

Syntheses and crystal structures of the cerium-based coordination polymers poly[(acetic acid)-bis(μ -5-carboxythiophene-2-carboxylato)bis(μ -thiophene-2,5-dicarboxylato)dicerium(III)] and poly[(μ -acetato)aqua(μ_4 -thiophene-2,5-dicarboxylato)cerium(III)]

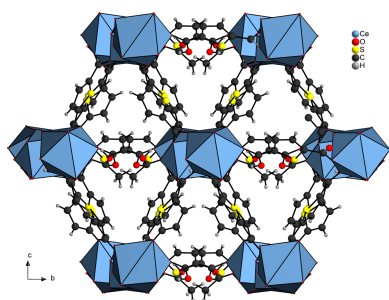
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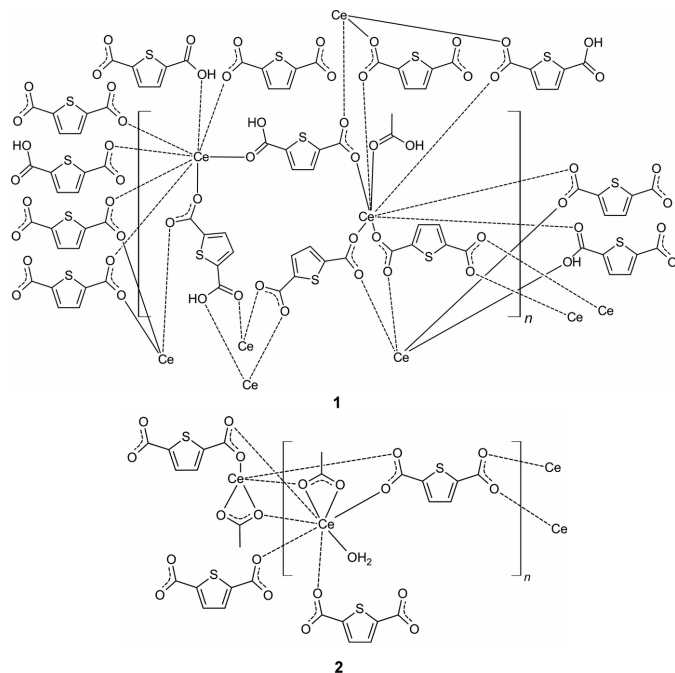
The title compounds, $[\text{Ce}_2(\text{C}_6\text{H}_3\text{SO}_4)_2(\text{C}_6\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{COOH})]_n$ (**1**) and $[\text{Ce}(\text{CH}_3\text{COO})(\text{C}_6\text{H}_2\text{SO}_4)(\text{H}_2\text{O})]_n$ (**2**) were synthesized by solvothermal reaction of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 2,5-thiophenedicarboxylic acid (H_2TDC , $\text{C}_6\text{H}_4\text{SO}_4$) and acetic acid in acetonitrile or ethanol/water, respectively. These compounds were obtained as single crystals among other crystalline phases. Both compounds belong to the family of three-dimensional coordination polymers. The asymmetric unit of **1** consists of two Ce^{III} cations, two TDC^{2-} dianions, two HTDC^- anions and one acetic acid ligand, all of them located in general positions. The two Ce^{III} cations are each coordinated by eight oxygen atoms in the form of distorted square antiprisms. These are bridged by carboxylate and carboxylic acid groups, forming mono-periodic hybrid inorganic building units (IBUs), which are connected into a three-dimensional network by the TDC^{2-} and HTDC^- ligands. Compound **2** has an asymmetric unit composed of one Ce^{III} cation, one TDC^{2-} dianion, one acetate anion and one water molecule in general positions. The cerium atom is eightfold coordinated by oxygen atoms. Edge-sharing CeO_8 polyhedra form a dinuclear IBU (Ce_2O_{14}). This IBU is bridged by six TDC^{2-} linkers to nine other IBUs, forming a three-dimensional framework. Both title compounds exhibit additional $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. Powder X-ray diffraction shows that both compounds were not obtained as pure phases.

1. Chemical context

The search for new coordination polymers (CPs) (Batten *et al.*, 2009), especially metal–organic frameworks (MOFs) (Rowsell & Yaghi, 2004; Long & Yaghi, 2009) is still a very active field of research. As a result of the variety of possible metals, as well as inorganic and organic linker molecules, there are many opportunities to discover new compounds and to modify properties and structural behaviors of existing ones. CPs contain metal atoms/ions linked by ligands that extend in one, two or three dimensions. MOFs are a subclass of CPs that exclusively contain organic ligands, called linkers, that lead to the formation of two- or three-periodic networks. In addition, MOFs have potential pores (Batten *et al.*, 2013). As a result of their porosity and large specific surface areas, MOFs have potential applications in areas such as catalysis (Hu *et al.*, 2018; Li, 2018; Lammert *et al.*, 2015), gas storage (Li *et al.*, 2019; Sahayaraj *et al.*, 2023) and sensing (Shekhah *et al.*, 2011; Wang *et al.*, 2018). The properties of MOFs can often be tuned by the selection of metal ions and organic linkers (Sahayaraj *et al.*,



2023). In the case of cerium MOFs, their redox properties can be exploited in catalytic applications (Lammert *et al.*, 2015; Smolders *et al.*, 2018, 2020).



The variety of possible reactants is matched by the variety of synthesis conditions under which these compounds can be obtained. Therefore, there are multidimensional parameter spaces to explore, which could lead to the discovery of an enormous number of new compounds. A very useful tool for the screening of large parameter spaces is high-throughput methods (Stock, 2010). High-throughput methods make use of the concepts of automation, parallelization and miniaturization. Many syntheses can be carried out under the same

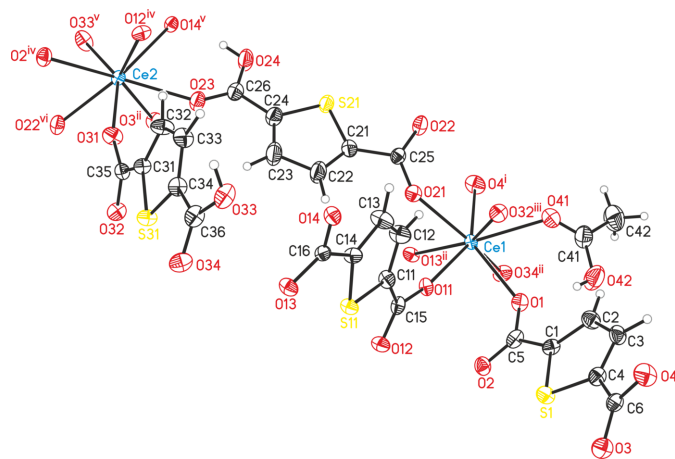


Figure 1
Crystal structure of compound **1** with atom labeling and displacement ellipsoids drawn at the 50% probability level. The HTDC[−] and TDC^{2−} fragments belonging to the oxygen atoms created by symmetry operations are omitted for clarity. Symmetry codes: (i) $-x + 1, -y + 2, z - \frac{1}{2}$; (ii) $-x + 1, -y + 1, z - \frac{1}{2}$; (iii) $x, y + 1, z$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$; (vi) $x, y - 1, z$.

Table 1
Selected bond lengths (Å) for **1**.

Ce1—O1	2.437 (5)	Ce2—O2 ^{iv}	2.481 (5)
Ce1—O4 ⁱ	2.259 (5)	Ce2—O3 ⁱⁱ	2.527 (5)
Ce1—O11	2.278 (4)	Ce2—O12 ^{iv}	2.518 (4)
Ce1—O13 ⁱⁱ	2.389 (4)	Ce2—O14 ^v	2.538 (4)
Ce1—O21	2.344 (5)	Ce2—O22 ^{vi}	2.502 (5)
Ce1—O32 ⁱⁱⁱ	2.288 (4)	Ce2—O23	2.555 (4)
Ce1—O34 ⁱⁱ	2.360 (5)	Ce2—O31	2.342 (5)
Ce1—O41	2.549 (5)	Ce2—O33 ^v	2.376 (5)

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

temperature-time program, while the influence of molar ratios of starting materials, solvent mixtures, concentration, *etc.* on the product formation can be studied simultaneously. Phase mixtures are often observed and high-throughput methods can also be used to optimize reaction conditions. In a systematic study of the chemical system Ce^{III}/2,5-thiophenedicarboxylic acid (H₂TDC) in different solvents two new CPs were discovered and structurally characterized by single crystal X-ray diffraction.

2. Structural commentary

Crystal structure of **1**

The asymmetric unit of [Ce₂(C₆H₃SO₄)₂(C₆H₂SO₄)₂(CH₃COOH)]_n (**1**) contains two Ce^{III} cations, two HTDC[−] anions, two TDC^{2−} dianions and one acetic acid molecule, all located in general positions (Fig. 1). Both Ce^{III} cations (Ce1 and Ce2) are coordinated by eight oxygen atoms, forming distorted square antiprisms. These oxygen atoms coordinating Ce1 belong to four TDC^{2−} dianions, three HTDC[−] anions and one acetic acid molecule. For Ce2, the oxygen atoms originate from four TDC^{2−} dianions and four HTDC[−] anions. While the binding mode of the carboxylate groups is exclusively bridging μ_2 -(O,O'), the binding modes of the carboxylic acid groups of HTDC[−] are monodentate μ_1 -(O) and bridging μ_2 -(O,O'). The carboxylic acid group of acetic acid exhibits the monodentate μ_1 -(O) binding mode. The Ce—O distances are in the range 2.259 (5)–2.555 (4) Å (Table 1). The binding modes of the ligands lead to an IBU consisting of CeO₈ polyhedra, which are bridged by carboxylate and carboxylic acid groups of TDC^{2−} and HTDC[−] anions, forming a monoperiodic chain extending along the crystallographic *a*-axis direction (Fig. 2).

