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Poly[[piperazine-1,4-dium [diaqua-tetrakis(μ -sulfanediyl diacetato)-dicerate(III)]] trihydrate]

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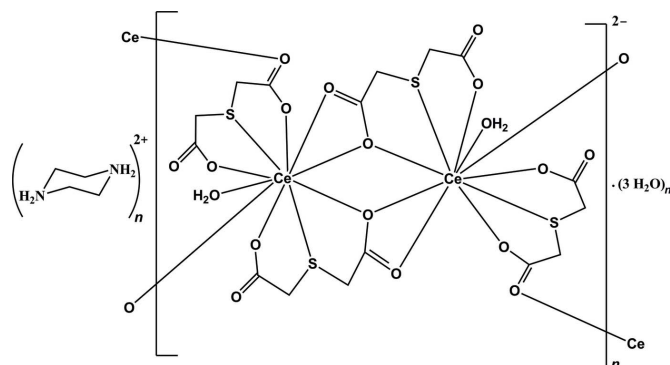
Received 17 December 2010; accepted 21 January 2011

Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; H-atom completeness 85%; disorder in solvent or counterion; R factor = 0.021; wR factor = 0.056; data-to-parameter ratio = 19.6.

The title compound, $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_4\text{S})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, features a polymeric anion with a centrosymmetric Ce_2O_2 core and a $\text{Ce} \cdots \text{Ce}$ distance of $4.3625(4)$ Å. The anions form ribbons $\{[\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_4\text{S})_4(\text{H}_2\text{O})_2]^{2-}\}_n$ extending along $[100]$. The doubly protonated piperazinium cations reside on centers of inversion and link the polymeric ribbons via $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonding. Each Ce^{III} cation is ten-coordinated by an O_2S donor set from two tridentate sulfanediyl diacetate (tda) ligands, one water molecule and three other tda O donors from adjacent $\{\text{Ce}(\text{tda})_2(\text{H}_2\text{O})\}$ units in a distorted bicapped cubic environment. Additional $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding involving the coordinated and solvent water molecules is also present. H atoms of the crystal water molecules could not be located and were not included in the refinement.

Related literature

For the structure determination of a bis-sulfanediyl diacetatonickelate(II), see: Delaunay *et al.* (1976). For a dinuclear sulfanediyl diacetato complex, see: Baggio *et al.* (1999). For an example with a solely bidentate coordination mode of the sulfanediyl diacetato ligand, see: Marek *et al.* (2003). For bond-valence-sum calculations, see: Zhang *et al.* (2004).



Experimental

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_4\text{S})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$
 $M_r = 1051.00$
 Triclinic, $P\bar{1}$
 $a = 6.4361(7)$ Å
 $b = 11.1135(12)$ Å
 $c = 12.5627(14)$ Å
 $\alpha = 96.693(4)^\circ$

$\beta = 104.646(3)^\circ$
 $\gamma = 101.192(3)^\circ$
 $V = 839.76(16)$ Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 3.01$ mm⁻¹
 $T = 90$ K
 $0.25 \times 0.22 \times 0.05$ mm

Data collection

Bruker SMART APEXII diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.520$, $T_{\max} = 0.864$

11816 measured reflections
 4482 independent reflections
 4433 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.056$
 $S = 1.11$
 4482 reflections
 229 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 1.79$ e Å⁻³
 $\Delta\rho_{\min} = -1.81$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ce1—S1	3.2903 (6)	Ce1—O7	2.5117 (15)
Ce1—S2	3.1445 (6)	Ce1—O8 ⁱ	2.5024 (15)
Ce1—O1	2.5359 (15)	Ce1—O3 ⁱⁱ	2.6137 (16)
Ce1—O4	2.5069 (14)	Ce1—O4 ⁱⁱ	2.6542 (15)
Ce1—O5	2.4278 (14)	Ce1—O9	2.6644 (15)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O9}-\text{H9C} \cdots \text{O7}^i$	0.82 (2)	2.00 (2)	2.793 (2)	163 (3)
$\text{O9}-\text{H9D} \cdots \text{O1}^{ii}$	0.83 (2)	1.92 (2)	2.729 (2)	167 (3)
$\text{N1}-\text{H1A} \cdots \text{O6}^{iii}$	0.92	1.84	2.732 (2)	162
$\text{N1}-\text{H1B} \cdots \text{O9}^{iv}$	0.92	2.10	2.988 (2)	161

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

MMO thanks the University of California, Davis, for the purchase of the X-ray diffractometer. Financial support from University of Kurdistan, Sanandaj, is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2442).

