

catena-Poly[[triaquachlorido- μ_3 -malonato-cerium(III)] hemihydrate]

Patrícia Silva, José A. Fernandes and Filipe A. Almeida Paz*

Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal
Correspondence e-mail: filipe.paz@ua.pt

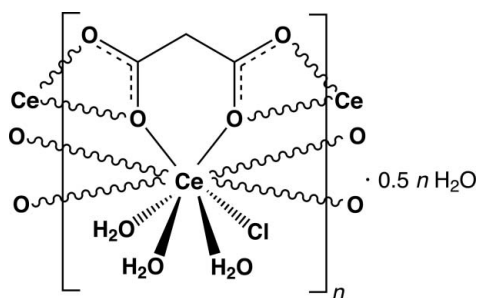
Received 30 October 2010; accepted 1 November 2010

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.021; wR factor = 0.053; data-to-parameter ratio = 17.6.

The asymmetric unit of the title compound, $[\{\text{Ce}(\text{C}_3\text{H}_2\text{O}_4)\text{Cl}(\text{H}_2\text{O})_3\} \cdot 0.5\text{H}_2\text{O}]_n$, contains a Ce^{3+} atom coordinated by a chloride anion, three water molecules and a malonate ligand, and one water molecule of crystallization with a factor of occupancy of 50%. The malonate ligand is bonded to three different symmetry-related metal atoms yielding a one-dimensional coordination polymer running parallel to the a axis. A supramolecular network composed of strong and highly directional $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds ensures a close and effective packing of adjacent polymeric chains.

Related literature

For general background to coordination compounds of malonates with lanthanides, see: Cañadillas-Delgado *et al.* (2006); Doreswamy *et al.* (2003, 2005); Hernández-Molina *et al.* (2000, 2002, 2003). For previous research from our group on coordination compounds of phosphonates, see: Cunha-Silva *et al.* (2007, 2009); Shi *et al.* (2008); Paz *et al.* (2004, 2005). For general background to the synthesis of coordination polymers using microwave heating, see: Klinowski *et al.* (2010).



Experimental

Crystal data

$[\text{Ce}(\text{C}_3\text{H}_2\text{O}_4)\text{Cl}(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O}$
 $M_r = 681.34$
 Monoclinic, $P2_1/c$
 $a = 7.6340$ (2) Å
 $b = 14.3065$ (3) Å
 $c = 8.7370$ (2) Å
 $\beta = 99.949$ (1)°
 $V = 939.87$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 5.13$ mm⁻¹
 $T = 150$ K
 $0.26 \times 0.16 \times 0.16$ mm

Data collection

Bruker X8 Kappa CCD APEXII diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
 $T_{\min} = 0.349$, $T_{\max} = 0.494$
 8271 measured reflections
 2514 independent reflections
 2481 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.053$
 $S = 1.17$
 2514 reflections
 143 parameters
 12 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 1.46$ e Å⁻³
 $\Delta\rho_{\min} = -1.77$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ce1—O1 ^W	2.4580 (17)	Ce1—O2 ^I	2.6083 (16)
Ce1—O3	2.4940 (16)	Ce1—O3 ⁱⁱ	2.6304 (17)
Ce1—O3 ^W	2.5525 (18)	Ce1—O4 ⁱⁱ	2.6487 (18)
Ce1—O1	2.5683 (16)	Ce1—O1 ^I	2.6793 (18)
Ce1—O2 ^W	2.5895 (17)	Ce1—Cl1	2.9086 (6)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1 ^W —H1 ^X ···Cl1 ⁱⁱⁱ	0.94 (1)	2.20 (2)	3.0967 (18)	159 (2)
O1 ^W —H1 ^Y ···O2 ^{iv}	0.94 (1)	1.71 (1)	2.652 (2)	174 (3)
O2 ^W —H2 ^X ···Cl1 ⁱ	0.94 (1)	2.11 (1)	3.0416 (19)	171 (3)
O2 ^W —H2 ^Y ···O4 ^w	0.94 (1)	1.94 (2)	2.816 (4)	153 (3)
O2 ^W —H2 ^Y ···O4 ^W	0.94 (1)	2.00 (2)	2.793 (4)	141 (3)
O3 ^W —H3 ^X ···O4 ^{vi}	0.95 (1)	1.86 (1)	2.798 (2)	173 (3)
O3 ^W —H3 ^Y ···O2 ^w	0.95 (3)	1.85 (3)	2.794 (3)	173 (3)
O4 ^W —H4 ^X ···Cl1 ⁱⁱ	0.95 (1)	2.38 (1)	3.326 (4)	176 (6)
O4 ^W —H4 ^Y ···O4 ^{vii}	0.95 (1)	2.26 (4)	3.083 (4)	144 (5)

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

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 2005); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2009); software used to prepare material for publication: SHELXTL.

