{3}$. The Flack parameter (Parsons *et al.*, 2013) of $-0.025(2)$ demonstrates the enantiomeric purity of the tested single crystal. The asymmetric unit consists of one crystallographically independent Eu^{III} ion, one tpa ligand, one Htpa molecule and one coordinated water molecule. As shown in Fig. 1, the structure of **1** consists of a discrete molecular complex $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3]$ and the Htpa molecule. In the discrete complex species, the deprotonated carboxylic group of tpa ligand adopts a $\mu_1\text{-}\kappa^2\text{O},\text{O}'$ -chelating coordination mode to the Eu^{III} ion. The central Eu^{III} ion is nine-coordinated with six oxygen atoms from three different tpa ligands and three oxygen atoms from coordinated water molecules. With the assistance of the *SHAPE* program (Llunell *et al.*, 2013), the

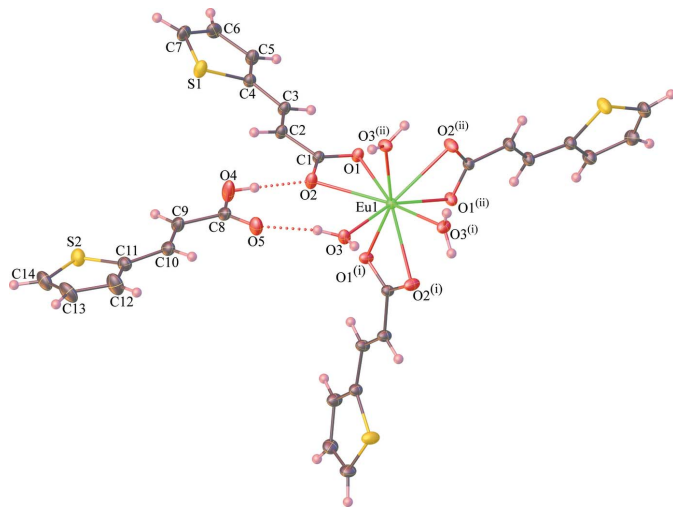


Figure 1
Molecular structure of the title compound **1**. Displacement ellipsoids are drawn at the 30% probability level. All hydrogen atoms were omitted for clarity. Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $-y + 1, x - y + 1, z$.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

C_g1 is the centroid of the S1/C4–C7 ring.

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O3---H3A}\cdots\text{O5}$	0.82 (1)	1.94 (2)	2.729 (3)	162 (3)
$\text{O3---H3B}\cdots\text{O1}^{\text{i}}$	0.82 (1)	1.89 (2)	2.693 (2)	165 (3)
$\text{O4---H4}\cdots\text{O2}$	0.84 (1)	1.78 (2)	2.614 (3)	177 (4)
$\text{C7---H7}\cdots C_g1^{\text{ii}}$	0.93	3.10	3.869 (3)	141

Symmetry codes: (i) $-x + y, -x + 1, z - 1$; (ii) $-x + y - \frac{2}{3}, -x - \frac{4}{3}, z - \frac{1}{3}$.

coordination geometry around the Eu^{III} center in **1** could be described as a distorted spherical tricapped trigonal prism [TCTPR-9; shape, D_{3h} symmetry; distortion (τ), 2.761], wherein a trigonal-prismatic geometry is formed by the vertical pairs: $\text{O1}\cdots\text{O3}'$, $\text{O1}'\cdots\text{O3}''$, and $\text{O1}''\cdots\text{O3}$, while the O2 , $\text{O2}'$, and $\text{O3}''$ atoms act as caps as shown in Fig. 2. The $\text{Eu}\text{---}\text{O}$ bond lengths range from 2.400 (2) to 2.511 (2) \AA , and the bond angles range from 51.62 (5) to 157.80 (6) $^\circ$, which are in the normal ranges of those observed in the reported europium(III) compounds (Behrsing *et al.*, 2016; Sun *et al.*, 2016; Alexander *et al.*, 2019). In addition, the $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3]$ complex interacts with the Htpa molecule through the formation of an $R_2^2(8)$ ring motif in terms of graph-set notation (Etter *et al.*, 1990).

3. Supramolecular features

As depicted in Fig. 3, the discrete complex $[\text{Eu}(\text{tpa})_3(\text{H}_2\text{O})_3]$ forms a supramolecular chain extending parallel to the c axis with its symmetry-related molecules through classical $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen-bonding interactions (Table 1) between the coordinated water molecules and the carboxylate groups of tpa ligands, which can be described by the $R_2^2(8)$ graph-set motif. The chains are further linked *via* $\text{C}\cdots\text{H}\cdots\pi$ interactions involving the thiophene moieties of adjacent tpa ligands [$\text{C7}\text{---}$

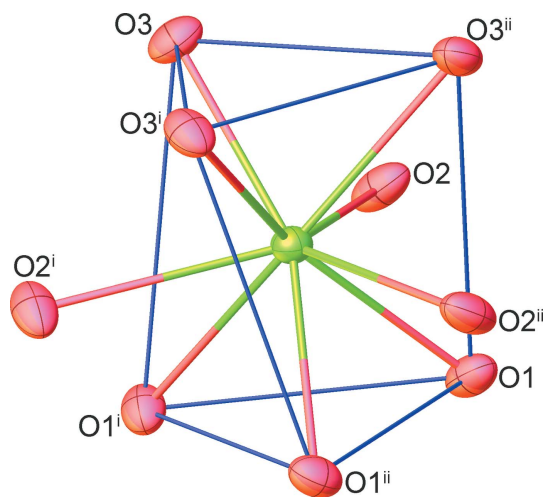


Figure 2
View of the distorted spherical tricapped trigonal prism (TCTPR-9) of the central Eu^{III} ion in the title compound **1**. Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $-y + 1, x - y + 1, z$.