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supplementary materials

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Poly[[piperazine-1,4-dium [diaquatetrakis(μ -sulfanediylodiacetato)dicerate(III)]] trihydrate]

M. Ghadermazi, M. M. Olmstead, S. Rostami and J. Attar Gharamaleki

Comment

Thiodiacetic acid is one class of dicarboxylic acid ligands that has been used for construction of coordination polymers. It is a versatile complexing agent with one sulfur and two oxygen donor atoms and can strongly complex metal ions. Although the structural study of sulfanediylodiacetate-transition metal compounds was initiated several decades ago (Delaunay, *et al.*, 1976), interest in the structural aspects of sulfanediylodiacetate compounds has remarkably increased in recent years, and many structures with *d*- and *f*-block metals are known to date. The ligand is usually tridentate, but at least one Mn(II) complex has been reported in which it is solely bidentate where the thioether S atom is not involved in bonding to the metal (Marek *et al.*, 2003). The ligand can be simply chelating or is involved in both bridging and chelating modes to give rise to dinuclear complexes (Baggio *et al.*, 1999).

The crystal structure of $\{(C_4H_{12}N_2)[Ce(C_4H_4O_4S)_2(H_2O)]_2 \cdot 3H_2O\}_n$ or $\{[(pipzH_2)[Ce(tda)_2(H_2O)]_2 \cdot 3H_2O\}_n$, where $tda = [S(CH_2COO)_2]^{2-}$, sulfanediylodiacetate, and $pipzH_2$ is doubly protonated piperazine, is composed of a polymeric dinuclear anion $[Ce(tda)_2(H_2O)]_2^{2-}$, $[pipzH_2]^{2+}$ cations, and three water molecules of hydration. The components of the structure are shown in Fig. 1. The sulfanediylodiacetate group involving S1 behaves as both a tridentate chelating ligand and a bridging ligand to form a centrosymmetric dimer. The $Ce1 \cdots Ce1^i$ ($i = 1 - x, 1 - y, -z$) distance is 4.3625 (4) Å. The sulfanediylodiacetate ligand involving S2 is also a tridentate chelating ligand while its oxygen, O8, coordinates to the Ce of an adjoining dimer and propagates the structure as a coordination polymer parallel to [100] (Fig. 2). The more distant $Ce1^{iii}$ ($iii = 1 + x, y, z$) is 6.4361 (7) Å away from Ce1. The local coordination of the Ce^{III} cations consists of two thioethers (S1 and S2) and four O atoms (O1, O4, O5 and O7) from two chelating sulfanediylodiacetate groups, three oxygen atoms (O3, O4 and O8) of the carboxylate moieties from other sulfanediylodiacetate groups, and one oxygen atom from the coordinated water molecule (O9), resulting in an S_2O_8 distorted bicapped cubic environment. The Ce—O and Ce—S distances are normal and are gathered in Table 1. Bond valence sum calculations (Zhang *et al.*, 2004) yield a value of 2.9, in agreement with the oxidation state +III for the cerium atom. The $[pipzH_2]^{2+}$ cations and water molecules are further engaged in hydrogen bonding between polymeric units (Table 2). Although the H atoms of the uncoordinated water molecules could not be located, $O \cdots O$ contacts between 2.58 and 2.86 Å suggest that these molecules also participate in $O—H \cdots O$ hydrogen bonding.

Experimental

The title compound was prepared by mixing two solutions containing 1.5 g (10 mmol) of 2,2'-thiodiacetic acid in 10 ml THF and 0.86 g (10 mmol) piperazine in 10 ml THF. A white precipitate was obtained after evaporating the solvent. An aqueous solution containing 0.34 g (1.5 mmol) of the obtained ion pair in 20 ml water was added dropwise to 0.21 g (0.5 mmol) $Ce(NO_3)_3 \cdot 6H_2O$ in 15 ml water. After 60 min stirring and heating to 303 K, the solution became clear. Yellow crystals of the title compound were obtained after allowing the mixture to stand for 3 weeks at room temperature to evaporate the solvent.

Refinement

The C-bound and N-bound hydrogen atoms were placed at calculated positions (C—H 0.99 Å, N—H 0.92 Å) and were treated as riding on their parent atoms with $U(\text{H})$ set to $1.2 U_{\text{eq}}(\text{C})$. The hydrogen atoms bonded to the coordinated water were located in a difference Fourier map and were refined with distance restraints of O—H 0.83 (2) Å and H···H 1.34 (4) Å and their isotropic displacement parameters allowed to refine. There are two sites for water molecules of hydration. One of the hydrate molecules is disordered with respect to a center of symmetry and was kept at 0.5 occupancy and refined with an isotropic displacement parameter. Hydrogen atoms bonded to the water molecules of crystallisation could not be reliably located and were eventually omitted from the refinement. The highest peak in the final difference map is 0.83 Å from Ce1 and the largest hole is 0.87 Å from the same atom.