We are grateful to the Fundação para a Ciência e a Tecnologia (FCT, Portugal) for their financial support through the R&D project PTDC/QUI-QUI/098098/2008 (FCOMP-01-0124-FEDER-010785), the PhD and post-doctoral research grants Nos. SFRH/BD/46601/2008 (to PS) and SFRH/BPD/

63736/2009 (to JAF), respectively, and also for specific funding for the purchase of the single-crystal diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2789).

References

- Brandenburg, K. (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2005). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2006). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cañadillas-Delgado, L., Pasán, J., Fabelo, O., Hernández-Molina, M., Lloret, F., Julve, M. & Ruiz-Pérez, C. (2006). *Inorg. Chem.* **45**, 10585–10594.
- Cunha-Silva, L., Lima, S., Ananias, D., Silva, P., Mafra, L., Carlos, L. D., Pillinger, M., Valente, A. A., Paz, F. A. A. & Rocha, J. (2009). *J. Mater. Chem.* **19**, 2618–2632.
- Cunha-Silva, L., Mafra, L., Ananias, D., Carlos, L. D., Rocha, J. & Paz, F. A. A. (2007). *Chem. Mater.* **19**, 3527–3538.
- Doreswamy, B. H., Mahendra, M., Sridhar, M. A., Prasad, J. S., Varughese, P. A., George, J. & Varghese, G. (2005). *Mater. Lett.* **59**, 1206–1213.
- Doreswamy, B. H., Mahendra, M., Sridhar, M. A., Prasad, J. S., Varughese, P. A., Saban, K. V. & Varghese, G. (2003). *J. Mol. Struct.* **659**, 81–88.
- Hernández-Molina, M., Lorenzo-Luis, P. A., Lopez, T., Ruiz-Pérez, C., Lloret, F. & Julve, M. (2000). *CrystEngComm*, **2**, 169–173.
- Hernández-Molina, M., Lorenzo-Luis, P., Ruiz-Pérez, C., Lopez, T., Martin, I. R., Anderson, K. M., Orpen, A. G., Bocanegra, E. H., Lloret, F. & Julve, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3462–3470.
- Hernández-Molina, M., Ruiz-Pérez, C., Lopez, T., Lloret, F. & Julve, M. (2003). *Inorg. Chem.* **42**, 5456–5458.
- Klinowski, J., Paz, F. A. A., Silva, P. & Rocha, J. (2010). *Dalton Trans.* doi:10.1039/C0DT00708K.
- Paz, F. A. A., Rocha, J., Klinowski, J., Trindade, T., Shi, F.-N. & Mafra, L. (2005). *Prog. Solid State Chem.* **33**, 113–125.
- Paz, F. A. A., Shi, F.-N., Klinowski, J., Rocha, J. & Trindade, T. (2004). *Eur. J. Inorg. Chem.* pp. 2759–2768.
- Sheldrick, G. M. (1998). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, F.-N., Trindade, T., Rocha, J. & Paz, F. A. A. (2008). *Cryst. Growth Des.* **8**, 3917–3920.

supplementary materials

Acta Cryst. (2010). E66, m1514-m1515 [doi:10.1107/S1600536810044727]

***catena*-Poly[[triquachlorido- μ_3 -malonato-cerium(III)] hemihydrate]**

P. Silva, J. A. Fernandes and F. A. Almeida Paz

Comment

The hydro-ionothermal reaction between tetraethyl-*p*-xylylenebisphosphonate (texbp) and $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ in pre-prepared homogeneous eutectic mixtures of choline chloride and malonic acid is known to lead to the phase-pure crystalline material $[\text{Ce}(\text{Hpmd})(\text{H}_2\text{O})]$ [where H_4pmd is 1,4-phenylenebis(methylene)diphosphonic acid, the hydrolysis product of texbp] (Shi *et al.*, 2008). Following our continuous interest in the preparation and study of the properties of metal-organic frameworks based on phosphonates (Cunha-Silva *et al.*, 2009; Cunha-Silva *et al.*, 2007; Paz *et al.*, 2005; Paz *et al.*, 2004), and our recent motivation to employ microwaves as an alternative heating source (Klinowski *et al.*, 2010), we decided to test the aforementioned synthetic conditions inside a microwave reactor. The use of microwave heating instead of hydro-ionothermal conditions resulted instead in the isolation of the title compound as a by-product, being composed of a one-dimensional polymer of Ce^{3+} with malonate residues. Noteworthy, this organic ligand can be found in a number of structures comprising lanthanide centres (Cañadillas-Delgado *et al.*, 2006; Hernández-Molina *et al.*, 2000; Hernández-Molina *et al.*, 2002; Hernández-Molina *et al.*, 2003; Doreswamy *et al.*, 2003; Doreswamy *et al.*, 2005) exhibiting several types of coordination modes such as unidentate, chelating and bridging.