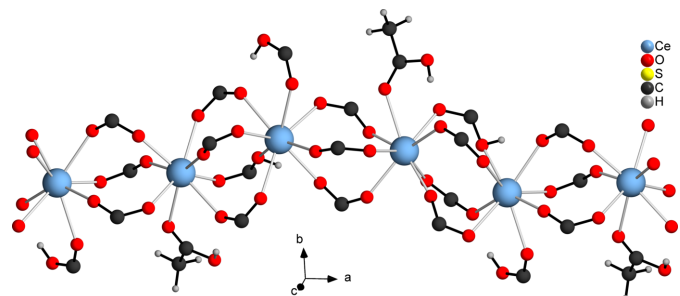


Figure 2
Monoperiodic chain of **1** composed of Ce^{III} cations, carboxylate groups and carboxylic acid groups.

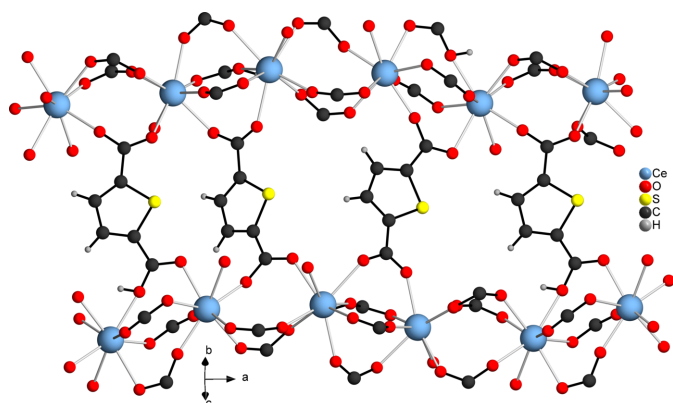


Figure 3
Connection of the monoperiodic chains of **1** by the TDC^{2-} and HTDC^- anions.

Each chain is interconnected to six other chains by TDC^{2-} and HTDC^- anions (Fig. 3), resulting in a hexagonal arrangement of the chains (Fig. 4). This gives rise to a CP with a three-dimensional network. The acetic acid does not participate in the formation of the network but completes the coordination sphere of Ce1 .

Crystal structure of **2**

The asymmetric unit of $[\text{Ce}(\text{C}_6\text{H}_2\text{SO}_4)(\text{CH}_3\text{COO})(\text{H}_2\text{O})]_n$ contains one Ce^{III} cation, one CH_3COO^- anion, one TDC^{2-} dianion and one water molecule, all of which are located in general positions (Fig. 5). The Ce^{III} cation is eightfold coordinated by oxygen atoms that originate from four TDC^{2-} dianions, two acetate ions and one water molecule, forming a distorted square antiprism. The carboxylate groups of the TDC^{2-} dianions coordinate the Ce^{III} cations exclusively in the bridging $\mu_2\text{-}(O,O')$ binding mode, while for the acetate ions the bridging chelate $\mu_2\text{-}(O,O',O')$ binding mode is observed. The $\text{Ce}-\text{O}$ distances are in the range 2.406 (2)–2.621 (2) Å (Table 2). Edge-sharing of the CeO_8 polyhedra leads to a dinuclear Ce_2O_{14} IBU. Each IBU is surrounded by six TDC^{2-}

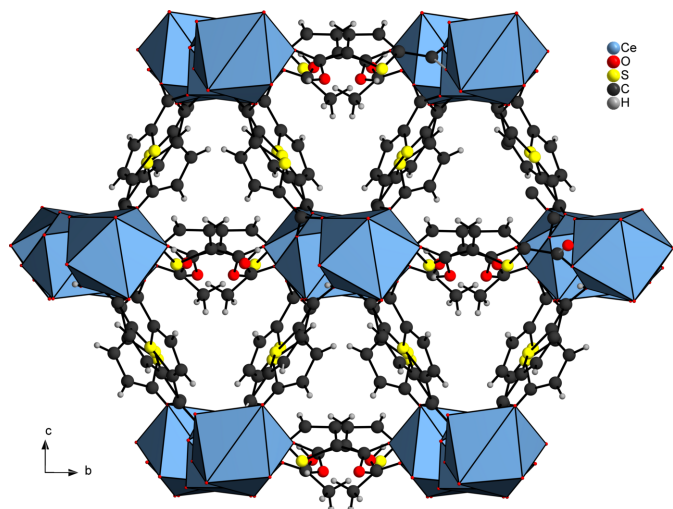


Figure 4
Crystal structure of **1** along the crystallographic a -axis. The CeO_8 units are represented by polyhedra.

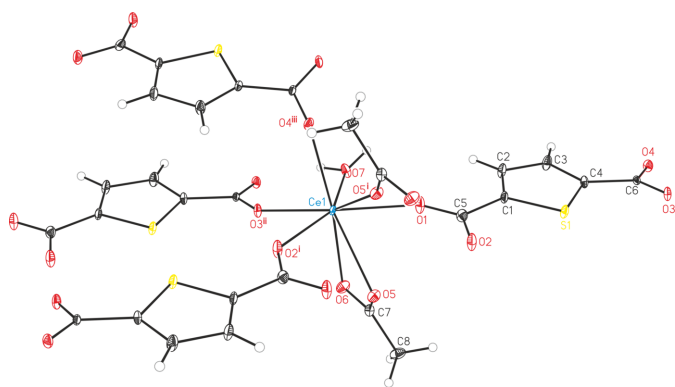


Figure 5
Crystal structure of compound **2** with atom labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z - 1$; (iii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$.

ligands (Fig. 6), which connect it to nine other IBUs, while each linker bridges three IBUs (Fig. 7). This gives rise to a CP with a three-dimensional network (Fig. 8).

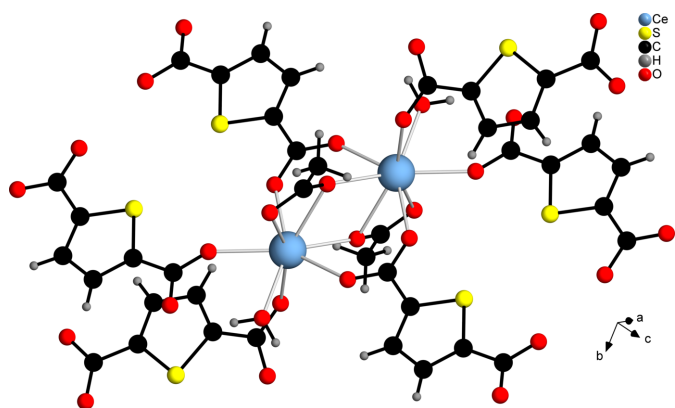


Figure 6
Connection of the CeO_8 polyhedra and the coordination of the linker molecules to the Ce_2O_{14} IBU of **2**.

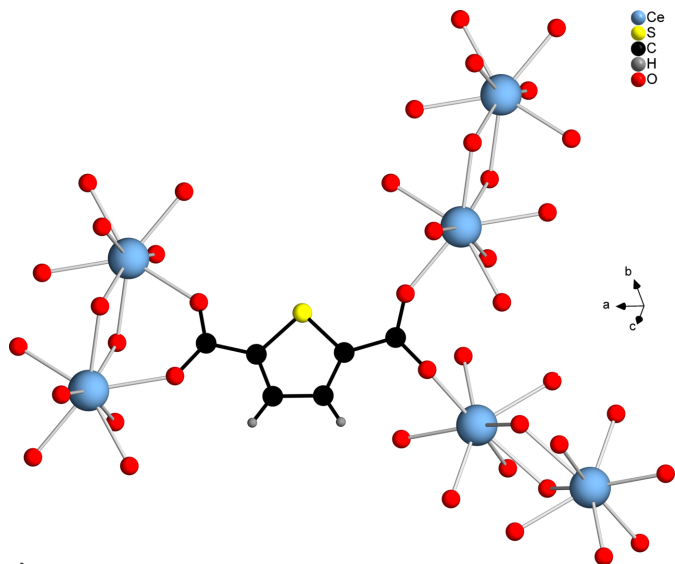


Figure 7
Bridging of three Ce_2O_{14} IBUs by one TDC^{2-} dianion in **2**.

Table 2
Selected bond lengths (Å) for **2**.