Figures

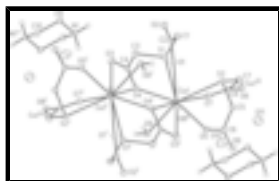


Fig. 1. Thermal ellipsoid plot of the title compound at the 50% probability level. Hydrogen atoms are removed for clarity except those bonded to the piperazine N atoms and the coordinated water molecule. Hydrogen atoms are drawn as spheres of arbitrary radius. Atoms that indicate the propagation of the coordination polymer are shown. Symmetry codes: i = 1 - x, 1 - y, -z; ii = x - 1, y z; iii = 1 + x, y, z; iv = -x, 1 - y, -z; v = -x, 2 - y, -z.

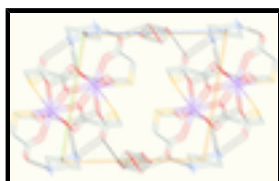


Fig. 2. A view down [100] of the polymeric structure.

Poly[[piperazine-1,4-dium [diaquatetrakis(μ-sulfanediyldiacetato)dicerate(III)]] trihydrate]

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_4\text{S})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$

$M_r = 1051.00$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.4361$ (7) Å

$b = 11.1135$ (12) Å

$c = 12.5627$ (14) Å

$\alpha = 96.693$ (4)°

$\beta = 104.646$ (3)°

$\gamma = 101.192$ (3)°

$V = 839.76$ (16) Å³

$Z = 1$

$F(000) = 520$

$D_x = 2.078$ Mg m⁻³

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

Cell parameters from 9880 reflections

$\theta = 2.7\text{--}31.5^\circ$

$\mu = 3.01$ mm⁻¹

$T = 90$ K

Plate, colourless

$0.25 \times 0.22 \times 0.05$ mm

Data collection

Bruker SMART APEXII
diffractometer

Radiation source: fine-focus sealed tube

4482 independent reflections

4433 reflections with $I > 2\sigma(I)$

graphite $R_{\text{int}} = 0.021$
 Detector resolution: 8.3 pixels mm^{-1} $\theta_{\text{max}} = 29.1^\circ$, $\theta_{\text{min}} = 2.8^\circ$
 ω scans $h = -8 \rightarrow 8$
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) $k = -15 \rightarrow 15$
 $T_{\text{min}} = 0.520$, $T_{\text{max}} = 0.864$ $l = -17 \rightarrow 17$
 11816 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.021$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.056$ H atoms treated by a mixture of independent and constrained refinement
 $S = 1.11$ $w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.9355P]$
 4482 reflections where $P = (F_o^2 + 2F_c^2)/3$
 229 parameters $(\Delta/\sigma)_{\text{max}} = 0.002$
 3 restraints $\Delta\rho_{\text{max}} = 1.79 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.81 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ce1	0.572270 (15)	0.396056 (9)	0.136487 (8)	0.00772 (4)	
S1	0.50618 (8)	0.61593 (5)	0.31570 (4)	0.01299 (10)	
S2	0.81761 (8)	0.37549 (4)	0.38182 (4)	0.01047 (9)	
O1	0.8397 (2)	0.60785 (14)	0.18806 (12)	0.0126 (3)	
O2	0.9817 (3)	0.81191 (14)	0.24661 (13)	0.0155 (3)	
O3	0.4131 (3)	0.75180 (14)	0.03785 (13)	0.0150 (3)	
O4	0.3790 (2)	0.55553 (13)	0.05890 (12)	0.0116 (3)	
O5	0.5613 (2)	0.18686 (13)	0.17676 (12)	0.0121 (3)	
O6	0.5126 (3)	0.02205 (15)	0.25991 (14)	0.0204 (3)	
O7	0.9607 (2)	0.36963 (14)	0.16697 (12)	0.0128 (3)	