The asymmetric unit of the title compound (see Scheme) comprises a chlorido, three water and one malonato (mal^{2-}) entities coordinated to Ce^{3+} , and one half-occupied water molecule of crystallization located in a generic crystallographic position: $[\text{CeCl}(\text{mal})(\text{H}_2\text{O})_3] \cdot 0.5(\text{H}_2\text{O})$. The coordination geometry of the metallic centre can be described as a highly distorted dodecahedron (Figure 1). For example, while the $\text{Ce1}-\text{O}_{\text{water}}$ distances range from 2.4580 (17) to 2.5895 (17) Å (see Table 1), the $\text{Ce1}-\text{Cl1}$ bond is considerably longer [2.9086 (6) Å]. The malonate ligand is, on the one hand, bound to the central Ce^{3+} *via* distal Ce—O bonds [distances of 2.5683 (16) and 2.4940 (16) Å], leading to the formation of a six-membered chelate ring. On the other, each carboxylate establishes a physical connection with a neighbouring metallic centre *via* proximal chelations [Ce—O distances in the 2.6083 (16) to 2.6793 (18) Å range - see Table 1], thus forming the four-membered chelate rings depicted in the chemical diagram. These two different coordination modes of the malonate ligand lead to the formation of a one-dimensional coordination polymer running parallel to the [100] direction (Figure 2). The intermetallic distances within the polymer are of 4.3832 (2) and 4.5091 (2) Å.

Due to the large number of donors and acceptors, the crystal structure of the title compound is rich in strong [D...A distances in the 2.652 (2)–3.326 (4) Å range] and highly directional [$\angle \text{D}-\text{H}\cdots\text{A}$ larger than *ca* 141 (3)°] hydrogen bonds (see Table 2). The hydrogen bonding interactions can be divided in three different types concerning the connectivity in relation to the polymeric chain. Intra-chain hydrogen bonds add stability to the coordination polymer by connecting three adjacent metal centres through a $\text{O3W}\cdots\text{O2W}\cdots\text{Cl}$ chain (blue dashed lines in Figure 2). The other two types of hydrogen bonds involve the crystal packing of adjacent coordination polymers: inter-chain interactions (green dashed lines in Figures 2 and 3) connect coordinated water molecules (O1W and O3W) of one polymer to the oxygen atoms of malonato ligands (O2 and O4 , respectively) of an adjacent polymer; the second type of inter-chain interactions occur *via* the half-occupied crystallization water molecule (O4W) forming $\text{O4}\cdots\text{O4W}\cdots\text{Cl1}$ chains (pink dashed lines in Figures 2 and 3). The extensive

supplementary materials

hydrogen bonding network described above leads to a series of strong connections among adjacent coordination polymers as depicted in Figure 3.

Experimental

The title compound was prepared following the procedure described elsewhere (Shi *et al.*, 2008), while replacing hydrothermal heating by microwave heating (Klinowski *et al.*, 2010). The reactive homogeneous suspension was transferred to a 10 ml IntelliVent reactor which was placed inside a CEM Focused MicrowaveTM Synthesis System Discover S-Class equipment. The reaction took place with constant magnetic stirring (controlled by the microwave equipment) and by monitoring the temperature and pressure inside the vessel. Experimental conditions: i) temperature of 120 °C; ii) power of 50 W; iii) reaction time of 45 minutes of microwave irradiation. A constant flow of air (*ca* 10 psi) ensured a close control of the temperature inside the vessel. After reacting a colourless solution was obtained. The resulting solution was then left to stand at ambient temperature until large block crystals grew by slow evaporation of the solvent over a period of six months.

Refinement

C-bound H atoms were located at their idealized positions and were included in the final structural model in riding-motion approximation with C—H distances of 0.99 Å. The isotropic displacement parameters for these atoms were fixed at $1.2 \times U_{eq}$ of the carbon atom to which they are attached.

All hydrogen atoms associated with the water molecules were directly located from difference Fourier maps and included in the structure with the O—H and H··H distances restrained to 0.95 (1) and 1.55 (1) Å, and with U_{iso} fixed at $1.5 \times U_{eq}$ of the O atom to which they are attached.

Figures

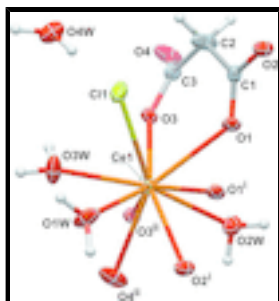


Fig. 1. Asymmetric unit of the title compound showing all non-hydrogen atoms as displacement ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radius [symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $1 - x, -y, 2 - z$]. The water molecule of crystallization, with fractional occupancy, is also depicted. For clarity, the coordination sphere of Ce1 was completed by generating by symmetry the remaining oxygen atoms.

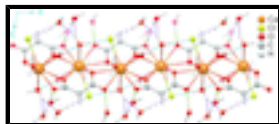


Fig. 2. Schematic representation of the one-dimensional chain coordination polymer composing the crystal structure of the title compound. Hydrogen bonds are represented as dashed lines: **blue** - intra-chain interactions; **pink** - hydrogen bonds with the water molecule of crystallization O4W; **green** - inter-chain interactions establishing direct supramolecular connections between adjacent polymers.