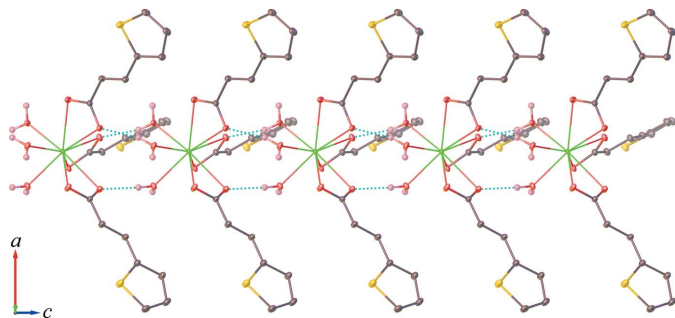


Figure 3
The one-dimensional hydrogen-bonded chain in the title compound **1** running parallel to the *c* axis.

$H7 \cdots Cg$ distance = 3.869 (3); symmetry code = $-\frac{2}{3} + y - x, -4/3 - x, -\frac{1}{3} + z$. As a result (illustrated in Fig. 4), a three-dimensional hydrogen-bonded network is created with large channels running along the crystallographic *c*-axis direction. The Htpa molecules are located in the cavities of the network, and are hydrogen bonded to both the tpa and water molecules through intermolecular $O-H \cdots O$ interactions with the $R_2^2(8)$ ring motif. It should be noted that no evidence for $\pi-\pi$ stacking interactions of neighboring aromatic thiophene rings is observed.

4. Hirshfeld surface analysis

The Hirshfeld surfaces and two-dimensional fingerprint plots was generated using *CrystalExplorer 21.5* (Spackman *et al.*, 2021) in order to quantify and visualize the intermolecular interactions in the crystal structure of the title compound **1**. As

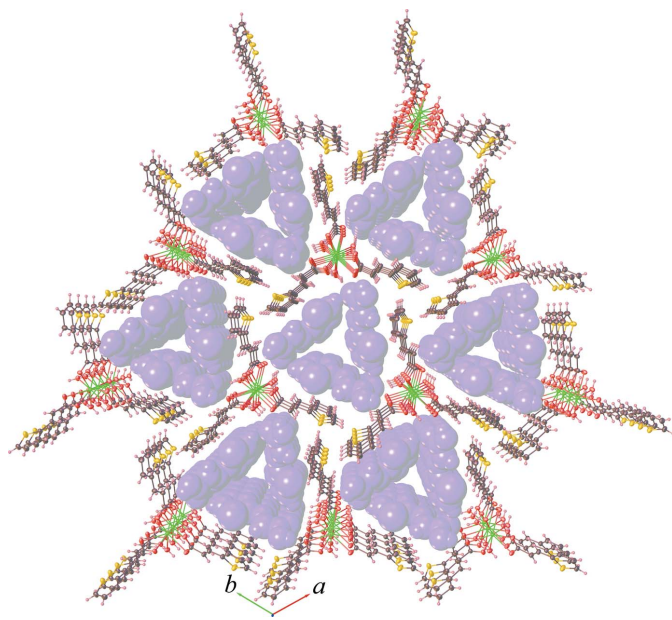


Figure 4
Crystal packing diagram of the title compound **1**, showing the three-dimensional hydrogen-bonded networks of the complex $[Eu(tpa)_3(H_2O)_3]$ species with the Htpa molecules in space-filling representation.