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O8	1.2946 (2)	0.33740 (14)	0.24070 (12)	0.0118 (3)	
O9	0.1631 (2)	0.30107 (14)	0.00472 (12)	0.0118 (3)	
H9C	0.092 (5)	0.329 (3)	0.043 (2)	0.024 (8)*	
H9D	0.146 (6)	0.332 (3)	-0.052 (2)	0.034 (9)*	
N1	0.1458 (3)	0.94944 (16)	0.08009 (15)	0.0121 (3)	
H1A	0.2761	0.9585	0.1349	0.015*	
H1B	0.0661	0.8687	0.0701	0.015*	
C1	0.7895 (4)	0.7018 (2)	0.35817 (17)	0.0144 (4)	
H1C	0.8004	0.7868	0.3965	0.017*	
H1D	0.8795	0.6601	0.4116	0.017*	
C2	0.8790 (3)	0.70996 (19)	0.25730 (16)	0.0117 (3)	
C3	0.3913 (4)	0.7073 (2)	0.21616 (18)	0.0174 (4)	
H3A	0.2354	0.7020	0.2151	0.021*	
H3B	0.4716	0.7955	0.2429	0.021*	
C4	0.3986 (3)	0.67031 (19)	0.09779 (16)	0.0114 (3)	
C5	0.6813 (4)	0.2163 (2)	0.37811 (18)	0.0164 (4)	
H5A	0.7899	0.1761	0.4223	0.020*	
H5B	0.5635	0.2172	0.4156	0.020*	
C6	0.5786 (3)	0.13566 (19)	0.26210 (17)	0.0126 (4)	
C7	1.0804 (3)	0.3580 (2)	0.36422 (17)	0.0159 (4)	
H7A	1.1962	0.4274	0.4151	0.019*	
H7B	1.1077	0.2799	0.3895	0.019*	
C8	1.1111 (3)	0.35473 (17)	0.24746 (16)	0.0100 (3)	
C9	0.0173 (3)	1.03697 (19)	0.11667 (17)	0.0134 (4)	
H9A	0.1071	1.1235	0.1328	0.016*	
H9B	-0.0169	1.0173	0.1861	0.016*	
C10	-0.1952 (3)	1.02600 (19)	0.02648 (17)	0.0133 (4)	
H10A	-0.2903	0.9413	0.0146	0.016*	
H10B	-0.2757	1.0867	0.0502	0.016*	
O10	0.0974 (4)	0.0278 (2)	0.41702 (19)	0.0388 (5)	
O11	0.4926 (7)	0.0607 (4)	0.5455 (3)	0.0312 (8)*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.00901 (6)	0.00557 (6)	0.00889 (6)	0.00190 (4)	0.00262 (4)	0.00197 (4)
S1	0.0153 (2)	0.0122 (2)	0.0120 (2)	0.00179 (17)	0.00535 (18)	0.00315 (17)
S2	0.0117 (2)	0.0087 (2)	0.0111 (2)	0.00170 (16)	0.00410 (16)	0.00140 (16)
O1	0.0135 (7)	0.0103 (6)	0.0125 (6)	0.0009 (5)	0.0036 (5)	-0.0009 (5)
O2	0.0177 (7)	0.0109 (7)	0.0174 (7)	0.0011 (5)	0.0058 (6)	0.0022 (5)
O3	0.0214 (7)	0.0108 (7)	0.0148 (7)	0.0063 (6)	0.0060 (6)	0.0038 (5)
O4	0.0133 (6)	0.0093 (6)	0.0130 (6)	0.0045 (5)	0.0034 (5)	0.0028 (5)
O5	0.0146 (7)	0.0089 (6)	0.0132 (6)	0.0033 (5)	0.0038 (5)	0.0032 (5)
O6	0.0244 (8)	0.0098 (7)	0.0199 (8)	-0.0015 (6)	-0.0035 (6)	0.0060 (6)
O7	0.0130 (6)	0.0150 (7)	0.0124 (6)	0.0052 (5)	0.0045 (5)	0.0045 (5)
O8	0.0112 (6)	0.0116 (6)	0.0135 (6)	0.0029 (5)	0.0045 (5)	0.0030 (5)
O9	0.0143 (7)	0.0103 (6)	0.0115 (6)	0.0027 (5)	0.0048 (5)	0.0023 (5)
N1	0.0129 (8)	0.0080 (7)	0.0144 (8)	0.0024 (6)	0.0016 (6)	0.0027 (6)