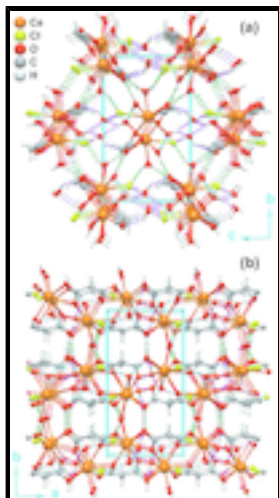


Fig. 3. Crystal packing viewed in perspective along the (a) [100] and (b) [001] directions of the unit cell. Hydrogen bonds represented as in Figure 2.

catena-Poly[[triaquachlorido- μ_3 -malonato-cerium(III)] hemihydrate]

Crystal data

[Ce(C₃H₂O₄)Cl(H₂O)₃] \cdot 0.5H₂O

M_r = 681.34

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 7.6340 (2) Å

b = 14.3065 (3) Å

c = 8.7370 (2) Å

β = 99.949 (1)°

V = 939.87 (4) Å³

Z = 2

$F(000)$ = 648

D_x = 2.408 Mg m⁻³

Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 6974 reflections

θ = 3.1–29.1°

μ = 5.13 mm⁻¹

T = 150 K

Block, colourless

0.26 \times 0.16 \times 0.16 mm

Data collection

Bruker X8 Kappa CCD APEXII diffractometer

Radiation source: fine-focus sealed tube graphite

ω and φ scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1998)

T_{\min} = 0.349, T_{\max} = 0.494

8271 measured reflections

2514 independent reflections

2481 reflections with $I > 2\sigma(I)$

R_{int} = 0.028

θ_{\max} = 29.1°, θ_{\min} = 3.7°

h = -7→10

k = -19→18

l = -11→11

Refinement

Refinement on F^2

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

supplementary materials

$$R[F^2 > 2\sigma(F^2)] = 0.021$$

$$wR(F^2) = 0.053$$

$$S = 1.17$$

2514 reflections

143 parameters

12 restraints

Primary atom site location: structure-invariant direct methods

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 1.2954P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 1.46 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.77 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXTL* (Sheldrick, 2008),

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

Extinction coefficient: 0.0139 (5)

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	0.742523 (15)	-0.079259 (8)	0.986480 (14)	0.00713 (7)	
Cl1	0.93077 (9)	-0.10017 (4)	1.30370 (7)	0.01792 (13)	
O1	0.9184 (2)	0.07240 (11)	1.0558 (2)	0.0110 (3)	
O2	1.1044 (2)	0.14538 (12)	1.23544 (19)	0.0126 (3)	
O3	0.5892 (2)	0.03721 (11)	1.12981 (19)	0.0100 (3)	
O4	0.4894 (2)	0.16117 (13)	1.2331 (2)	0.0187 (4)	
C1	0.9494 (3)	0.11752 (15)	1.1829 (3)	0.0089 (4)	
C2	0.8055 (3)	0.14023 (19)	1.2763 (3)	0.0166 (5)	
H2A	0.8375	0.1100	1.3793	0.020*	
H2B	0.8066	0.2086	1.2938	0.020*	
C3	0.6181 (3)	0.11199 (16)	1.2087 (3)	0.0113 (4)	
O1W	0.8161 (3)	-0.24629 (12)	1.0159 (2)	0.0186 (4)	
H1X	0.844 (5)	-0.2811 (19)	0.932 (2)	0.028*	
H1Y	0.844 (5)	-0.2812 (19)	1.1084 (19)	0.028*	
O2W	0.7066 (2)	0.03997 (12)	0.7602 (2)	0.0139 (3)	
H2X	0.815 (2)	0.065 (2)	0.740 (3)	0.021*	
H2Y	0.635 (3)	0.021 (2)	0.667 (2)	0.021*	
O3W	0.5195 (3)	-0.16461 (12)	1.1230 (2)	0.0185 (4)	
H3X	0.518 (5)	-0.2259 (10)	1.164 (4)	0.028*	
H3Y	0.439 (4)	-0.1266 (17)	1.167 (4)	0.028*	
O4W	0.4133 (5)	0.0545 (3)	0.5211 (4)	0.0186 (7)	0.50