Ce1—O1	2.422 (3)	Ce1—O5	2.621 (2)
Ce1—O2 ⁱ	2.428 (3)	Ce1—O5 ⁱ	2.466 (2)
Ce1—O3 ⁱⁱⁱ	2.406 (2)	Ce1—O6	2.551 (3)
Ce1—O4 ⁱⁱⁱ	2.443 (2)	Ce1—O7	2.503 (3)

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

3. Supramolecular features

Supramolecular features of **1**

Additionally, **1** exhibits hydrogen bonds (O—H···O) between HTDC[−] and TDC^{2−} anions (O33—H33···O22 and O24—H24···O14) as well as acetic acid and TDC^{2−}

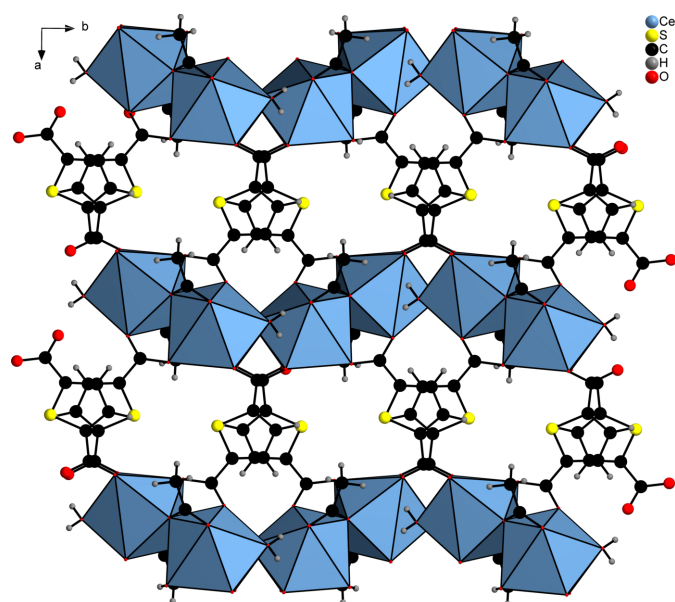


Figure 8
Crystal structure of **2** along the crystallographic *c*-axis. The Ce₂O₁₄ IBUs are represented by polyhedra.

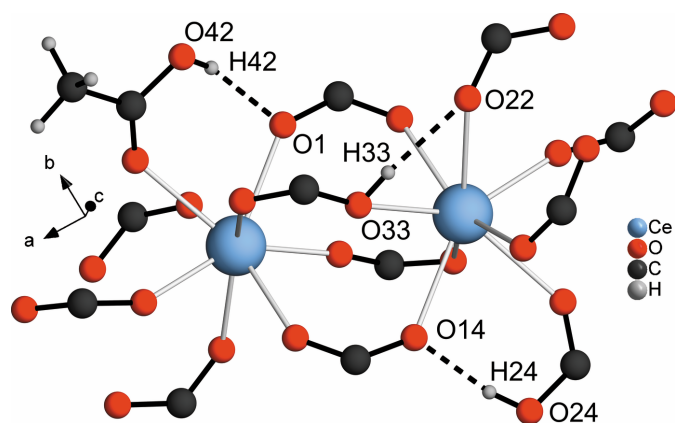


Figure 9
Hydrogen bonds in **1**. The carboxylic acid groups and carboxylate are related to HTDC[−] anions and TDC^{2−} dianions, which are not shown completely for the sake of clarity. The hydrogen bonding is shown with dashed lines.

Table 3
Hydrogen-bond geometry (Å, °) for **1**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C12—H12···O21	0.95	2.55	3.283 (8)	134
C12—H12···O32 ⁱⁱⁱ	0.95	2.55	3.329 (9)	140
O24—H24···O14 ^v	0.84	1.77	2.599 (7)	168
O33—H33···O22 ^{vii}	0.85 (3)	2.06 (5)	2.871 (7)	159 (11)
C32—H32···O12 ^{iv}	0.95	2.55	3.449 (8)	158
O42—H42···O1	0.84	1.89	2.671 (8)	155

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

Table 4
Hydrogen-bond geometry (Å, °) for **2**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C8—H8B···O3 ^{iv}	0.98	2.65	3.497 (5)	145
O7—H7A···O4 ⁱⁱ	0.86 (2)	2.02 (2)	2.829 (4)	156 (4)
O7—H7B···O6 ^v	0.85 (2)	1.95 (2)	2.795 (4)	168 (5)

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

(O42—H42···O1, Fig. 9). The H···O distances and O—H···O angles (Table 3) indicate the presence of strong hydrogen bonds (1.5–2.2 Å, 130–180°; Desiraju & Steiner, 1999). In addition, C—H···O hydrogen bonds are found, indicating the presence of weak hydrogen bonds.

Supramolecular features of **2**

In **2**, hydrogen bonds (O—H···O) are present between the hydrogen atoms of the water molecules and the TDC^{2−} (O7—H4A···O4) and the acetate anions (O7—H4B···O6). The presence of these hydrogen bonds leads to the stabilization of the network through the connection with two adjacent IBUs (Fig. 10). The H···O distances and O—H···O angles (Table 4) indicate the presence of strong hydrogen bonds (1.5–2.2 Å, 130–180°; Desiraju & Steiner, 1999). For C—H···O hydrogen bonds, only weak interactions can be assumed.

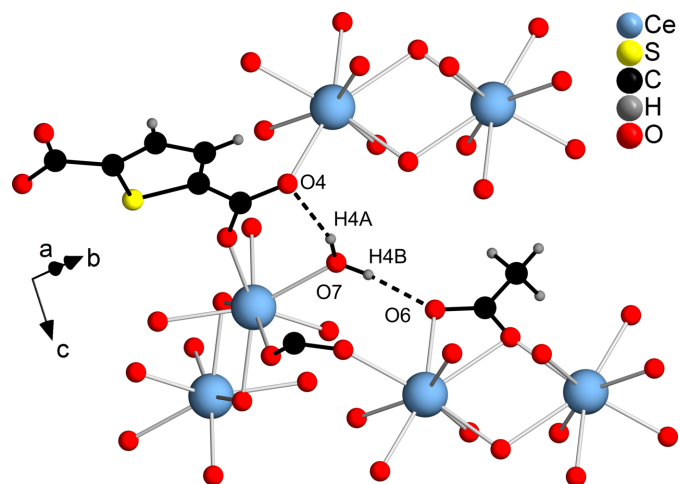


Figure 10
Hydrogen bonds in **2**. The bridging carboxylate group is related to a TDC^{2−} dianion, which was omitted for clarity. The hydrogen bonding is shown with dashed lines.

4. Database survey

A search for crystal structures containing Ce and TDC²⁻ anions in the Cambridge Structural Database (CSD version 5.45, last update September 2024; Groom *et al.*, 2016) revealed two structures containing Ce^{III} cations, namely [Ce₆(TDC)₉-(*N,N*-diethylformamide)₅(H₂O)₃]_n (refcode UMEKUU; Yawer *et al.*, 2016) and [Ce₂(TDC)₃(*N,N'*-dimethylacetamide)₂(H₂O)]_n (VUZNEM; Kumar *et al.*, 2020). Extending the search to any lanthanide cation except Ce results in 150 hits. Restricting the search to the cell parameters of **1** (reduced cell, 5% tolerance) yields nine hits with eight unique compounds, none of which is isostructural to **1**. Restricting the search to the cell parameters of **2** (reduced cell, 5% tolerance) gives 24 hits with 16 unique compounds. Eight of the compounds have the composition [Ln(TDC)(CH₃COO)(H₂O)]_n (*Ln* = Pr, Nd, Eu, Gd, Tb, Dy) (refcodes: KILCAL, KILCEP, KILCIT, KILCOZ, KILCUF, KILDAM (Ren *et al.*, 2012), KILCUF01 (Yuan *et al.*, 2022) (deposited without coordinates) and KILCUF02 (Han *et al.*, 2024)], which are isostructural to **2**. Another six results are published as [Ln(TDC)-(CH₃COO)(H₂O)]_n (*Ln* = Sm, Eu, Gd, Tb, Dy) and are also isostructural to **2** [refcodes: FEFXEF, FEFWIZ, FEFWUL, FEFWOF, FEFXAS (Han *et al.*, 2017) and FEFWIZ01 (Han *et al.*, 2020)]. Another ten results are for compounds structurally related to **2** with acetate anions being replaced by nitrate anions [Ln(TDC)(NO₃)(H₂O)]_n (*Ln* = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) [refcodes: ICOREZ, ICORID, ICOROJ, ICORUP, ICOSAW, ICOSEA, ICOSIE, ICOSOK, ICOSUO (Sun *et al.*, 2011) and ICOROJ01 (Adcock *et al.*, 2018)].

5. Synthesis and crystallization

Synthesis of **1**

Single crystals of the title compound were obtained by applying the high-throughput method as described in the literature with our custom-made high-throughput setup (Radke *et al.*, 2023) and were placed in a Memmert UFP400 oven. 36.7 mg (0.21332 mmol) of H₂TDC (abcr, 97%) were inserted into a 2 mL Teflon vial. 80 µL (0.0640 mmol) of Ce(NO₃)₃·6H₂O [abcr, 99.9% Ce (REO)] in acetonitrile (*c* = 0.1333 mol L⁻¹), 320 µL of acetonitrile and 610 µL of acetic acid were added. The reactor was sealed, placed in an oven and heated to 423 K within 1 h. This temperature was held for 3 h and afterwards the reactor was cooled down to room temperature within 1 h. The reaction mixture was filtered off and washed three times with 3 mL of acetonitrile and dried under air. Comparison of the experimental powder pattern of **1** with that calculated from single crystal data reveal that this batch is contaminated with a very small amount of an unknown crystalline phase (Fig. 11).