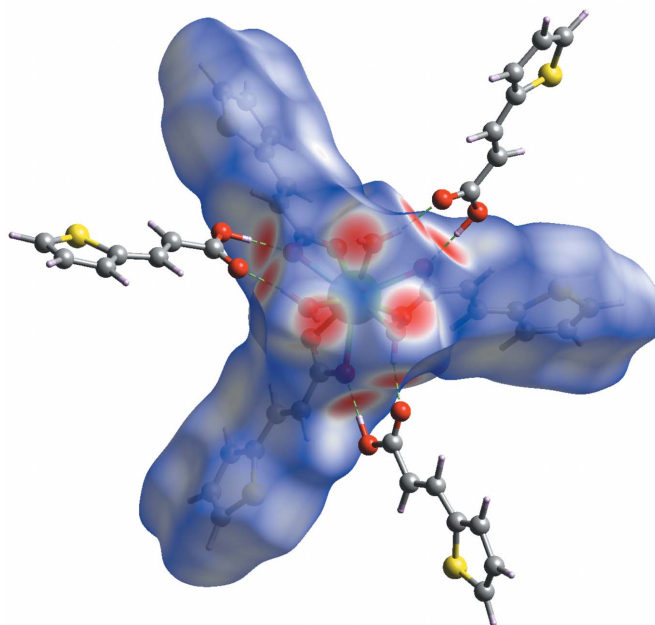
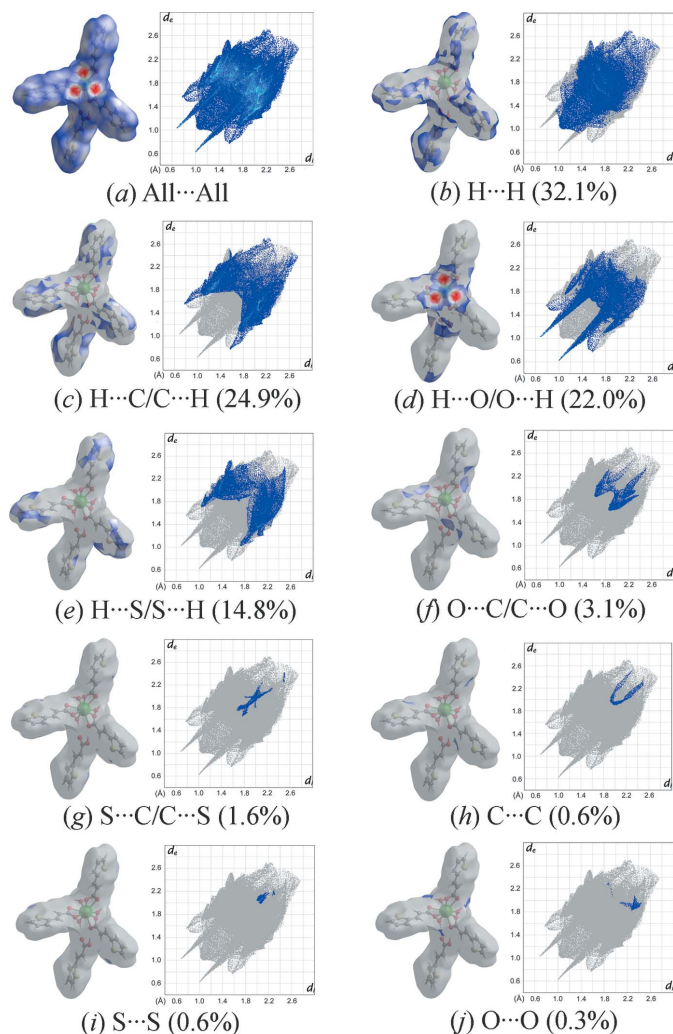


Figure 5
Hirshfeld surface mapped over d_{norm} of the title compound **1**, highlighting the $O-H \cdots O$ interactions.

can be seen in Fig. 5, the Hirshfeld surfaces mapped over d_{norm} shows the most intense red spots around the carboxylate groups and water molecules resulting from the $O-H \cdots O$ hydrogen-bonding interactions between the complex $[Eu(tpa)_3(H_2O)_3]$ species and the Htpa molecules. Furthermore, analysis of the two-dimensional fingerprint plots, Fig. 6, reveals that $H \cdots H$ (32.1%) contacts, which represent van der Waals interactions, are the major contributors toward the Hirshfeld surface. Meanwhile, $H \cdots C/C \cdots H$ (24.9%, *i.e.* $C-H \cdots \pi$) and $H \cdots O/O \cdots H$ (22.0%, *i.e.* $O-H \cdots O$) contacts also make a significant contribution. The $H \cdots S/S \cdots H$ (14.8%), $C \cdots O/O \cdots C$ (3.1%) and $C \cdots S/S \cdots C$ (1.6%) contacts make a small contribution to the entire Hirshfeld surface. Therefore, it can be concluded that $O-H \cdots O$ and $C-H \cdots \pi$ hydrogen bonds as well as $H \cdots H$ and $H \cdots S$ van der Waals contacts contribute significantly to the overall stability of the packing arrangement of the crystal structure of the title compound **1**.

5. Infrared spectroscopy

The infrared (IR) spectrum of the title compound **1** was recorded on a Perkin Elmer model Spectrum 100 spectrometer using the attenuated total reflectance (ATR) mode in the range of $650-4000 \text{ cm}^{-1}$. As can be seen in Fig. 7, the broad absorption bands in the region $3020-3400 \text{ cm}^{-1}$ are assigned to the stretching vibrations of the hydroxyl ($O-H$) groups. The band at 2978 cm^{-1} corresponds to the $C-H$ stretching vibrations. The strong band at 1670 cm^{-1} indicates the existence of the carboxylic groups while the strong bands appearing in the region $1305-1610 \text{ cm}^{-1}$ can be ascribed to the asymmetric and symmetric stretching vibrations of the

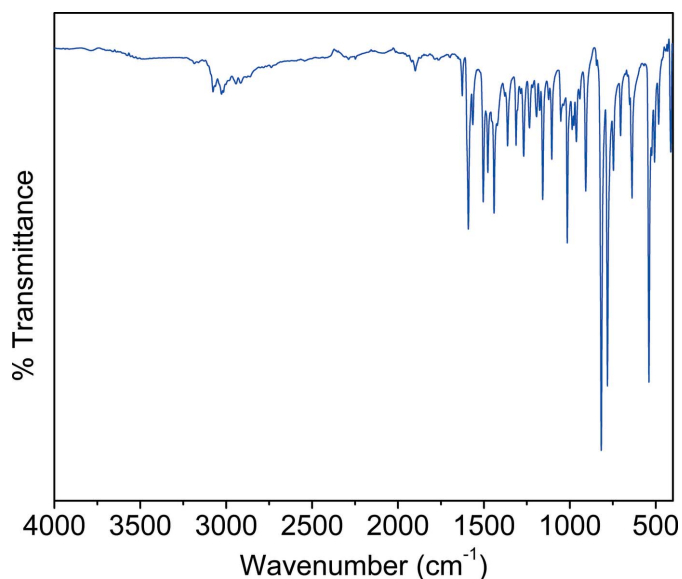

Figure 6

Two-dimensional fingerprint plots of the title compound **1**, showing (a) all interactions, and those delineated into (b) H...H, (c) H...C/C...H, (d) H...O/O...H, (e) H...S/S...H, (f) O...C/C...O, (g) S...C/C...S, (h) C...C, (i) S...S, and (j) O...O contacts [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

carboxylate groups. The bands at 705 and 750 cm^{-1} can be assigned to C—S stretching vibrations.