H4X	0.318 (7)	0.066 (4)	0.576 (8)	0.028*	0.50
H4Y	0.435 (9)	0.109 (3)	0.465 (7)	0.028*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.00713 (9)	0.00740 (9)	0.00779 (9)	-0.00056 (4)	0.00394 (5)	-0.00129 (3)
Cl1	0.0202 (3)	0.0217 (3)	0.0116 (3)	-0.0073 (2)	0.0020 (2)	0.0043 (2)
O1	0.0114 (8)	0.0119 (7)	0.0108 (8)	-0.0008 (6)	0.0051 (6)	-0.0046 (6)
O2	0.0086 (8)	0.0182 (8)	0.0116 (7)	-0.0021 (6)	0.0034 (6)	-0.0050 (6)
O3	0.0094 (8)	0.0096 (7)	0.0118 (7)	-0.0012 (6)	0.0040 (6)	-0.0031 (6)
O4	0.0094 (8)	0.0192 (8)	0.0285 (10)	0.0005 (7)	0.0062 (7)	-0.0146 (7)
C1	0.0091 (10)	0.0076 (9)	0.0108 (9)	0.0003 (7)	0.0038 (8)	0.0005 (7)
C2	0.0078 (11)	0.0253 (12)	0.0180 (11)	-0.0024 (9)	0.0061 (9)	-0.0128 (10)
C3	0.0095 (10)	0.0140 (10)	0.0118 (10)	-0.0024 (8)	0.0062 (8)	-0.0034 (8)
O1W	0.0330 (11)	0.0132 (8)	0.0111 (8)	0.0097 (8)	0.0078 (7)	0.0013 (6)
O2W	0.0112 (8)	0.0178 (8)	0.0133 (8)	-0.0016 (6)	0.0036 (6)	0.0001 (6)
O3W	0.0198 (9)	0.0112 (7)	0.0288 (10)	0.0021 (7)	0.0159 (8)	0.0049 (7)
O4W	0.0189 (19)	0.0240 (18)	0.0134 (16)	0.0028 (16)	0.0043 (14)	0.0011 (14)

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

Ce1—O1W	2.4580 (17)	O3—Ce1 ⁱⁱ	2.6304 (17)
Ce1—O3	2.4940 (16)	O4—C3	1.256 (3)
Ce1—O3W	2.5525 (18)	O4—Ce1 ⁱⁱ	2.6487 (18)
Ce1—O1	2.5683 (16)	C1—C2	1.512 (3)
Ce1—O2W	2.5895 (17)	C1—Ce1 ⁱ	3.038 (2)
Ce1—O2 ⁱ	2.6083 (16)	C2—C3	1.505 (3)
Ce1—O3 ⁱⁱ	2.6304 (17)	C2—H2A	0.9900
Ce1—O4 ⁱⁱ	2.6487 (18)	C2—H2B	0.9900
Ce1—O1 ⁱ	2.6793 (18)	C3—Ce1 ⁱⁱ	3.014 (2)
Ce1—Cl1	2.9086 (6)	O1W—H1X	0.943 (10)
Ce1—C3 ⁱⁱ	3.014 (2)	O1W—H1Y	0.943 (10)
Ce1—C1 ⁱ	3.038 (2)	O2W—H2X	0.944 (10)
O1—C1	1.271 (3)	O2W—H2Y	0.941 (10)
O1—Ce1 ⁱ	2.6793 (18)	O3W—H3X	0.947 (10)
O2—C1	1.258 (3)	O3W—H3Y	0.95 (3)
O2—Ce1 ⁱ	2.6083 (16)	O4W—H4X	0.947 (10)
O3—C3	1.271 (3)	O4W—H4Y	0.947 (10)
O1W—Ce1—O3	135.69 (6)	O3 ⁱⁱ —Ce1—C3 ⁱⁱ	24.86 (5)
O1W—Ce1—O3W	69.19 (6)	O4 ⁱⁱ —Ce1—C3 ⁱⁱ	24.56 (6)
O3—Ce1—O3W	71.11 (5)	O1 ⁱ —Ce1—C3 ⁱⁱ	137.52 (6)
O1W—Ce1—O1	134.11 (7)	Cl1—Ce1—C3 ⁱⁱ	140.88 (5)
O3—Ce1—O1	65.71 (5)	O1W—Ce1—C1 ⁱ	72.16 (6)
O3W—Ce1—O1	131.12 (6)	O3—Ce1—C1 ⁱ	146.63 (6)