Synthesis of **2**

Single crystals of the title compound were obtained by applying the high-throughput method mentioned above. Different amounts of H₂O, EtOH and acetic acid were used to synthesize single crystals suitable for single-crystal X-ray diffraction (sample *A*) and the product containing larger

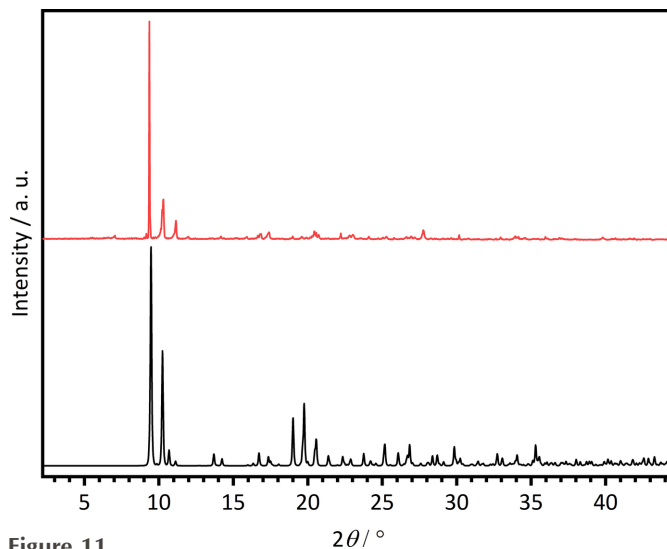


Figure 11
Comparison of the calculated (black) PXRd pattern with the measured one (red) of **1**.

amounts of **2** (sample *B*). In both syntheses, 9.2 mg (0.0533 mmol) of H₂TDC (abcr, 97%) were inserted into a 2 mL Teflon vial and 400 µL (0.0533 mmol) of Ce(NO₃)₃·6H₂O [abcr, 99.9% Ce (REO)] in H₂O/EtOH (68:32) (*c* = 0.1333 mol L⁻¹) were used. For sample *A*, 131 µL of H₂O/EtOH (68:32) and 469 µL of acetic acid, and for sample *B*, 470 µL of H₂O/EtOH (68:32) and 130 µL of acetic acid were added. The reactor was sealed, placed in an oven and heated to 423 K within 24 h. This temperature was held for 192 h and afterwards the reactor was cooled down to room temperature within 48 h. The reaction mixture was filtered off and washed with H₂O/EtOH (68:32) and dried in air. Compound **2** was not obtained phase pure, as demonstrated by powder X-ray diffraction (Fig. 12). While sample *A* contained single crystals with large amounts of unidentified byproduct, the majority of sample *B* can be assigned to microcrystalline **2**.

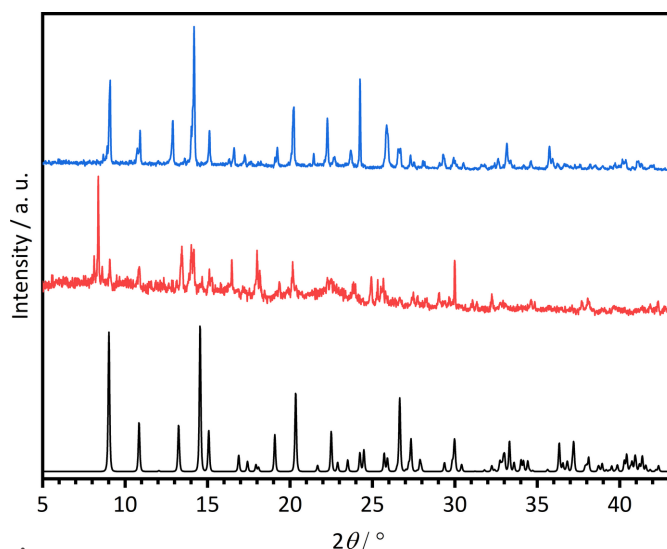


Figure 12
Comparison of the calculated (black) PXRd pattern with the measured ones from sample *A* (red) and sample *B* (blue) of **2**.

Table 5
Experimental details.

	1	2
Crystal data		
Chemical formula	[Ce ₂ (C ₆ H ₃ O ₄ S) ₂ (C ₆ H ₂ OS) ₂ (C ₂ H ₄ O ₂)]	[Ce(C ₂ H ₃ O ₂)(C ₆ H ₂ O ₄ S)(H ₂ O)]
<i>M_r</i>	1022.85	387.32
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.91596 (13), 11.08917 (9), 17.25666 (13)	10.0310 (1), 14.6755 (1), 7.6765 (1)
α , β , γ (°)	90, 90, 90	90, 102.354 (1), 90
<i>V</i> (Å ³)	3428.43 (5)	1103.89 (2)
<i>Z</i>	4	4
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α
μ (mm ⁻¹)	23.23	33.89
Crystal size (mm)	0.08 × 0.08 × 0.03	0.12 × 0.10 × 0.08
Data collection		
Diffractometer	XtaLAB Synergy, Dualflex, HyPix	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T</i> _{min} , <i>T</i> _{max}	0.601, 1.000	0.301, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	29513, 7126, 7101	13515, 2360, 2349
<i>R</i> _{int}	0.022	0.025
(sin θ/λ) _{max} (Å ⁻¹)	0.637	0.639
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.067, 1.05	0.027, 0.077, 1.15
No. of reflections	7126	2360
No. of parameters	458	162
No. of restraints	2	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.43, -1.05	1.43, -1.30
Absolute structure	Refined as an inversion twin	—
Absolute structure parameter	0.491 (4)	—

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2014/4* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 1999), *XP* in *SHELXL-PC* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Experimental details

The powder X-ray diffraction patterns were collected on a Stoe Stadi P with a MYTHEN2 1K detector and Cu *K*α1 radiation.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5.

Refinement of 1

The C—H H atoms were located in difference maps but were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with *U*_{iso}(H) = 1.2*U*_{eq}(C) (1.5 for methyl H atoms) using a riding model. The O—H H atoms at O24 and O42 were clearly located in difference maps but were finally positioned with idealized geometry, allowed to rotate but not to tip and were refined with *U*_{iso}(H) = 1.5*U*_{eq}(O) using a riding model. It is noted that some electron density is also found close to O1, which make a hydrogen bond to O42. Because the O...O distance between O42 and O1 is relatively short and the C—O distances C41—O42 and C5—O1 are clearly elongated, it cannot be excluded that the H atom is disordered over both sites. Considering these two H atoms, one must assume that compound **1** is a mixed-valence compound, consisting of Ce^{III} and Ce^{IV}, but bond-valence calculations using *PLATON*

(Spek, 2009) leads to very similar values for both Ce centers, which deviate only slightly from that expected for Ce^{III}. Moreover, because this compound was not obtained as a pure phase, this cannot experimentally proven. Therefore, we assumed that the oxidation state is retained during the synthesis and in this case, one O—H H atom is missing for charge balance. In this context, it is noted that no reasonable electron density was found close to O atoms for carboxylate groups where the C—O distances are slightly different, but for one carboxylate group that shows comparable C—O bond lengths, a reasonable electron density maxima is observed at O33, which would make a hydrogen bond to O22. If an H atom is assigned to this maximum, the corresponding H atom can be refined isotropically, leading to a reasonable temperature factor. This leads to an elongated O—H distance, which indicates that the situation is similar to that between O1 and O42, where the H atom might be disordered. Therefore, the H atom at O33 (H33) was refined with restraints. Finally, it is noted that all carboxylate O atoms except O24 and O42 are coordinated to Ce cations, which might be responsible for the fact that in this case the C—O bond lengths are slightly elongated and not very different. This might also be responsible for the problems in the location of the final H atom and it can also not be excluded that the H atoms are disordered over at least two different sites.

The crystal is twinned by inversion and therefore, a twin-refinement was performed [BASF parameter: 0.491 (4)].

Refinement of 2

The C—H H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model. The O—H H atoms were located in difference maps and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ using restraints.

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Syntheses and crystal structures of the cerium-based coordination polymers poly[(acetic acid)bis(μ -5-carboxythiophene-2-carboxylato)bis(μ -thiophene-2,5-dicarboxylato)dicerium(III)] and poly[(μ -acetato)aqua(μ_4 -thiophene-2,5-dicarboxylato)cerium(III)]

Niklas Ruser, Christian Näther and Norbert Stock

Computing details

Poly[(acetic acid)bis(μ -5-carboxythiophene-2-carboxylato)bis(μ -thiophene-2,5-dicarboxylato)dicerium(III)] (1)

Crystal data

[Ce₂(C₆H₃O₄S)₂(C₆H₂OS)₂(C₂H₄O₂)₂]

$M_r = 1022.85$

Orthorhombic, *Pna*2₁

$a = 17.91596$ (13) Å

$b = 11.08917$ (9) Å

$c = 17.25666$ (13) Å

$V = 3428.43$ (5) Å³

$Z = 4$

$F(000) = 1976$

$D_x = 1.982$ Mg m⁻³

Cu *K* α radiation, $\lambda = 1.54184$ Å

Cell parameters from 25594 reflections

$\theta = 2.5$ – 78.6°

$\mu = 23.23$ mm⁻¹

$T = 100$ K

Block, red

$0.08 \times 0.08 \times 0.03$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.601$, $T_{\max} = 1.000$

29513 measured reflections

7126 independent reflections

7101 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 79.4^\circ$, $\theta_{\min} = 4.7^\circ$