6. Thermal stability

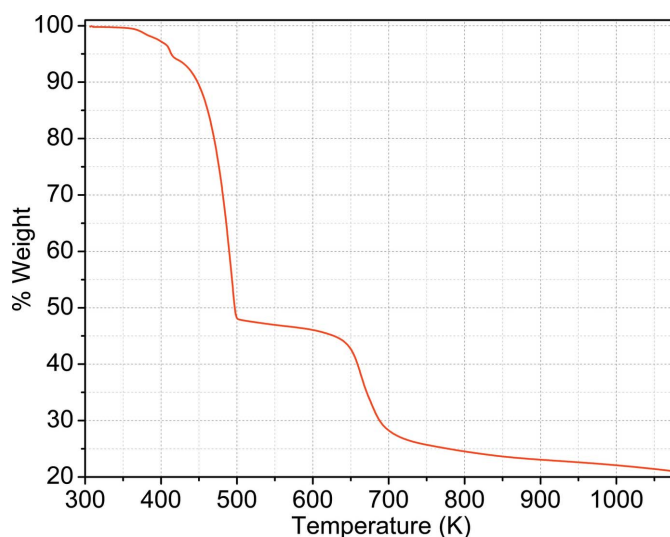
The thermal stability of the title compound **1** was studied by thermogravimetric analysis (TGA). The sample was studied on TGA55 TA Instrument from room temperature to 1073 K under a N_2 atmosphere (heating rate of $10^\circ\text{C min}^{-1}$). As shown in Fig. 8, the TGA curve of **1** displays two steps of weight loss. The first weight loss of 52.1% from 325–500 K can be ascribed to the removal of water and Htpa molecules (calculated 50.7%). Then the structure begins to collapse at around 630 K.


Figure 7

IR spectrum of the title compound **1**.

7. Database survey

A ConQuest search for the metal complexes bearing the thiopheneacrylate ligand in the Cambridge Structural Database (CSD version 5.42, September 2021 update; Bruno *et al.*, 2002; Groom *et al.*, 2016) resulted in ten hits, namely, the complexes with the Mo^{V} ion (GAKPUF, Vrdoljak *et al.*, 2010; DAMRUG, Alberding *et al.*, 2011), Sb^{V} ion (GIFPET, GIFPIX, Sarwar *et al.*, 2018), Sn^{IV} ion (NUJGII, Danish *et al.*, 1996; RIWBII, Parvez *et al.*, 1997; TEDTIF, TEDTOL, Danish *et al.*, 1995), Ga^{III} ion (YUWCAV, Uhl *et al.*, 2010), and Pd^{II} ion (ZIJNAK, Vasseur *et al.*, 2018). In these complexes, the tpa ligand displays four distinct coordination modes with the carboxylate anions being monodentate $\mu_1\text{-}\kappa^1\text{O}$ (GIFPET, GIFPIX), bidentate chelating $\mu_1\text{-}\kappa^2\text{O},\text{O}'$ (RIWBII, ZIJNAK, similar to that found in the title compound **1**) and $\mu_2\text{-}\kappa\text{O}:\kappa\text{O}$


Figure 8

TGA curve of the title compound **1**.

(DAMRUG, GAKPUF, NUJGII, YUWCAV), or bidentate bridging μ_2 - $\kappa O:\kappa O'$ (TEDTIF, TEDTOL). In addition, 69 hits for lanthanide complexes with the $[Ln(\text{COO})_3(\text{H}_2\text{O})_3]$ coordination sphere similar to that in the title compound **1** were found. Twelve of them *viz.* CSD refcodes HIVCEW, HIVCIA, HIVCOG, HIVCUM, HIVDAT (Marques *et al.*, 2013), LOMNAE (Tsaryuk *et al.*, 2014), VUSGIZ, VUSGOF, VUSGUL (Zeng & Pan, 1992), XILLUA (Kameshwar *et al.*, 2007a), XILNUC (Kameshwar *et al.*, 2007b), and YENHOO (Rzaczynska & Belskii, 1994) crystallized in the trigonal system with space group *R*3, and the central Ln^{3+} cation exhibiting a nine-coordinated tricapped trigonal–prismatic (TTP) geometry.

8. Synthesis and crystallization

All reagents were purchased as analytical grade and used without further purification. The Htpa ligand (30.8 mg, 0.2 mmol) was dissolved in an isopropanol solution (2 ml) and was then added dropwise to an aqueous solution (5 ml) of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (44.61 mg, 0.1 mmol). The mixture was stirred for 1 h at room temperature and then filtered to remove any undissolved solid. The solution was slowly evaporated at room temperature. Colorless block-shaped crystals of **1** were obtained in 20% yield (8.9 mg) based on Eu^{3+} source.

9. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were refined in the riding-model approximation with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms bounded to oxygen atoms of coordinated water (O3) and carboxylic acid (O4) were located from difference-Fourier maps but were refined with distance restraints of $O-H = 0.84 \pm 0.01 \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The thiophene ring of the Htpa molecule was found to be disordered over two positions and the site occupancies of the disordered fragments were refined to 0.778 (4) and 0.222 (4). The restraints of the SADI, RIGU and FLAT commands were applied to accommodate the disordered thiophene ring.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Eu}(\text{C}_7\text{H}_5\text{O}_2\text{S})_3(\text{H}_2\text{O})_3] \cdot 3\text{C}_7\text{H}_6\text{O}_2\text{S}$
M_r	1128.05
Crystal system, space group	Trigonal, <i>R</i> 3
Temperature (K)	296
a, c (\AA)	26.5369 (6), 5.9386 (1)
V (\AA^3)	3621.72 (17)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.62
Crystal size (mm)	$0.28 \times 0.22 \times 0.12$
Data collection	
Diffractometer	Bruker D8 QUEST CMOS
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.690, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	54319, 4921, 4921
R_{int}	0.036
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.015, 0.032, 1.07
No. of reflections	4921
No. of parameters	252
No. of restraints	88
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.21, −0.25
Absolute structure	Flack x determined using 2459 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	−0.024 (2)

Computer programs: APEX4 and SAINT (Bruker, 2019), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), and OLEX2 (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structure of a new europium(III) compound based on thiopheneacrylic acid

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Computing details

Data collection: *APEX4* (Bruker, 2019); cell refinement: *SAINTE* (Bruker, 2019); data reduction: *SAINTE* (Bruker, 2019); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Olex2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

Triaquatris[3-(thiophen-2-yl)prop-2-enoato- κ^2O,O']europium(III)-3-(thiophen-2-yl)prop-2-enoic acid (1/3)

Crystal data

[Eu(C₇H₅O₂S)₃(H₂O)₃]₃C₇H₆O₂S
M_r = 1128.05
 Trigonal, *R*3
a = 26.5369 (6) Å
c = 5.9386 (1) Å
V = 3621.72 (17) Å³
Z = 3
F(000) = 1710

D_x = 1.552 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 9889 reflections
 θ = 2.7–30.4°
 μ = 1.62 mm⁻¹
T = 296 K
 Block, colourless
 0.28 × 0.22 × 0.12 mm

Data collection

Bruker D8 QUEST CMOS
 diffractometer
 Radiation source: sealed x-ray tube, Mo
 Graphite monochromator
 Detector resolution: 7.39 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
T_{min} = 0.690, *T_{max}* = 0.746

54319 measured reflections
 4921 independent reflections
 4921 reflections with *I* > 2σ(*I*)
R_{int} = 0.036
 θ_{max} = 30.6°, θ_{min} = 2.7°
h = -37→37
k = -37→37
l = -8→8

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.015
wR(*F*²) = 0.032
S = 1.07
 4921 reflections
 252 parameters
 88 restraints
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 0.9645P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.21 e Å⁻³
 Δρ_{min} = -0.25 e Å⁻³
 Extinction correction: SHELXL-2018/3
 (Sheldrick, 2015b),
 $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00059 (8)

Absolute structure: Flack x determined using
 2459 quotients $[(F^-)-(F)]/[(F^+)+(F)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: -0.024 (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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Eu1	0.333333	0.666667	0.48411 (2)	0.02639 (5)	
S1	0.36988 (4)	0.42204 (3)	0.93748 (13)	0.05608 (18)	
S2	0.07634 (8)	0.25613 (8)	0.0719 (3)	0.0619 (4)	0.778 (4)
S2A	0.0659 (6)	0.3006 (7)	-0.330 (2)	0.075 (2)	0.222 (4)
O1	0.36847 (8)	0.62424 (7)	0.7756 (3)	0.0377 (3)	
O2	0.30981 (8)	0.56296 (7)	0.5258 (3)	0.0445 (4)	
O3	0.26557 (8)	0.60435 (7)	0.2042 (3)	0.0391 (3)	
H3A	0.2574 (13)	0.5703 (7)	0.197 (5)	0.031 (7)*	
H3B	0.2612 (13)	0.6169 (12)	0.083 (3)	0.051 (8)*	
O4	0.24635 (12)	0.45449 (9)	0.3997 (5)	0.0819 (8)	
H4	0.2673 (14)	0.4894 (8)	0.436 (6)	0.077 (11)*	
O5	0.22298 (10)	0.48956 (8)	0.1065 (4)	0.0591 (5)	
C1	0.34166 (10)	0.57296 (10)	0.6978 (4)	0.0327 (4)	
C2	0.34785 (11)	0.52549 (10)	0.7943 (4)	0.0405 (5)	
H2	0.330251	0.489999	0.719057	0.049*	
C3	0.37665 (11)	0.52981 (11)	0.9802 (4)	0.0403 (5)	
H3	0.391555	0.564646	1.059115	0.048*	
C4	0.38750 (10)	0.48571 (10)	1.0746 (4)	0.0395 (5)	
C5	0.41575 (12)	0.48962 (11)	1.2707 (4)	0.0477 (6)	
H5	0.428911	0.520927	1.369331	0.057*	
C6	0.42297 (13)	0.44089 (13)	1.3086 (5)	0.0548 (7)	
H6	0.441164	0.436683	1.435195	0.066*	
C7	0.40079 (14)	0.40149 (13)	1.1425 (5)	0.0541 (7)	
H7	0.402122	0.367138	1.139609	0.065*	
C8	0.21768 (11)	0.44876 (11)	0.2140 (5)	0.0476 (6)	
C9	0.17650 (12)	0.38762 (11)	0.1581 (5)	0.0513 (6)	
H9	0.174401	0.358161	0.249464	0.062*	
C10	0.14254 (11)	0.37414 (12)	-0.0201 (5)	0.0496 (6)	
H10	0.148027	0.405028	-0.110983	0.060*	0.778 (4)
H10A	0.146668	0.403635	-0.116266	0.060*	0.222 (4)
C11	0.0978 (3)	0.3170 (2)	-0.0906 (16)	0.050 (2)	0.778 (4)
C11A	0.0989 (6)	0.3144 (9)	-0.070 (5)	0.051 (7)	0.222 (4)
C12	0.0688 (7)	0.3046 (7)	-0.282 (2)	0.080 (3)	0.778 (4)
H12	0.072978	0.332514	-0.386972	0.097*	0.778 (4)
C12A	0.0791 (12)	0.2676 (11)	0.049 (5)	0.085 (11)	0.222 (4)