supplementary materials

O1W—Ce1—O2W	135.43 (6)	O3W—Ce1—C1 ⁱ	140.97 (6)
O3—Ce1—O2W	86.92 (5)	O1—Ce1—C1 ⁱ	81.37 (6)
O3W—Ce1—O2W	132.90 (6)	O2W—Ce1—C1 ⁱ	74.66 (6)
O1—Ce1—O2W	66.78 (6)	O2 ⁱ —Ce1—C1 ⁱ	24.25 (6)
O1W—Ce1—O2 ⁱ	66.52 (6)	O3 ⁱⁱ —Ce1—C1 ⁱ	128.90 (6)
O3—Ce1—O2 ⁱ	157.66 (5)	O4 ⁱⁱ —Ce1—C1 ⁱ	92.55 (6)
O3W—Ce1—O2 ⁱ	126.49 (6)	O1 ⁱ —Ce1—C1 ⁱ	24.68 (6)
O1—Ce1—O2 ⁱ	101.46 (5)	C11—Ce1—C1 ⁱ	98.57 (4)
O2W—Ce1—O2 ⁱ	70.93 (5)	C3 ⁱⁱ —Ce1—C1 ⁱ	113.88 (6)
O1W—Ce1—O3 ⁱⁱ	116.75 (6)	C1—O1—Ce1	130.24 (15)
O3—Ce1—O3 ⁱⁱ	62.43 (6)	C1—O1—Ce1 ⁱ	93.64 (14)
O3W—Ce1—O3 ⁱⁱ	67.32 (6)	Ce1—O1—Ce1 ⁱ	118.46 (6)
O1—Ce1—O3 ⁱⁱ	109.09 (5)	C1—O2—Ce1 ⁱ	97.36 (13)
O2W—Ce1—O3 ⁱⁱ	65.58 (5)	C3—O3—Ce1	141.45 (15)
O2 ⁱ —Ce1—O3 ⁱⁱ	108.72 (5)	C3—O3—Ce1 ⁱⁱ	94.72 (14)
O1W—Ce1—O4 ⁱⁱ	75.98 (6)	Ce1—O3—Ce1 ⁱⁱ	117.57 (6)
O3—Ce1—O4 ⁱⁱ	110.26 (5)	C3—O4—Ce1 ⁱⁱ	94.24 (14)
O3W—Ce1—O4 ⁱⁱ	73.16 (6)	O2—C1—O1	120.1 (2)
O1—Ce1—O4 ⁱⁱ	143.27 (6)	O2—C1—C2	117.4 (2)
O2W—Ce1—O4 ⁱⁱ	76.65 (6)	O1—C1—C2	122.5 (2)
O2 ⁱ —Ce1—O4 ⁱⁱ	68.32 (5)	O2—C1—Ce1 ⁱ	58.39 (12)
O3 ⁱⁱ —Ce1—O4 ⁱⁱ	48.92 (5)	O1—C1—Ce1 ⁱ	61.67 (12)
O1W—Ce1—O1 ⁱ	80.87 (6)	C2—C1—Ce1 ⁱ	175.81 (16)
O3—Ce1—O1 ⁱ	126.38 (5)	C3—C2—C1	117.41 (19)
O3W—Ce1—O1 ⁱ	145.13 (6)	C3—C2—H2A	107.9
O1—Ce1—O1 ⁱ	61.54 (6)	C1—C2—H2A	107.9
O2W—Ce1—O1 ⁱ	81.26 (6)	C3—C2—H2B	107.9
O2 ⁱ —Ce1—O1 ⁱ	48.93 (5)	C1—C2—H2B	107.9
O3 ⁱⁱ —Ce1—O1 ⁱ	145.80 (5)	H2A—C2—H2B	107.2
O4 ⁱⁱ —Ce1—O1 ⁱ	117.21 (5)	O4—C3—O3	119.7 (2)
O1W—Ce1—C11	74.57 (5)	O4—C3—C2	120.1 (2)
O3—Ce1—C11	77.74 (4)	O3—C3—C2	120.2 (2)
O3W—Ce1—C11	76.42 (5)	O4—C3—Ce1 ⁱⁱ	61.20 (12)
O1—Ce1—C11	73.15 (4)	O3—C3—Ce1 ⁱⁱ	60.43 (12)
O2W—Ce1—C11	139.90 (4)	C2—C3—Ce1 ⁱⁱ	167.62 (17)
O2 ⁱ —Ce1—C11	117.38 (4)	Ce1—O1W—H1X	120.7 (18)
O3 ⁱⁱ —Ce1—C11	132.52 (4)	Ce1—O1W—H1Y	128.3 (18)
O4 ⁱⁱ —Ce1—C11	143.42 (5)	H1X—O1W—H1Y	109.8 (14)
O1 ⁱ —Ce1—C11	78.76 (4)	Ce1—O2W—H2X	114 (2)
O1W—Ce1—C3 ⁱⁱ	94.47 (7)	Ce1—O2W—H2Y	116.0 (19)
O3—Ce1—C3 ⁱⁱ	85.75 (6)	H2X—O2W—H2Y	110.2 (15)