C1	0.0165 (9)	0.0130 (9)	0.0118 (9)	0.0006 (7)	0.0033 (7)	0.0007 (7)
C2	0.0108 (8)	0.0120 (9)	0.0112 (8)	0.0022 (7)	0.0018 (7)	0.0015 (7)
C3	0.0234 (10)	0.0202 (10)	0.0123 (9)	0.0137 (8)	0.0049 (8)	0.0025 (7)
C4	0.0103 (8)	0.0123 (9)	0.0118 (8)	0.0047 (7)	0.0020 (7)	0.0021 (7)
C5	0.0209 (10)	0.0105 (9)	0.0132 (9)	−0.0015 (7)	−0.0010 (8)	0.0056 (7)
C6	0.0114 (8)	0.0096 (8)	0.0160 (9)	0.0026 (7)	0.0015 (7)	0.0036 (7)
C7	0.0112 (9)	0.0255 (11)	0.0114 (9)	0.0052 (8)	0.0033 (7)	0.0031 (8)
C8	0.0123 (8)	0.0048 (8)	0.0128 (8)	0.0011 (6)	0.0041 (7)	0.0010 (6)
C9	0.0172 (9)	0.0098 (8)	0.0132 (9)	0.0041 (7)	0.0037 (7)	0.0014 (7)
C10	0.0144 (9)	0.0114 (9)	0.0154 (9)	0.0039 (7)	0.0055 (7)	0.0027 (7)
O10	0.0566 (14)	0.0248 (10)	0.0376 (11)	0.0073 (9)	0.0213 (10)	0.0010 (8)

Geometric parameters (Å, °)

Ce1—S1	3.2903 (6)	O9—H9D	0.825 (18)
Ce1—S2	3.1445 (6)	N1—C10 ⁱⁱⁱ	1.495 (3)
Ce1—O1	2.5359 (15)	N1—C9	1.497 (3)
Ce1—O4	2.5069 (14)	N1—H1A	0.9200
Ce1—O5	2.4278 (14)	N1—H1B	0.9200
Ce1—O7	2.5117 (15)	C1—C2	1.524 (3)
Ce1—O8 ⁱ	2.5024 (15)	C1—H1C	0.9900
Ce1—O3 ⁱⁱ	2.6137 (16)	C1—H1D	0.9900
Ce1—O4 ⁱⁱ	2.6542 (15)	C3—C4	1.511 (3)
Ce1—O9	2.6644 (15)	C3—H3A	0.9900
S1—C1	1.798 (2)	C3—H3B	0.9900
S1—C3	1.806 (2)	C5—C6	1.531 (3)
S2—C7	1.804 (2)	C5—H5A	0.9900
S2—C5	1.805 (2)	C5—H5B	0.9900
O1—C2	1.287 (2)	C7—C8	1.526 (3)
O2—C2	1.236 (3)	C7—H7A	0.9900
O3—C4	1.248 (2)	C7—H7B	0.9900
O4—C4	1.282 (2)	C9—C10	1.513 (3)
O5—C6	1.262 (2)	C9—H9A	0.9900
O6—C6	1.246 (3)	C9—H9B	0.9900
O7—C8	1.262 (2)	C10—H10A	0.9900
O8—C8	1.255 (2)	C10—H10B	0.9900
O9—H9C	0.817 (17)		
O5—Ce1—O8 ⁱ	69.44 (5)	C8—O7—Ce1	136.54 (13)
O5—Ce1—O4	150.35 (5)	C8—O8—Ce1 ^{iv}	140.41 (13)
O8 ⁱ —Ce1—O4	91.13 (5)	Ce1—O9—H9C	101 (2)
O5—Ce1—O7	74.48 (5)	Ce1—O9—H9D	109 (3)
O8 ⁱ —Ce1—O7	131.20 (5)	H9C—O9—H9D	108 (3)
O4—Ce1—O7	133.20 (5)	C10 ⁱⁱⁱ —N1—C9	111.17 (15)
O5—Ce1—O1	138.75 (5)	C10 ⁱⁱⁱ —N1—H1A	109.4
O8 ⁱ —Ce1—O1	121.49 (5)	C9—N1—H1A	109.4
O4—Ce1—O1	70.37 (5)	C10 ⁱⁱⁱ —N1—H1B	109.4