H12A	0.092117	0.267347	0.194105	0.102*	0.222 (4)
C13	0.0297 (3)	0.2428 (3)	-0.3118 (14)	0.080 (2)	0.778 (4)
H13	0.007440	0.226422	-0.440497	0.095*	0.778 (4)
C13A	0.0345 (12)	0.2148 (11)	-0.063 (4)	0.063 (6)	0.222 (4)
H13A	0.016090	0.177634	-0.001909	0.076*	0.222 (4)
C14	0.0292 (4)	0.2116 (4)	-0.1301 (15)	0.073 (2)	0.778 (4)
H14	0.006362	0.171352	-0.117203	0.087*	0.778 (4)
C14A	0.0245 (10)	0.2287 (9)	-0.269 (5)	0.075 (8)	0.222 (4)
H14A	-0.002560	0.201670	-0.368413	0.090*	0.222 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.02863 (5)	0.02863 (5)	0.02191 (6)	0.01432 (3)	0.000	0.000
S1	0.0759 (5)	0.0441 (3)	0.0540 (4)	0.0343 (3)	-0.0218 (3)	-0.0081 (3)
S2	0.0656 (9)	0.0470 (7)	0.0633 (8)	0.0208 (6)	-0.0086 (6)	-0.0082 (5)
S2A	0.067 (4)	0.078 (4)	0.069 (5)	0.029 (3)	-0.032 (3)	-0.025 (3)
O1	0.0486 (10)	0.0343 (8)	0.0331 (8)	0.0229 (7)	-0.0127 (7)	-0.0072 (6)
O2	0.0589 (10)	0.0349 (8)	0.0390 (8)	0.0228 (8)	-0.0222 (7)	-0.0056 (6)
O3	0.0454 (9)	0.0355 (9)	0.0316 (8)	0.0168 (8)	-0.0122 (7)	0.0017 (7)
O4	0.0987 (18)	0.0395 (11)	0.0989 (19)	0.0282 (12)	-0.0581 (15)	-0.0183 (11)
O5	0.0659 (13)	0.0417 (10)	0.0584 (12)	0.0184 (9)	-0.0173 (10)	-0.0091 (9)
C1	0.0378 (11)	0.0333 (10)	0.0296 (10)	0.0197 (9)	-0.0047 (8)	-0.0011 (8)
C2	0.0485 (13)	0.0355 (11)	0.0410 (11)	0.0236 (10)	-0.0105 (10)	-0.0018 (9)
C3	0.0484 (13)	0.0383 (11)	0.0400 (12)	0.0260 (10)	-0.0104 (10)	-0.0042 (9)
C4	0.0435 (12)	0.0381 (11)	0.0391 (11)	0.0220 (10)	-0.0072 (9)	0.0003 (9)
C5	0.0566 (15)	0.0428 (13)	0.0455 (13)	0.0264 (12)	-0.0154 (11)	-0.0030 (10)
C6	0.0565 (16)	0.0552 (15)	0.0552 (15)	0.0298 (13)	-0.0139 (12)	0.0118 (12)
C7	0.0628 (17)	0.0456 (14)	0.0621 (17)	0.0333 (13)	-0.0067 (14)	0.0098 (12)
C8	0.0432 (13)	0.0411 (12)	0.0607 (15)	0.0229 (11)	-0.0098 (11)	-0.0137 (11)
C9	0.0528 (15)	0.0400 (13)	0.0625 (17)	0.0243 (12)	-0.0142 (12)	-0.0133 (11)
C10	0.0483 (14)	0.0447 (13)	0.0571 (15)	0.0242 (11)	-0.0070 (11)	-0.0108 (11)
C11	0.049 (4)	0.046 (2)	0.054 (3)	0.022 (2)	-0.009 (3)	-0.009 (2)
C11A	0.025 (9)	0.058 (6)	0.069 (15)	0.019 (6)	-0.010 (8)	-0.028 (8)
C12	0.073 (5)	0.065 (4)	0.069 (5)	0.008 (4)	-0.025 (4)	-0.012 (4)
C12A	0.090 (17)	0.054 (8)	0.083 (15)	0.014 (8)	-0.008 (10)	-0.023 (8)
C13	0.055 (3)	0.074 (5)	0.070 (3)	0.003 (3)	-0.021 (2)	-0.018 (3)
C13A	0.063 (11)	0.051 (7)	0.074 (15)	0.027 (7)	-0.002 (9)	-0.016 (7)
C14	0.058 (3)	0.055 (3)	0.073 (5)	0.003 (2)	-0.002 (3)	-0.018 (3)
C14A	0.061 (12)	0.026 (7)	0.096 (15)	-0.011 (6)	-0.021 (10)	-0.002 (7)