$h = -12 \rightarrow 20$

$k = -13 \rightarrow 14$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.067$

$S = 1.05$

7126 reflections

458 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 4.6448P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.43$ e Å⁻³

$\Delta\rho_{\min} = -1.05$ e Å⁻³

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.491 (4)

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. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ce1	0.46380 (2)	0.80027 (2)	0.28586 (2)	0.01453 (8)
Ce2	0.18976 (2)	−0.15909 (3)	0.29904 (2)	0.01616 (8)
O1	0.5601 (3)	0.9287 (4)	0.3419 (3)	0.0244 (9)
O2	0.6600 (3)	0.8289 (4)	0.3874 (3)	0.0262 (10)
O3	0.7403 (3)	1.0927 (5)	0.6792 (3)	0.0284 (10)
O4	0.6311 (3)	1.1855 (5)	0.7001 (3)	0.0324 (11)
S1	0.68606 (9)	0.97752 (15)	0.52658 (9)	0.0247 (3)
C1	0.6206 (3)	0.9991 (6)	0.4542 (4)	0.0213 (12)
C2	0.5756 (4)	1.0967 (6)	0.4703 (4)	0.0273 (14)
H2	0.537576	1.124358	0.436258	0.033*
C3	0.5914 (4)	1.1509 (6)	0.5416 (4)	0.0257 (13)
H3	0.564755	1.218090	0.561729	0.031*
C4	0.6500 (4)	1.0959 (6)	0.5794 (4)	0.0229 (13)
C5	0.6152 (4)	0.9125 (6)	0.3899 (4)	0.0231 (12)
C6	0.6772 (4)	1.1245 (6)	0.6581 (4)	0.0210 (12)
O11	0.5337 (2)	0.6800 (4)	0.3645 (3)	0.0192 (9)
O12	0.6233 (2)	0.5628 (4)	0.4117 (3)	0.0242 (9)
O13	0.5094 (2)	0.3635 (4)	0.7003 (3)	0.0215 (9)
O14	0.4058 (2)	0.4679 (4)	0.7275 (2)	0.0200 (8)
S11	0.54976 (8)	0.49323 (13)	0.55758 (8)	0.0202 (3)
C11	0.5132 (4)	0.5817 (6)	0.4845 (4)	0.0218 (12)
C12	0.4420 (4)	0.6152 (7)	0.4994 (4)	0.0299 (14)
H12	0.412376	0.661448	0.464759	0.036*
C13	0.4165 (4)	0.5740 (7)	0.5722 (4)	0.0301 (15)
H13	0.368422	0.591469	0.592429	0.036*
C14	0.4687 (3)	0.5061 (6)	0.6106 (4)	0.0198 (12)
C15	0.5601 (4)	0.6078 (5)	0.4161 (3)	0.0197 (12)
C16	0.4612 (3)	0.4414 (6)	0.6848 (4)	0.0172 (12)
O21	0.3820 (3)	0.6444 (4)	0.3206 (3)	0.0239 (10)
O22	0.2682 (3)	0.6609 (4)	0.2674 (3)	0.0276 (11)
O23	0.2292 (3)	0.0610 (4)	0.3147 (3)	0.0299 (11)
O24	0.1564 (4)	0.1784 (5)	0.2421 (4)	0.0438 (15)
H24	0.130628	0.115383	0.238411	0.066*
S21	0.23213 (9)	0.40527 (14)	0.26857 (10)	0.0277 (3)
C21	0.3077 (4)	0.4717 (6)	0.3126 (4)	0.0276 (14)
C22	0.3471 (5)	0.3929 (7)	0.3566 (6)	0.044 (2)
H22	0.390305	0.414617	0.385313	0.053*
C23	0.3170 (5)	0.2748 (7)	0.3551 (6)	0.044 (2)

H23	0.337410	0.208507	0.382821	0.053*
C24	0.2546 (4)	0.2677 (6)	0.3087 (4)	0.0303 (14)
C25	0.3202 (3)	0.6025 (5)	0.2991 (4)	0.0219 (11)
C26	0.2124 (4)	0.1592 (5)	0.2890 (5)	0.0287 (14)
O31	0.2886 (3)	-0.1471 (4)	0.3875 (3)	0.0289 (11)
O32	0.4117 (3)	-0.1330 (4)	0.3991 (3)	0.0252 (9)
O33	0.3789 (3)	0.2171 (4)	0.7121 (3)	0.0297 (11)
H33	0.334 (2)	0.193 (9)	0.717 (7)	0.044*
O34	0.4761 (3)	0.1068 (5)	0.6798 (3)	0.0279 (10)
S31	0.41620 (8)	-0.01107 (14)	0.54570 (9)	0.0223 (3)
C31	0.3376 (3)	-0.0379 (6)	0.4919 (3)	0.0182 (11)
C32	0.2764 (4)	0.0208 (7)	0.5203 (4)	0.0271 (14)
H32	0.227951	0.015883	0.498103	0.032*
C33	0.2940 (4)	0.0900 (6)	0.5868 (4)	0.0265 (14)
H33A	0.258660	0.137317	0.614346	0.032*
C34	0.3674 (4)	0.0811 (6)	0.6069 (3)	0.0209 (12)
C35	0.3462 (4)	-0.1112 (5)	0.4215 (4)	0.0194 (12)
C36	0.4093 (4)	0.1370 (6)	0.6702 (4)	0.0247 (13)
O41	0.4239 (3)	1.0183 (5)	0.2643 (3)	0.0365 (12)
O42	0.5238 (4)	1.1350 (6)	0.2716 (5)	0.0552 (18)
H42	0.535686	1.084306	0.305602	0.083*
C41	0.4562 (5)	1.1099 (7)	0.2450 (5)	0.0397 (19)
C42	0.4262 (6)	1.2017 (9)	0.1916 (7)	0.056 (3)
H42A	0.460229	1.211191	0.147552	0.084*
H42B	0.421445	1.278750	0.218924	0.084*
H42C	0.377096	1.176024	0.172853	0.084*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.02098 (15)	0.01503 (14)	0.00758 (14)	0.00154 (9)	0.00108 (12)	0.00061 (11)
Ce2	0.02058 (15)	0.01835 (14)	0.00956 (14)	-0.00248 (10)	-0.00244 (13)	0.00005 (11)
O1	0.030 (2)	0.025 (2)	0.018 (2)	-0.0008 (18)	-0.0033 (18)	0.0006 (18)
O2	0.032 (3)	0.023 (2)	0.024 (3)	0.0029 (19)	-0.003 (2)	-0.0046 (18)
O3	0.031 (3)	0.033 (2)	0.021 (2)	0.001 (2)	-0.0032 (19)	-0.0059 (19)
O4	0.035 (3)	0.040 (3)	0.022 (3)	0.006 (2)	0.003 (2)	-0.013 (2)
S1	0.0263 (8)	0.0282 (7)	0.0195 (7)	0.0050 (6)	-0.0035 (6)	-0.0081 (6)
C1	0.021 (3)	0.027 (3)	0.015 (3)	-0.002 (2)	0.000 (2)	-0.006 (2)
C2	0.027 (3)	0.030 (3)	0.025 (3)	0.004 (3)	0.001 (3)	-0.003 (3)
C3	0.029 (3)	0.023 (3)	0.025 (3)	0.004 (2)	0.001 (3)	-0.006 (2)
C4	0.025 (3)	0.024 (3)	0.019 (3)	-0.002 (2)	0.003 (2)	-0.005 (2)
C5	0.029 (3)	0.025 (3)	0.015 (3)	-0.007 (3)	0.001 (2)	-0.001 (2)
C6	0.024 (3)	0.021 (3)	0.017 (3)	-0.002 (2)	-0.001 (2)	-0.004 (2)
O11	0.028 (2)	0.0177 (18)	0.012 (2)	0.0019 (16)	0.0016 (17)	0.0038 (17)
O12	0.020 (2)	0.030 (2)	0.022 (2)	0.0043 (18)	0.0020 (16)	0.0052 (18)
O13	0.022 (2)	0.026 (2)	0.016 (2)	0.0053 (18)	0.0021 (17)	0.0087 (17)
O14	0.024 (2)	0.0199 (19)	0.0166 (19)	0.0025 (16)	0.0033 (17)	0.0037 (17)
S11	0.0190 (6)	0.0258 (7)	0.0158 (7)	0.0035 (5)	0.0021 (5)	0.0087 (6)