supplementary materials

O7—Ce1—O1	70.20 (5)	C9—N1—H1B	109.4
O5—Ce1—O3 ⁱⁱ	69.93 (5)	H1A—N1—H1B	108.0
O8 ⁱ —Ce1—O3 ⁱⁱ	121.93 (5)	C2—C1—S1	110.59 (14)
O4—Ce1—O3 ⁱⁱ	105.26 (5)	C2—C1—H1C	109.5
O7—Ce1—O3 ⁱⁱ	71.75 (5)	S1—C1—H1C	109.5
O1—Ce1—O3 ⁱⁱ	116.48 (5)	C2—C1—H1D	109.5
O5—Ce1—O4 ⁱⁱ	119.23 (5)	S1—C1—H1D	109.5
O8 ⁱ —Ce1—O4 ⁱⁱ	144.10 (5)	H1C—C1—H1D	108.1
O4—Ce1—O4 ⁱⁱ	64.63 (6)	O2—C2—O1	124.50 (19)
O7—Ce1—O4 ⁱⁱ	82.62 (5)	O2—C2—C1	119.06 (18)
O1—Ce1—O4 ⁱⁱ	76.75 (5)	O1—C2—C1	116.43 (18)
O3 ⁱⁱ —Ce1—O4 ⁱⁱ	49.44 (5)	C4—C3—S1	115.90 (15)
O5—Ce1—O9	85.38 (5)	C4—C3—H3A	108.3
O8 ⁱ —Ce1—O9	66.23 (5)	S1—C3—H3A	108.3
O4—Ce1—O9	65.95 (5)	C4—C3—H3B	108.3
O7—Ce1—O9	141.72 (5)	S1—C3—H3B	108.3
O1—Ce1—O9	135.87 (5)	H3A—C3—H3B	107.4
O3 ⁱⁱ —Ce1—O9	70.84 (5)	O3—C4—O4	121.12 (19)
O4 ⁱⁱ —Ce1—O9	79.35 (5)	O3—C4—C3	119.05 (19)
O5—Ce1—S2	63.64 (4)	O4—C4—C3	119.73 (18)
O8 ⁱ —Ce1—S2	70.54 (4)	C6—C5—S2	116.14 (15)
O4—Ce1—S2	132.01 (3)	C6—C5—H5A	108.3
O7—Ce1—S2	64.42 (3)	S2—C5—H5A	108.3
O1—Ce1—S2	82.04 (4)	C6—C5—H5B	108.3
O3 ⁱⁱ —Ce1—S2	122.24 (4)	S2—C5—H5B	108.3
O4 ⁱⁱ —Ce1—S2	145.36 (3)	H5A—C5—H5B	107.4
O9—Ce1—S2	133.47 (3)	O6—C6—O5	124.6 (2)
C4 ⁱⁱ —Ce1—S2	139.09 (4)	O6—C6—C5	116.06 (18)
O5—Ce1—S1	120.96 (4)	O5—C6—C5	119.27 (18)
O8 ⁱ —Ce1—S1	62.01 (4)	C8—C7—S2	117.92 (15)
O4—Ce1—S1	62.43 (4)	C8—C7—H7A	107.8
O7—Ce1—S1	115.38 (4)	S2—C7—H7A	107.8
O1—Ce1—S1	60.23 (4)	C8—C7—H7B	107.8
O3 ⁱⁱ —Ce1—S1	167.65 (3)	S2—C7—H7B	107.8
O4 ⁱⁱ —Ce1—S1	119.75 (3)	H7A—C7—H7B	107.2
O9—Ce1—S1	102.88 (3)	O8—C8—O7	124.80 (19)
C4 ⁱⁱ —Ce1—S1	144.33 (4)	O8—C8—C7	114.35 (17)
S2—Ce1—S1	69.898 (14)	O7—C8—C7	120.85 (18)
C1—S1—C3	99.14 (11)	N1—C9—C10	110.34 (16)
C1—S1—Ce1	95.72 (7)	N1—C9—H9A	109.6
C3—S1—Ce1	97.65 (7)	C10—C9—H9A	109.6
C7—S2—C5	101.63 (11)	N1—C9—H9B	109.6
C7—S2—Ce1	100.18 (7)	C10—C9—H9B	109.6
C5—S2—Ce1	97.24 (7)	H9A—C9—H9B	108.1