Geometric parameters (Å, °)

Eu1—O1 ⁱ	2.4868 (16)	C3—C4	1.451 (3)
Eu1—O1 ⁱⁱ	2.4868 (16)	C4—C5	1.361 (3)
Eu1—O1	2.4868 (16)	C5—H5	0.9300
Eu1—O2 ⁱⁱ	2.5113 (16)	C5—C6	1.417 (4)
Eu1—O2	2.5112 (16)	C6—H6	0.9300

Eu1—O2 ⁱ	2.5113 (16)	C6—C7	1.340 (4)
Eu1—O3 ⁱ	2.3996 (15)	C7—H7	0.9300
Eu1—O3 ⁱⁱ	2.3997 (15)	C8—C9	1.471 (3)
Eu1—O3	2.3997 (15)	C9—H9	0.9300
S1—C4	1.716 (2)	C9—C10	1.318 (4)
S1—C7	1.703 (3)	C10—H10	0.9300
S2—C11	1.715 (9)	C10—H10A	0.9300
S2—C14	1.710 (7)	C10—C11	1.443 (6)
S2A—C11A	1.72 (3)	C10—C11A	1.452 (17)
S2A—C14A	1.70 (2)	C11—C12	1.322 (14)
O1—C1	1.266 (3)	C11A—C12A	1.29 (3)
O2—O4 ⁱⁱⁱ	11.564 (3)	C12—H12	0.9300
O2—C1	1.266 (3)	C12—C13	1.446 (15)
O3—H3A	0.818 (13)	C12A—H12A	0.9300
O3—H3B	0.826 (13)	C12A—C13A	1.47 (3)
O4—H4	0.836 (14)	C13—H13	0.9300
O4—C8	1.305 (3)	C13—C14	1.358 (9)
O5—C8	1.203 (3)	C13A—H13A	0.9300
C1—C2	1.466 (3)	C13A—C14A	1.34 (2)
C2—H2	0.9300	C14—H14	0.9300
C2—C3	1.315 (3)	C14A—H14A	0.9300
C3—H3	0.9300		
O1 ⁱ —Eu1—O1 ⁱⁱ	76.88 (6)	C2—C3—H3	116.7
O1 ⁱ —Eu1—O1	76.88 (6)	C2—C3—C4	126.5 (2)
O1 ⁱⁱ —Eu1—O1	76.88 (6)	C4—C3—H3	116.7
O1—Eu1—O2 ⁱⁱ	79.32 (6)	C3—C4—S1	123.01 (17)
O1—Eu1—O2 ⁱ	126.87 (6)	C5—C4—S1	110.47 (18)
O1 ⁱⁱ —Eu1—O2	126.87 (6)	C5—C4—C3	126.4 (2)
O1 ⁱ —Eu1—O2 ⁱ	51.62 (5)	C4—C5—H5	123.6
O1 ⁱⁱ —Eu1—O2 ⁱⁱ	51.62 (5)	C4—C5—C6	112.8 (2)
O1 ⁱⁱ —Eu1—O2 ⁱ	79.33 (6)	C6—C5—H5	123.6
O1—Eu1—O2	51.62 (5)	C5—C6—H6	123.6
O1 ⁱ —Eu1—O2	79.33 (6)	C7—C6—C5	112.8 (2)
O1 ⁱ —Eu1—O2 ⁱⁱ	126.87 (6)	C7—C6—H6	123.6
O2 ⁱⁱ —Eu1—O2	119.037 (14)	S1—C7—H7	124.1
O2 ⁱ —Eu1—O2	119.040 (14)	C6—C7—S1	111.7 (2)
O2 ⁱ —Eu1—O2 ⁱⁱ	119.038 (14)	C6—C7—H7	124.1
O3 ⁱ —Eu1—O1	157.80 (6)	O4—C8—C9	112.8 (2)
O3 ⁱ —Eu1—O1 ⁱⁱ	91.68 (6)	O5—C8—O4	123.0 (2)
O3 ⁱⁱ —Eu1—O1 ⁱⁱ	119.45 (5)	O5—C8—C9	124.1 (3)
O3 ⁱⁱ —Eu1—O1 ⁱ	157.80 (6)	C8—C9—H9	119.6
O3—Eu1—O1 ⁱⁱ	157.80 (6)	C10—C9—C8	120.7 (3)
O3 ⁱⁱ —Eu1—O1	91.68 (6)	C10—C9—H9	119.7
O3—Eu1—O1	119.45 (5)	C9—C10—H10	116.2
O3—Eu1—O1 ⁱ	91.68 (6)	C9—C10—H10A	119.2
O3 ⁱ —Eu1—O1 ⁱ	119.45 (5)	C9—C10—C11	127.5 (5)
O3—Eu1—O2 ⁱⁱ	141.12 (6)	C9—C10—C11A	121.6 (13)