C11	0.026 (3)	0.023 (3)	0.017 (3)	0.001 (2)	0.006 (2)	0.007 (2)
C12	0.026 (3)	0.039 (4)	0.025 (3)	0.004 (3)	0.003 (3)	0.015 (3)
C13	0.026 (3)	0.042 (4)	0.022 (3)	0.009 (3)	0.006 (3)	0.012 (3)
C14	0.017 (3)	0.027 (3)	0.015 (3)	-0.001 (2)	0.001 (2)	0.010 (2)
C15	0.028 (3)	0.018 (3)	0.014 (3)	-0.004 (2)	0.004 (2)	0.001 (2)
C16	0.017 (3)	0.019 (3)	0.016 (3)	-0.002 (2)	-0.0022 (19)	0.006 (2)
O21	0.026 (2)	0.025 (2)	0.020 (2)	0.0007 (16)	-0.0014 (17)	-0.0063 (17)
O22	0.036 (3)	0.021 (2)	0.025 (3)	-0.0049 (17)	-0.009 (2)	0.0027 (17)
O23	0.034 (2)	0.022 (2)	0.033 (3)	-0.0054 (18)	-0.006 (2)	0.0018 (19)
O24	0.044 (3)	0.022 (2)	0.065 (4)	-0.006 (2)	-0.024 (3)	0.006 (2)
S21	0.0290 (8)	0.0203 (6)	0.0338 (9)	-0.0040 (5)	-0.0056 (6)	0.0016 (6)
C21	0.027 (3)	0.022 (3)	0.033 (4)	0.001 (2)	-0.002 (2)	-0.001 (3)
C22	0.044 (4)	0.024 (3)	0.064 (6)	-0.007 (3)	-0.022 (4)	0.003 (3)
C23	0.049 (5)	0.023 (3)	0.060 (6)	-0.005 (3)	-0.017 (4)	0.005 (4)
C24	0.033 (3)	0.026 (3)	0.032 (4)	-0.003 (3)	-0.002 (3)	-0.001 (3)
C25	0.025 (3)	0.021 (3)	0.020 (3)	-0.002 (2)	0.000 (2)	-0.003 (3)
C26	0.030 (3)	0.025 (3)	0.032 (4)	-0.003 (2)	0.000 (3)	0.000 (3)
O31	0.028 (2)	0.032 (3)	0.027 (3)	0.0014 (19)	-0.011 (2)	-0.013 (2)
O32	0.028 (2)	0.029 (2)	0.018 (2)	-0.0017 (19)	0.0069 (18)	-0.0082 (19)
O33	0.042 (3)	0.027 (2)	0.020 (2)	-0.008 (2)	0.012 (2)	-0.0117 (19)
O34	0.027 (2)	0.036 (3)	0.021 (2)	-0.005 (2)	-0.0036 (18)	-0.007 (2)
S31	0.0204 (7)	0.0285 (7)	0.0178 (7)	0.0003 (5)	-0.0019 (5)	-0.0110 (6)
C31	0.020 (3)	0.023 (3)	0.012 (3)	-0.001 (2)	0.000 (2)	-0.005 (2)
C32	0.019 (3)	0.041 (4)	0.021 (3)	0.001 (3)	-0.004 (2)	-0.013 (3)
C33	0.029 (3)	0.027 (3)	0.023 (3)	0.004 (3)	0.005 (3)	-0.014 (3)
C34	0.026 (3)	0.024 (3)	0.013 (3)	0.000 (2)	0.000 (2)	-0.009 (2)
C35	0.024 (3)	0.019 (3)	0.016 (3)	0.001 (2)	-0.005 (2)	-0.001 (2)
C36	0.033 (4)	0.025 (3)	0.015 (3)	-0.003 (3)	0.002 (3)	-0.008 (2)
O41	0.035 (3)	0.033 (3)	0.042 (3)	0.005 (2)	-0.001 (2)	-0.001 (2)
O42	0.061 (4)	0.038 (3)	0.067 (5)	-0.013 (3)	-0.015 (3)	0.012 (3)
C41	0.050 (5)	0.030 (4)	0.039 (5)	0.000 (3)	-0.009 (3)	-0.001 (3)
C42	0.069 (7)	0.040 (5)	0.060 (7)	0.006 (4)	-0.001 (5)	0.015 (4)

Geometric parameters (Å, °)

Ce1—O1	2.437 (5)	C13—H13	0.9500
Ce1—O4 ⁱ	2.259 (5)	C13—C14	1.371 (9)
Ce1—O11	2.278 (4)	C14—C16	1.474 (8)
Ce1—O13 ⁱⁱ	2.389 (4)	O21—C25	1.257 (7)
Ce1—O21	2.344 (5)	O22—C25	1.259 (8)
Ce1—O32 ⁱⁱⁱ	2.288 (4)	O23—C26	1.214 (8)
Ce1—O34 ⁱⁱ	2.360 (5)	O24—H24	0.8400
Ce1—O41	2.549 (5)	O24—C26	1.306 (9)
Ce2—O2 ^{iv}	2.481 (5)	S21—C21	1.718 (7)
Ce2—O3 ⁱⁱ	2.527 (5)	S21—C24	1.723 (7)
Ce2—O12 ^{iv}	2.518 (4)	C21—C22	1.356 (11)
Ce2—O14 ^v	2.538 (4)	C21—C25	1.486 (8)
Ce2—O22 ^{vi}	2.502 (5)	C22—H22	0.9500

Ce2—O23	2.555 (4)	C22—C23	1.416 (10)
Ce2—O31	2.342 (5)	C23—H23	0.9500
Ce2—O33 ^v	2.376 (5)	C23—C24	1.378 (11)
O1—C5	1.301 (8)	C24—C26	1.462 (9)
O2—C5	1.226 (8)	O31—C35	1.252 (8)
O3—C6	1.240 (8)	O32—C35	1.260 (8)
O4—C6	1.290 (8)	O33—H33	0.85 (3)
S1—C1	1.730 (6)	O33—C36	1.268 (8)
S1—C4	1.724 (6)	O34—C36	1.255 (9)
C1—C2	1.377 (9)	S31—C31	1.713 (6)
C1—C5	1.470 (8)	S31—C34	1.710 (6)
C2—H2	0.9500	C31—C32	1.366 (9)
C2—C3	1.400 (9)	C31—C35	1.469 (8)
C3—H3	0.9500	C32—H32	0.9500
C3—C4	1.378 (10)	C32—C33	1.417 (9)
C4—C6	1.478 (9)	C33—H33A	0.9500
O11—C15	1.287 (8)	C33—C34	1.363 (10)
O12—C15	1.239 (8)	C34—C36	1.463 (8)
O13—C16	1.249 (7)	O41—C41	1.215 (10)
O14—C16	1.270 (7)	O42—H42	0.8400
S11—C11	1.727 (6)	O42—C41	1.324 (10)
S11—C14	1.722 (6)	C41—C42	1.475 (12)
C11—C12	1.354 (10)	C42—H42A	0.9800
C11—C15	1.478 (8)	C42—H42B	0.9800
C12—H12	0.9500	C42—H42C	0.9800
C12—C13	1.412 (9)		
O1—Ce1—O41	72.69 (16)	C16—O13—Ce1 ^{viii}	142.8 (4)
O4 ⁱ —Ce1—O1	138.75 (17)	C16—O14—Ce2 ^x	132.9 (4)
O4 ⁱ —Ce1—O11	147.65 (18)	C14—S11—C11	91.2 (3)
O4 ⁱ —Ce1—O13 ⁱⁱ	78.45 (19)	C12—C11—S11	112.0 (5)
O4 ⁱ —Ce1—O21	75.46 (18)	C12—C11—C15	129.4 (6)
O4 ⁱ —Ce1—O32 ⁱⁱⁱ	103.31 (19)	C15—C11—S11	118.6 (5)
O4 ⁱ —Ce1—O34 ⁱⁱ	78.76 (18)	C11—C12—H12	123.7
O4 ⁱ —Ce1—O41	68.09 (19)	C11—C12—C13	112.6 (6)
O11—Ce1—O1	73.52 (16)	C13—C12—H12	123.7
O11—Ce1—O13 ⁱⁱ	79.19 (16)	C12—C13—H13	123.6
O11—Ce1—O21	76.09 (16)	C14—C13—C12	112.8 (6)
O11—Ce1—O32 ⁱⁱⁱ	84.53 (17)	C14—C13—H13	123.6
O11—Ce1—O34 ⁱⁱ	117.81 (16)	C13—C14—S11	111.3 (5)
O11—Ce1—O41	142.83 (17)	C13—C14—C16	128.7 (5)
O13 ⁱⁱ —Ce1—O1	123.16 (16)	C16—C14—S11	119.9 (4)
O13 ⁱⁱ —Ce1—O41	133.41 (17)	O11—C15—C11	117.7 (6)
O21—Ce1—O1	140.50 (16)	O12—C15—O11	123.0 (6)
O21—Ce1—O13 ⁱⁱ	73.96 (16)	O12—C15—C11	119.3 (5)
O21—Ce1—O34 ⁱⁱ	143.69 (17)	O13—C16—O14	125.1 (6)
O21—Ce1—O41	124.15 (16)	O13—C16—C14	117.4 (5)
O32 ⁱⁱⁱ —Ce1—O1	76.14 (16)	O14—C16—C14	117.5 (5)