C2—O1—Ce1	138.15 (13)	N1 ⁱⁱⁱ —C10—C9	110.03 (17)
C4—O3—Ce1 ⁱⁱ	95.97 (12)	N1 ⁱⁱⁱ —C10—H10A	109.7
C4—O4—Ce1	131.30 (13)	C9—C10—H10A	109.7
C4—O4—Ce1 ⁱⁱ	93.20 (12)	N1 ⁱⁱⁱ —C10—H10B	109.7
Ce1—O4—Ce1 ⁱⁱ	115.37 (5)	C9—C10—H10B	109.7
C6—O5—Ce1	136.68 (13)	H10A—C10—H10B	108.2
O5—Ce1—S1—C1	108.05 (8)	O1—Ce1—O4—Ce1 ⁱⁱ	84.25 (6)
O8 ⁱ —Ce1—S1—C1	146.53 (8)	O3 ⁱⁱ —Ce1—O4—Ce1 ⁱⁱ	-28.92 (7)
O4—Ce1—S1—C1	-105.85 (8)	O4 ⁱⁱ —Ce1—O4—Ce1 ⁱⁱ	0.0
O7—Ce1—S1—C1	21.53 (8)	O9—Ce1—O4—Ce1 ⁱⁱ	-89.30 (6)
O1—Ce1—S1—C1	-23.78 (8)	S2—Ce1—O4—Ce1 ⁱⁱ	142.97 (3)
O3 ⁱⁱ —Ce1—S1—C1	-101.58 (18)	S1—Ce1—O4—Ce1 ⁱⁱ	150.14 (7)
O4 ⁱⁱ —Ce1—S1—C1	-74.64 (8)	O8 ⁱ —Ce1—O5—C6	-53.69 (19)
O9—Ce1—S1—C1	-159.61 (8)	O4—Ce1—O5—C6	-105.6 (2)
S2—Ce1—S1—C1	68.49 (7)	O7—Ce1—O5—C6	92.87 (19)
O5—Ce1—S1—C3	-151.90 (9)	O1—Ce1—O5—C6	61.1 (2)
O8 ⁱ —Ce1—S1—C3	-113.42 (9)	O3 ⁱⁱ —Ce1—O5—C6	168.7 (2)
O4—Ce1—S1—C3	-5.79 (9)	O4 ⁱⁱ —Ce1—O5—C6	164.92 (18)
O7—Ce1—S1—C3	121.59 (9)	O9—Ce1—O5—C6	-120.01 (19)
O1—Ce1—S1—C3	76.28 (9)	S2—Ce1—O5—C6	24.12 (18)
O3 ⁱⁱ —Ce1—S1—C3	-1.53 (19)	S1—Ce1—O5—C6	-17.8 (2)
O4 ⁱⁱ —Ce1—S1—C3	25.42 (9)	O5—Ce1—O7—C8	-65.42 (18)
O9—Ce1—S1—C3	-59.56 (9)	O8 ⁱ —Ce1—O7—C8	-22.1 (2)
S2—Ce1—S1—C3	168.54 (8)	O4—Ce1—O7—C8	127.01 (18)
O5—Ce1—S2—C7	84.51 (9)	O1—Ce1—O7—C8	92.90 (19)
O8 ⁱ —Ce1—S2—C7	160.59 (9)	O3 ⁱⁱ —Ce1—O7—C8	-138.95 (19)
O4—Ce1—S2—C7	-126.28 (9)	O4 ⁱⁱ —Ce1—O7—C8	171.42 (19)
O7—Ce1—S2—C7	-0.10 (9)	O9—Ce1—O7—C8	-126.28 (18)
O1—Ce1—S2—C7	-71.91 (9)	S2—Ce1—O7—C8	2.38 (17)
O3 ⁱⁱ —Ce1—S2—C7	44.46 (9)	S1—Ce1—O7—C8	51.92 (19)
O4 ⁱⁱ —Ce1—S2—C7	-19.46 (10)	C3—S1—C1—C2	-56.27 (16)
O9—Ce1—S2—C7	138.09 (9)	Ce1—S1—C1—C2	42.45 (15)
S1—Ce1—S2—C7	-133.04 (8)	Ce1—O1—C2—O2	-159.61 (15)
O5—Ce1—S2—C5	-18.75 (9)	Ce1—O1—C2—C1	20.0 (3)
O8 ⁱ —Ce1—S2—C5	57.33 (9)	S1—C1—C2—O2	132.49 (17)
O4—Ce1—S2—C5	130.46 (9)	S1—C1—C2—O1	-47.1 (2)
O7—Ce1—S2—C5	-103.36 (9)	C1—S1—C3—C4	87.74 (18)
O1—Ce1—S2—C5	-175.16 (9)	Ce1—S1—C3—C4	-9.35 (18)
O3 ⁱⁱ —Ce1—S2—C5	-58.80 (9)	Ce1 ⁱⁱ —O3—C4—O4	-5.3 (2)
O4 ⁱⁱ —Ce1—S2—C5	-122.72 (10)	Ce1 ⁱⁱ —O3—C4—C3	178.13 (16)
O9—Ce1—S2—C5	34.83 (9)	Ce1—O4—C4—O3	133.58 (17)
S1—Ce1—S2—C5	123.70 (8)	Ce1 ⁱⁱ —O4—C4—O3	5.2 (2)
O5—Ce1—O1—C2	-97.7 (2)	Ce1—O4—C4—C3	-49.9 (3)
O8 ⁱ —Ce1—O1—C2	-3.5 (2)	Ce1 ⁱⁱ —O4—C4—C3	-178.26 (17)