O3—Eu1—O2	67.86 (5)	C11—C10—H10	116.2
O3 ⁱⁱ —Eu1—O2 ⁱⁱ	67.86 (5)	C11A—C10—H10A	119.2
O3 ⁱⁱ —Eu1—O2 ⁱ	141.12 (6)	C10—C11—S2	122.5 (7)
O3 ⁱ —Eu1—O2	141.12 (6)	C12—C11—S2	111.9 (8)
O3 ⁱ —Eu1—O2 ⁱ	67.86 (5)	C12—C11—C10	125.6 (10)
O3 ⁱⁱ —Eu1—O2	78.67 (7)	C10—C11A—S2A	117 (2)
O3 ⁱ —Eu1—O2 ⁱⁱ	78.67 (7)	C12A—C11A—S2A	111.6 (16)
O3—Eu1—O2 ⁱ	78.67 (7)	C12A—C11A—C10	131 (3)
O3 ⁱ —Eu1—O3 ⁱⁱⁱ	77.30 (7)	C11—C12—H12	123.7
O3—Eu1—O3 ⁱⁱ	77.30 (7)	C11—C12—C13	112.6 (12)
O3 ⁱ —Eu1—O3	77.30 (7)	C13—C12—H12	123.7
C7—S1—C4	92.19 (13)	C11A—C12A—H12A	122.7
C14—S2—C11	92.3 (5)	C11A—C12A—C13A	115 (3)
C14A—S2A—C11A	91.3 (14)	C13A—C12A—H12A	122.7
C1—O1—Eu1	95.50 (12)	C12—C13—H13	123.9
Eu1—O2—O4 ⁱⁱⁱ	150.31 (5)	C14—C13—C12	112.2 (8)
C1—O2—Eu1	94.35 (13)	C14—C13—H13	123.9
C1—O2—O4 ⁱⁱⁱ	109.24 (13)	O3 ⁱⁱ —C13A—H13A	143.0
Eu1—O3—H3A	119 (2)	C12A—C13A—H13A	125.4
Eu1—O3—H3B	122 (2)	C14A—C13A—C12A	109 (2)
H3A—O3—H3B	113 (3)	C14A—C13A—H13A	125.4
C8—O4—H4	112 (3)	S2—C14—H14	124.6
O1—C1—C2	122.4 (2)	C13—C14—S2	110.8 (6)
O2—C1—O1	118.50 (19)	C13—C14—H14	124.6
O2—C1—C2	119.0 (2)	S2A—C14A—H14A	123.3
C1—C2—H2	117.9	C13A—C14A—S2A	113 (2)
C3—C2—C1	124.3 (2)	C13A—C14A—H14A	123.3
C3—C2—H2	117.9		
Eu1—O1—C1—O2	-1.5 (2)	C7—S1—C4—C3	175.6 (2)
Eu1—O1—C1—C2	176.2 (2)	C7—S1—C4—C5	-0.3 (2)
Eu1—O2—C1—O1	1.5 (2)	C8—C9—C10—C11	-176.2 (4)
Eu1—O2—C1—C2	-176.33 (19)	C8—C9—C10—C11A	-175.8 (6)
S1—C4—C5—C6	0.0 (3)	C9—C10—C11—S2	7.3 (6)
S2—C11—C12—C13	-4.1 (14)	C9—C10—C11—C12	-172.7 (10)
S2A—C11A—C12A—C13A	0.4 (6)	C9—C10—C11A—S2A	-169.2 (7)
O1—C1—C2—C3	6.8 (4)	C9—C10—C11A—C12A	11.0 (8)
O2—C1—C2—C3	-175.5 (3)	C10—C11—C12—C13	175.8 (6)
O3 ⁱⁱ —C13A—C14A—S2A	-5.5 (5)	C10—C11A—C12A—C13A	-179.8 (3)
O4 ⁱⁱⁱ —O2—C1—O1	163.18 (17)	C11—S2—C14—C13	-1.1 (6)
O4 ⁱⁱⁱ —O2—C1—C2	-14.6 (2)	C11—C12—C13—C14	3.4 (14)
O4—C8—C9—C10	177.6 (3)	C11A—S2A—C14A—C13A	-0.2 (5)
O5—C8—C9—C10	0.6 (5)	C11A—C12A—C13A—O3 ⁱⁱ	18.1 (16)
C1—C2—C3—C4	-175.5 (2)	C11A—C12A—C13A—C14A	-0.5 (8)
C2—C3—C4—S1	6.9 (4)	C12—C13—C14—S2	-1.0 (9)
C2—C3—C4—C5	-177.8 (3)	C12A—C13A—C14A—S2A	0.5 (7)
C3—C4—C5—C6	-175.7 (3)	C14—S2—C11—C10	-176.9 (4)
C4—S1—C7—C6	0.6 (3)	C14—S2—C11—C12	3.1 (9)

C4—C5—C6—C7	0.4 (4)	C14A—S2A—C11A—C10	-179.9 (2)
C5—C6—C7—S1	-0.7 (4)	C14A—S2A—C11A—C12A	-0.1 (4)

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

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the S1/C4—C7 ring.

<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>
O3—H3A \cdots O5	0.82 (1)	1.94 (2)	2.729 (3)	162 (3)
O3—H3B \cdots O1 ^{iv}	0.82 (1)	1.89 (2)	2.693 (2)	165 (3)
O4—H4 \cdots O2	0.84 (1)	1.78 (2)	2.614 (3)	177 (4)
C7—H7 \cdots Cg1 ^v	0.93	3.10	3.869 (3)	141

Symmetry codes: (iv) $-x+y, -x+1, z-1$; (v) $-x+y-2/3, -x-4/3, z-1/3$.