O32 ⁱⁱⁱ —Ce1—O13 ⁱⁱ	148.81 (17)	C25—O21—Ce1	138.4 (4)
O32 ⁱⁱⁱ —Ce1—O21	76.40 (16)	C25—O22—Ce2 ⁱⁱⁱ	136.9 (4)
O32 ⁱⁱⁱ —Ce1—O34 ⁱⁱ	134.98 (18)	C26—O23—Ce2	138.5 (5)
O32 ⁱⁱⁱ —Ce1—O41	72.77 (18)	C26—O24—H24	109.5
O34 ⁱⁱ —Ce1—O1	74.31 (16)	C21—S21—C24	91.0 (3)
O34 ⁱⁱ —Ce1—O13 ⁱⁱ	76.18 (17)	C22—C21—S21	112.4 (5)
O34 ⁱⁱ —Ce1—O41	66.45 (18)	C22—C21—C25	129.7 (7)
O2 ^{iv} —Ce2—O3 ⁱⁱ	146.16 (16)	C25—C21—S21	117.9 (5)
O2 ^{iv} —Ce2—O12 ^{iv}	75.25 (16)	C21—C22—H22	123.6
O2 ^{iv} —Ce2—O14 ^v	125.11 (15)	C21—C22—C23	112.8 (7)
O2 ^{iv} —Ce2—O22 ^{vi}	69.48 (17)	C23—C22—H22	123.6
O2 ^{iv} —Ce2—O23	136.00 (16)	C22—C23—H23	124.1
O3 ⁱⁱ —Ce2—O14 ^v	76.98 (15)	C24—C23—C22	111.8 (7)
O3 ⁱⁱ —Ce2—O23	70.81 (17)	C24—C23—H23	124.1
O12 ^{iv} —Ce2—O3 ⁱⁱ	137.97 (16)	C23—C24—S21	111.9 (5)
O12 ^{iv} —Ce2—O14 ^v	79.70 (15)	C23—C24—C26	127.0 (7)
O12 ^{iv} —Ce2—O23	69.15 (16)	C26—C24—S21	120.9 (5)
O14 ^v —Ce2—O23	73.03 (14)	O21—C25—O22	126.2 (5)
O22 ^{vi} —Ce2—O3 ⁱⁱ	77.01 (16)	O21—C25—C21	116.5 (6)
O22 ^{vi} —Ce2—O12 ^{iv}	140.61 (16)	O22—C25—C21	117.3 (5)
O22 ^{vi} —Ce2—O14 ^v	135.69 (15)	O23—C26—O24	124.3 (6)
O22 ^{vi} —Ce2—O23	129.04 (15)	O23—C26—C24	121.6 (7)
O31—Ce2—O2 ^{iv}	78.76 (18)	O24—C26—C24	114.0 (6)
O31—Ce2—O3 ⁱⁱ	98.17 (17)	C35—O31—Ce2	161.2 (5)
O31—Ce2—O12 ^{iv}	80.23 (17)	C35—O32—Ce1 ^{vi}	134.8 (4)
O31—Ce2—O14 ^v	142.75 (15)	Ce2 ^x —O33—H33	68 (7)
O31—Ce2—O22 ^{vi}	76.28 (16)	C36—O33—Ce2 ^x	170.6 (5)
O31—Ce2—O23	70.59 (16)	C36—O33—H33	104 (7)
O31—Ce2—O33 ^v	146.68 (17)	C36—O34—Ce1 ^{viii}	114.9 (4)
O33 ^v —Ce2—O2 ^{iv}	80.68 (18)	C34—S31—C31	91.0 (3)
O33 ^v —Ce2—O3 ⁱⁱ	84.75 (18)	C32—C31—S31	112.5 (5)
O33 ^v —Ce2—O12 ^{iv}	119.17 (16)	C32—C31—C35	130.1 (6)
O33 ^v —Ce2—O14 ^v	70.38 (15)	C35—C31—S31	117.2 (5)
O33 ^v —Ce2—O22 ^{vi}	72.06 (16)	C31—C32—H32	124.1
O33 ^v —Ce2—O23	139.62 (16)	C31—C32—C33	111.7 (6)
C5—O1—Ce1	135.2 (4)	C33—C32—H32	124.1
C5—O2—Ce2 ^{vii}	137.4 (5)	C32—C33—H33A	123.8
C6—O3—Ce2 ^{viii}	127.5 (4)	C34—C33—C32	112.5 (6)
C6—O4—Ce1 ^{ix}	152.4 (5)	C34—C33—H33A	123.8
C4—S1—C1	91.3 (3)	C33—C34—S31	112.3 (5)
C2—C1—S1	111.1 (5)	C33—C34—C36	130.8 (6)
C2—C1—C5	128.8 (6)	C36—C34—S31	116.9 (5)
C5—C1—S1	119.9 (5)	O31—C35—O32	124.2 (6)
C1—C2—H2	123.3	O31—C35—C31	118.5 (6)
C1—C2—C3	113.4 (6)	O32—C35—C31	117.3 (6)
C3—C2—H2	123.3	O33—C36—C34	120.2 (6)
C2—C3—H3	123.8	O34—C36—O33	121.4 (6)
C4—C3—C2	112.3 (6)	O34—C36—C34	118.3 (6)

C4—C3—H3	123.8	C41—O41—Ce1	134.3 (5)
C3—C4—S1	111.9 (5)	C41—O42—H42	109.5
C3—C4—C6	126.2 (6)	O41—C41—O42	121.1 (8)
C6—C4—S1	121.7 (5)	O41—C41—C42	125.0 (8)
O1—C5—C1	116.1 (6)	O42—C41—C42	113.8 (8)
O2—C5—O1	125.3 (6)	C41—C42—H42A	109.5
O2—C5—C1	118.5 (6)	C41—C42—H42B	109.5
O3—C6—O4	124.7 (6)	C41—C42—H42C	109.5
O3—C6—C4	120.6 (6)	H42A—C42—H42B	109.5
O4—C6—C4	114.7 (6)	H42A—C42—H42C	109.5
C15—O11—Ce1	168.0 (4)	H42B—C42—H42C	109.5
C15—O12—Ce2 ^{vii}	107.9 (4)		

Symmetry codes: (i) $-x+1, -y+2, z-1/2$; (ii) $-x+1, -y+1, z-1/2$; (iii) $x, y+1, z$; (iv) $x-1/2, -y+1/2, z$; (v) $-x+1/2, y-1/2, z-1/2$; (vi) $x, y-1, z$; (vii) $x+1/2, -y+1/2, z$; (viii) $-x+1, -y+1, z+1/2$; (ix) $-x+1, -y+2, z+1/2$; (x) $-x+1/2, y+1/2, z+1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12 \cdots O21	0.95	2.55	3.283 (8)	134
C12—H12 \cdots O32 ⁱⁱⁱ	0.95	2.55	3.329 (9)	140
O24—H24 \cdots O14 ^v	0.84	1.77	2.599 (7)	168
O33—H33 \cdots O22 ^{xi}	0.85 (3)	2.06 (5)	2.871 (7)	159 (11)
C32—H32 \cdots O12 ^{iv}	0.95	2.55	3.449 (8)	158
O42—H42 \cdots O1	0.84	1.89	2.671 (8)	155

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

Poly[(μ -acetato) aqua(μ_4 -thiophene-2,5-dicarboxylato) cerium(III)] (2)

Crystal data

$[\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_6\text{H}_2\text{O}_4\text{S})(\text{H}_2\text{O})]$

$M_r = 387.32$

Monoclinic, $P2_1/c$

$a = 10.0310$ (1) \AA

$b = 14.6755$ (1) \AA

$c = 7.6765$ (1) \AA

$\beta = 102.354$ (1) $^\circ$

$V = 1103.89$ (2) \AA^3

$Z = 4$

$F(000) = 740$

$D_x = 2.330$ Mg m^{-3}

Cu $K\alpha$ radiation, $\lambda = 1.54184$ \AA

Cell parameters from 10498 reflections

$\theta = 3.1\text{--}79.9^\circ$

$\mu = 33.89$ mm^{-1}

$T = 100$ K

Block, colorless

$0.12 \times 0.10 \times 0.08$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
diffractometer

Radiation source: micro-focus sealed X-ray
tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm^{-1}

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.301$, $T_{\max} = 1.000$

13515 measured reflections

2360 independent reflections

2349 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 80.3^\circ$, $\theta_{\min} = 4.5^\circ$

$h = -12 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.077$

$S = 1.15$

2360 reflections

162 parameters

3 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 2.3818P]$

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

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 1.43 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -1.30 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL2016/6*