O3W—Ce1—C3 ⁱⁱ	64.67 (6)	Ce1—O3W—H3X	132.1 (19)
O1—Ce1—C3 ⁱⁱ	130.83 (6)	Ce1—O3W—H3Y	116.4 (19)
O2W—Ce1—C3 ⁱⁱ	72.81 (6)	H3X—O3W—H3Y	109 (3)
O2 ⁱ —Ce1—C3 ⁱⁱ	90.33 (6)	H4X—O4W—H4Y	110.0 (16)
O1W—Ce1—O1—C1	-84.6 (2)	C1 ⁱ —Ce1—O3—C3	-23.8 (3)
O3—Ce1—O1—C1	46.42 (19)	O1W—Ce1—O3—Ce1 ⁱⁱ	-101.07 (10)
O3W—Ce1—O1—C1	16.4 (2)	O3W—Ce1—O3—Ce1 ⁱⁱ	-73.68 (8)
O2W—Ce1—O1—C1	143.9 (2)	O1—Ce1—O3—Ce1 ⁱⁱ	129.82 (8)
O2 ⁱ —Ce1—O1—C1	-152.87 (19)	O2W—Ce1—O3—Ce1 ⁱⁱ	63.96 (7)
O3 ⁱⁱ —Ce1—O1—C1	92.5 (2)	O2 ⁱ —Ce1—O3—Ce1 ⁱⁱ	71.47 (16)
O4 ⁱⁱ —Ce1—O1—C1	138.16 (18)	O3 ⁱⁱ —Ce1—O3—Ce1 ⁱⁱ	0.0
O1 ⁱ —Ce1—O1—C1	-123.6 (2)	O4 ⁱⁱ —Ce1—O3—Ce1 ⁱⁱ	-10.60 (9)
Cl1—Ce1—O1—C1	-37.46 (19)	O1 ⁱ —Ce1—O3—Ce1 ⁱⁱ	140.74 (6)
C3 ⁱⁱ —Ce1—O1—C1	106.6 (2)	Cl1—Ce1—O3—Ce1 ⁱⁱ	-153.33 (7)
C1 ⁱ —Ce1—O1—C1	-139.21 (18)	C3 ⁱⁱ —Ce1—O3—Ce1 ⁱⁱ	-9.01 (7)
O1W—Ce1—O1—Ce1 ⁱ	39.03 (11)	C1 ⁱ —Ce1—O3—Ce1 ⁱⁱ	119.68 (10)
O3—Ce1—O1—Ce1 ⁱ	170.01 (9)	Ce1 ⁱ —O2—C1—O1	-0.2 (2)
O3W—Ce1—O1—Ce1 ⁱ	139.96 (7)	Ce1 ⁱ —O2—C1—C2	179.99 (18)
O2W—Ce1—O1—Ce1 ⁱ	-92.54 (8)	Ce1—O1—C1—O2	133.00 (19)
O2 ⁱ —Ce1—O1—Ce1 ⁱ	-29.27 (8)	Ce1 ⁱ —O1—C1—O2	0.2 (2)
O3 ⁱⁱ —Ce1—O1—Ce1 ⁱ	-143.90 (7)	Ce1—O1—C1—C2	-47.2 (3)
O4 ⁱⁱ —Ce1—O1—Ce1 ⁱ	-98.25 (10)	Ce1 ⁱ —O1—C1—C2	180.0 (2)
O1 ⁱ —Ce1—O1—Ce1 ⁱ	0.0	Ce1—O1—C1—Ce1 ⁱ	132.79 (18)
Cl1—Ce1—O1—Ce1 ⁱ	86.13 (7)	O2—C1—C2—C3	176.4 (2)
C3 ⁱⁱ —Ce1—O1—Ce1 ⁱ	-129.82 (8)	O1—C1—C2—C3	-3.4 (4)
C1 ⁱ —Ce1—O1—Ce1 ⁱ	-15.61 (7)	Ce1 ⁱⁱ —O4—C3—O3	-15.7 (2)
O1W—Ce1—O3—C3	115.4 (2)	Ce1 ⁱⁱ —O4—C3—C2	165.9 (2)
O3W—Ce1—O3—C3	142.8 (3)	Ce1—O3—C3—O4	163.95 (17)
O1—Ce1—O3—C3	-13.7 (2)	Ce1 ⁱⁱ —O3—C3—O4	15.9 (2)
O2W—Ce1—O3—C3	-79.6 (2)	Ce1—O3—C3—C2	-17.7 (4)
O2 ⁱ —Ce1—O3—C3	-72.1 (3)	Ce1 ⁱⁱ —O3—C3—C2	-165.7 (2)
O3 ⁱⁱ —Ce1—O3—C3	-143.5 (3)	Ce1—O3—C3—Ce1 ⁱⁱ	148.1 (2)
O4 ⁱⁱ —Ce1—O3—C3	-154.1 (2)	C1—C2—C3—O4	-146.9 (2)
O1 ⁱ —Ce1—O3—C3	-2.8 (3)	C1—C2—C3—O3	34.7 (3)
Cl1—Ce1—O3—C3	63.1 (2)	C1—C2—C3—Ce1 ⁱⁱ	-54.5 (8)
C3 ⁱⁱ —Ce1—O3—C3	-152.5 (2)		

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

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

<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>
O1W—H1X \cdots Cl1 ⁱⁱⁱ	0.94 (1)	2.20 (2)	3.0967 (18)	159 (2)

supplementary materials

O1W—H1Y...O2 ^{iv}	0.94 (1)	1.71 (1)	2.652 (2)	174 (3)
O2W—H2X...C11 ⁱ	0.94 (1)	2.11 (1)	3.0416 (19)	171 (3)
O2W—H2Y...O4W ^v	0.94 (1)	1.94 (2)	2.816 (4)	153 (3)
O2W—H2Y...O4W	0.94 (1)	2.00 (2)	2.793 (4)	141 (3)
O3W—H3X...O4 ^{vi}	0.95 (1)	1.86 (1)	2.798 (2)	173 (3)
O3W—H3Y...O2W ⁱⁱ	0.95 (3)	1.85 (3)	2.794 (3)	173 (3)
O4W—H4X...C11 ⁱⁱ	0.95 (1)	2.38 (1)	3.326 (4)	176 (6)
O4W—H4Y...O4 ^{vii}	0.95 (1)	2.26 (4)	3.083 (4)	144 (5)

Symmetry codes: (iii) $x, -y-1/2, z-1/2$; (iv) $-x+2, y-1/2, -z+5/2$; (i) $-x+2, -y, -z+2$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, y-1/2, -z+5/2$; (ii) $-x+1, -y, -z+2$; (vii) $x, y, z-1$.