supplementary materials

O4—Ce1—O1—C2	75.31 (19)	Ce1—O4—C4—Ce1 ⁱⁱ	128.35 (15)
O7—Ce1—O1—C2	-130.4 (2)	S1—C3—C4—O3	-150.05 (17)
O3 ⁱⁱ —Ce1—O1—C2	173.03 (18)	S1—C3—C4—O4	33.4 (3)
O4 ⁱⁱ —Ce1—O1—C2	142.8 (2)	C7—S2—C5—C6	-79.97 (18)
O9—Ce1—O1—C2	83.8 (2)	Ce1—S2—C5—C6	22.04 (17)
S2—Ce1—O1—C2	-64.81 (19)	Ce1—O5—C6—O6	160.71 (16)
S1—Ce1—O1—C2	6.54 (18)	Ce1—O5—C6—C5	-17.5 (3)
O5—Ce1—O4—C4	135.03 (17)	S2—C5—C6—O6	170.16 (17)
O8 ⁱ —Ce1—O4—C4	87.52 (17)	S2—C5—C6—O5	-11.5 (3)
O7—Ce1—O4—C4	-69.76 (19)	C5—S2—C7—C8	98.32 (18)
O1—Ce1—O4—C4	-35.69 (17)	Ce1—S2—C7—C8	-1.33 (17)
O3 ⁱⁱ —Ce1—O4—C4	-148.85 (17)	Ce1 ^{iv} —O8—C8—O7	32.5 (3)
O4 ⁱⁱ —Ce1—O4—C4	-119.94 (19)	Ce1 ^{iv} —O8—C8—C7	-146.95 (16)
O9—Ce1—O4—C4	150.77 (18)	Ce1—O7—C8—O8	176.41 (13)
S2—Ce1—O4—C4	23.04 (19)	Ce1—O7—C8—C7	-4.1 (3)
S1—Ce1—O4—C4	30.20 (16)	S2—C7—C8—O8	-177.31 (15)
O5—Ce1—O4—Ce1 ⁱⁱ	-105.03 (10)	S2—C7—C8—O7	3.2 (3)
O8 ⁱ —Ce1—O4—Ce1 ⁱⁱ	-152.54 (6)	C10 ⁱⁱⁱ —N1—C9—C10	57.6 (2)
O7—Ce1—O4—Ce1 ⁱⁱ	50.18 (9)	N1—C9—C10—N1 ⁱⁱⁱ	-57.0 (2)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9C \cdots O7 ⁱ	0.82 (2)	2.00 (2)	2.793 (2)	163 (3)
O9—H9D \cdots O1 ⁱⁱ	0.83 (2)	1.92 (2)	2.729 (2)	167 (3)
N1—H1A \cdots O6 ^v	0.92	1.84	2.732 (2)	162
N1—H1B \cdots O9 ^{vi}	0.92	2.10	2.988 (2)	161

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

Fig. 1

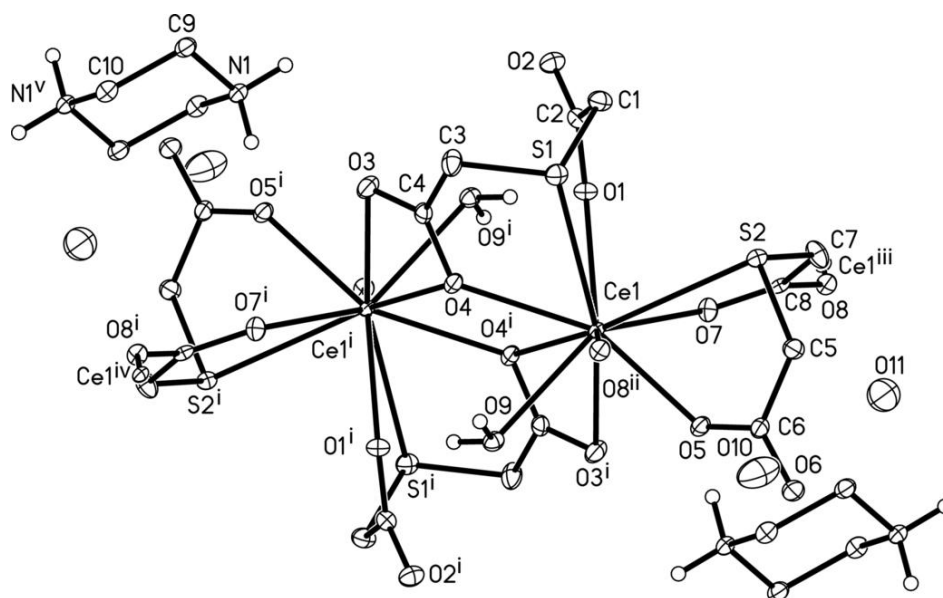


Fig. 2