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00097 (10)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ce1	0.39777 (2)	0.61197 (2)	0.39322 (2)	0.00537 (11)
S1	0.97823 (9)	0.62456 (6)	0.89764 (12)	0.00924 (18)
C1	0.8335 (3)	0.6693 (2)	0.7640 (5)	0.0091 (7)
C2	0.8385 (4)	0.7628 (3)	0.7551 (5)	0.0120 (7)
H2	0.766359	0.799189	0.690202	0.014*
C3	0.9626 (4)	0.7987 (2)	0.8530 (5)	0.0123 (7)
H3	0.984488	0.861789	0.859212	0.015*
C4	1.0481 (3)	0.7316 (2)	0.9386 (5)	0.0081 (6)
C5	0.7227 (4)	0.6083 (2)	0.6703 (5)	0.0102 (7)
O1	0.6225 (3)	0.64614 (19)	0.5702 (4)	0.0139 (5)
O2	0.7387 (3)	0.52357 (18)	0.6960 (4)	0.0140 (5)
C6	1.1848 (3)	0.7417 (2)	1.0561 (4)	0.0068 (6)
O3	1.2357 (2)	0.67297 (17)	1.1434 (3)	0.0102 (5)
O4	1.2436 (2)	0.81927 (17)	1.0629 (3)	0.0095 (5)
O5	0.5659 (3)	0.48401 (17)	0.3371 (3)	0.0110 (5)
O6	0.5347 (3)	0.59880 (18)	0.1501 (4)	0.0122 (5)
C7	0.6028 (3)	0.5302 (2)	0.2133 (5)	0.0077 (6)
C8	0.7282 (4)	0.5017 (3)	0.1529 (5)	0.0136 (7)
H8A	0.743427	0.542620	0.058242	0.016*
H8B	0.716894	0.439144	0.107223	0.016*
H8C	0.806844	0.504409	0.253655	0.016*
O7	0.4453 (3)	0.77851 (18)	0.3711 (3)	0.0121 (5)
H7A	0.387 (4)	0.807 (3)	0.291 (5)	0.018*
H7B	0.484 (5)	0.816 (3)	0.452 (5)	0.018*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.00288 (14)	0.00494 (15)	0.00770 (14)	0.00049 (5)	-0.00018 (9)	0.00042 (5)
S1	0.0047 (4)	0.0073 (4)	0.0142 (4)	-0.0007 (3)	-0.0013 (3)	0.0008 (3)
C1	0.0040 (15)	0.0136 (17)	0.0087 (15)	-0.0003 (12)	-0.0006 (12)	-0.0001 (12)
C2	0.0061 (16)	0.0130 (18)	0.0149 (18)	0.0005 (12)	-0.0021 (13)	0.0017 (13)
C3	0.0088 (15)	0.0073 (16)	0.0182 (17)	0.0007 (12)	-0.0025 (13)	0.0023 (13)
C4	0.0050 (15)	0.0097 (16)	0.0086 (15)	-0.0022 (12)	-0.0008 (12)	0.0006 (12)
C5	0.0076 (17)	0.0100 (18)	0.0129 (18)	-0.0026 (11)	0.0019 (14)	-0.0007 (12)
O1	0.0087 (11)	0.0122 (13)	0.0177 (13)	-0.0028 (10)	-0.0041 (10)	0.0027 (11)
O2	0.0095 (12)	0.0116 (13)	0.0173 (13)	-0.0013 (9)	-0.0051 (10)	0.0021 (10)
C6	0.0038 (15)	0.0112 (16)	0.0052 (15)	-0.0005 (12)	0.0006 (12)	-0.0011 (12)
O3	0.0071 (11)	0.0121 (12)	0.0091 (11)	0.0001 (9)	-0.0030 (9)	0.0018 (9)
O4	0.0071 (11)	0.0082 (12)	0.0122 (11)	-0.0025 (9)	0.0000 (9)	-0.0007 (9)
O5	0.0106 (12)	0.0126 (12)	0.0107 (11)	0.0020 (9)	0.0039 (9)	0.0030 (9)
O6	0.0123 (13)	0.0101 (11)	0.0148 (13)	0.0026 (10)	0.0046 (10)	0.0033 (10)
C7	0.0074 (15)	0.0065 (15)	0.0086 (14)	-0.0010 (12)	0.0006 (12)	0.0023 (12)
C8	0.0126 (17)	0.0115 (17)	0.0195 (17)	-0.0005 (13)	0.0093 (14)	-0.0016 (14)
O7	0.0131 (13)	0.0106 (12)	0.0102 (12)	-0.0024 (10)	-0.0030 (10)	-0.0006 (9)

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

Ce1—Ce1 ⁱ	4.0320 (3)	C3—H3	0.9500
Ce1—O1	2.422 (3)	C3—C4	1.377 (5)
Ce1—O2 ⁱ	2.428 (3)	C4—C6	1.479 (4)
Ce1—O3 ⁱⁱ	2.406 (2)	C5—O1	1.257 (5)
Ce1—O4 ⁱⁱⁱ	2.443 (2)	C5—O2	1.263 (4)
Ce1—O5	2.621 (2)	C6—O3	1.258 (4)
Ce1—O5 ⁱ	2.466 (2)	C6—O4	1.277 (4)
Ce1—O6	2.551 (3)	O5—C7	1.285 (4)
Ce1—C7	2.965 (4)	O6—C7	1.254 (4)
Ce1—O7	2.503 (3)	C7—C8	1.491 (5)
S1—C1	1.719 (3)	C8—H8A	0.9800
S1—C4	1.722 (4)	C8—H8B	0.9800
C1—C2	1.375 (5)	C8—H8C	0.9800
C1—C5	1.488 (5)	O7—H7A	0.861 (19)
C2—H2	0.9500	O7—H7B	0.854 (19)
C2—C3	1.411 (5)		
O1—Ce1—Ce1 ⁱ	67.00 (6)	O7—Ce1—C7	101.68 (9)
O1—Ce1—O2 ⁱ	136.75 (9)	C1—S1—C4	91.09 (17)
O1—Ce1—O4 ⁱⁱⁱ	103.58 (9)	C2—C1—S1	112.1 (3)
O1—Ce1—O5	71.71 (9)	C2—C1—C5	127.4 (3)
O1—Ce1—O5 ⁱ	72.22 (9)	C5—C1—S1	120.4 (3)
O1—Ce1—O6	81.02 (10)	C1—C2—H2	123.7
O1—Ce1—C7	71.95 (10)	C1—C2—C3	112.5 (3)
O1—Ce1—O7	70.61 (9)	C3—C2—H2	123.7

O2 ⁱ —Ce1—Ce1 ⁱ	69.76 (6)	C2—C3—H3	124.0
O2 ⁱ —Ce1—O4 ⁱⁱⁱ	96.07 (9)	C4—C3—C2	112.0 (3)
O2 ⁱ —Ce1—O5 ⁱ	75.06 (9)	C4—C3—H3	124.0
O2 ⁱ —Ce1—O5	73.16 (8)	C3—C4—S1	112.2 (3)
O2 ⁱ —Ce1—O6	95.20 (9)	C3—C4—C6	128.4 (3)
O2 ⁱ —Ce1—C7	86.69 (9)	C6—C4—S1	119.4 (3)
O2 ⁱ —Ce1—O7	152.22 (8)	O1—C5—C1	116.5 (3)
O3 ⁱⁱ —Ce1—Ce1 ⁱ	145.65 (6)	O1—C5—O2	126.1 (3)
O3 ⁱⁱ —Ce1—O1	139.39 (9)	O2—C5—C1	117.4 (3)
O3 ⁱⁱ —Ce1—O2 ⁱ	80.56 (8)	C5—O1—Ce1	141.1 (2)
O3 ⁱⁱ —Ce1—O4 ⁱⁱⁱ	82.77 (8)	C5—O2—Ce1 ⁱ	135.8 (2)
O3 ⁱⁱ —Ce1—O5 ⁱ	146.62 (8)	O3—C6—C4	117.5 (3)
O3 ⁱⁱ —Ce1—O5	118.98 (8)	O3—C6—O4	124.2 (3)
O3 ⁱⁱ —Ce1—O6	79.80 (9)	O4—C6—C4	118.3 (3)
O3 ⁱⁱ —Ce1—C7	101.36 (9)	C6—O3—Ce1 ^{iv}	148.4 (2)
O3 ⁱⁱ —Ce1—O7	71.86 (8)	C6—O4—Ce1 ^v	133.3 (2)
O4 ⁱⁱⁱ —Ce1—Ce1 ⁱ	116.42 (6)	Ce1 ⁱ —O5—Ce1	104.82 (9)
O4 ⁱⁱⁱ —Ce1—O5	152.47 (8)	C7—O5—Ce1 ⁱ	155.3 (2)
O4 ⁱⁱⁱ —Ce1—O5 ⁱ	77.58 (8)	C7—O5—Ce1	92.3 (2)
O4 ⁱⁱⁱ —Ce1—O6	157.36 (8)	C7—O6—Ce1	96.4 (2)
O4 ⁱⁱⁱ —Ce1—C7	175.38 (9)	O5—C7—Ce1	62.02 (18)
O4 ⁱⁱⁱ —Ce1—O7	77.54 (9)	O5—C7—C8	118.5 (3)
O5 ⁱ —Ce1—Ce1 ⁱ	38.93 (6)	O6—C7—Ce1	58.74 (19)
O5 ⁱ —Ce1—O5	36.25 (5)	O6—C7—O5	119.4 (3)
O5 ⁱ —Ce1—O5	75.18 (9)	O6—C7—C8	122.1 (3)
O5 ⁱ —Ce1—O6	124.42 (8)	C8—C7—Ce1	166.9 (2)
O5 ⁱ —Ce1—C7	25.65 (9)	C7—C8—H8A	109.5
O5 ⁱ —Ce1—C7	99.64 (9)	C7—C8—H8B	109.5
O5 ⁱ —Ce1—O7	128.22 (8)	C7—C8—H8C	109.5
O6—Ce1—Ce1 ⁱ	85.93 (6)	H8A—C8—H8B	109.5
O6—Ce1—O5	50.13 (8)	H8A—C8—H8C	109.5
O6—Ce1—C7	24.85 (9)	H8B—C8—H8C	109.5
C7—Ce1—Ce1 ⁱ	61.08 (6)	Ce1—O7—H7A	114 (3)
O7—Ce1—Ce1 ⁱ	137.38 (6)	Ce1—O7—H7B	129 (3)
O7—Ce1—O5	123.36 (8)	H7A—O7—H7B	111 (4)
O7—Ce1—O6	83.35 (9)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8B \cdots O3 ^{vi}	0.98	2.65	3.497 (5)	145
O7—H7A \cdots O4 ⁱⁱ	0.86 (2)	2.02 (2)	2.829 (4)	156 (4)
O7—H7B \cdots O6 ^{vii}	0.85 (2)	1.95 (2)	2.795 (4)	168 (5)

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