Fig. 1

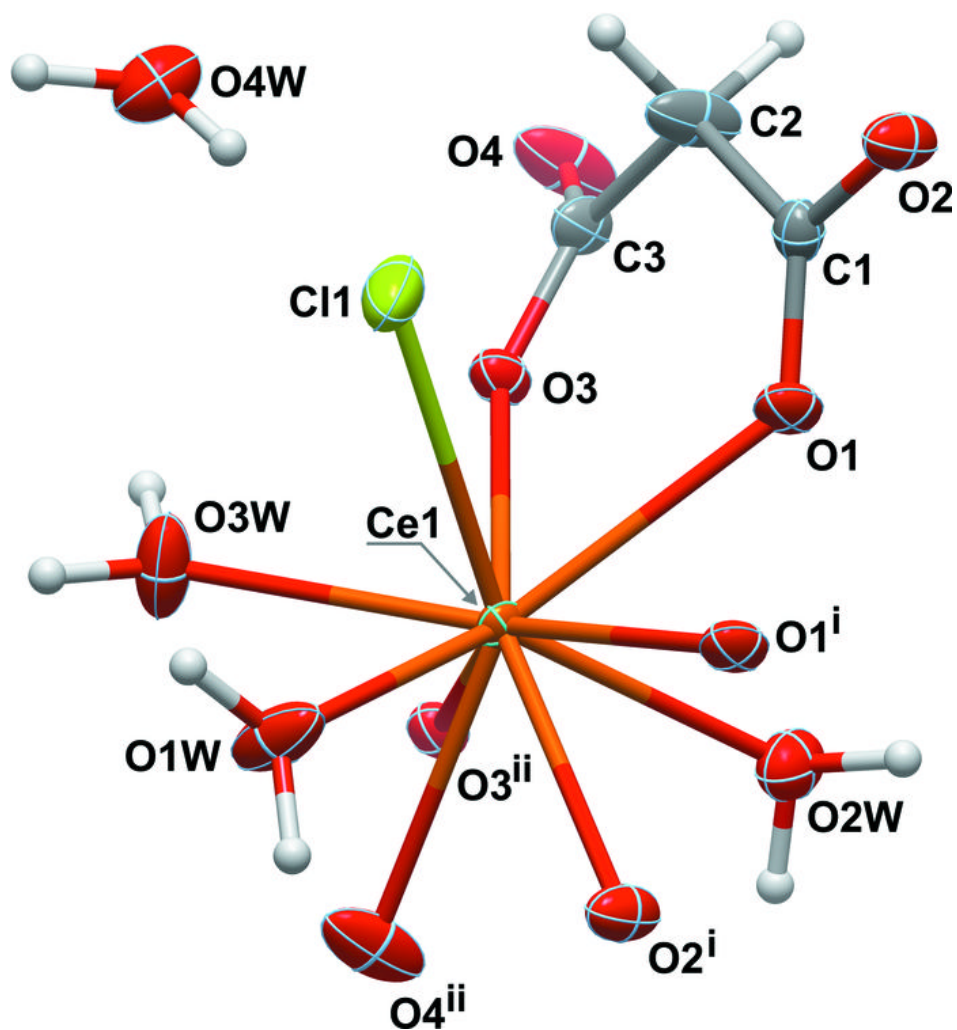


Fig. 2

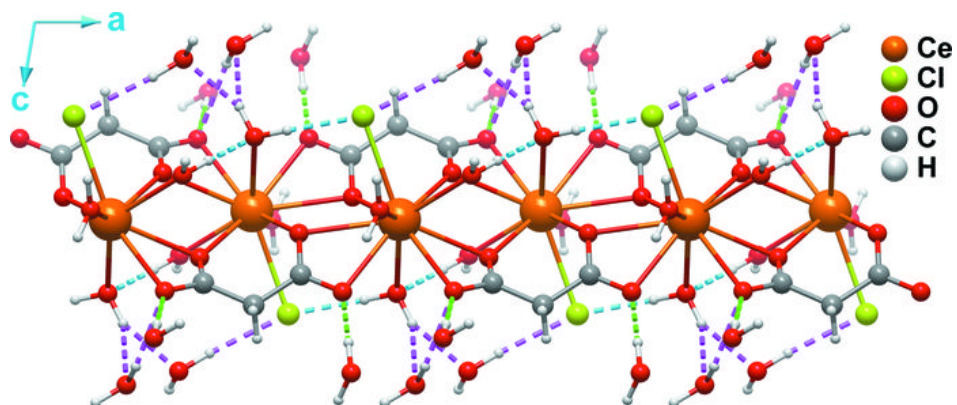


Fig. 3

