



# Hydrothermal synthesis and crystal structure of a new lanthanum(III) coordination polymer with fumaric acid

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The title compound, poly[diaquatrakis( $\mu_4$ -but-2-enedioato)-( $\mu_2$ -but-2-enedioic acid)dilanthanum(III)],  $[\text{La}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2]_n$ , was synthesized by the reaction of lanthanum chloride pentahydrate with fumaric acid under hydrothermal conditions. The asymmetric unit comprises an  $\text{La}^{\text{III}}$  cation, one and a half fumarate dianions ( $\text{L}^{2-}$ ), one a half-molecule of fumaric acid ( $\text{H}_2\text{L}$ ) and one coordinated water molecule. Each  $\text{La}^{\text{III}}$  cation has the same nine-coordinate environment and is surrounded by eight O atoms from seven distinct fumarate moieties, including one protonated fumarate unit and one water molecule in a distorted tricapped trigonal-prismatic environment. The  $\text{LaO}_8(\text{H}_2\text{O})$  polyhedra centres are edge-shared through three carboxylate bridges of the fumarate ligand, forming chains in three dimensions to construct the MOF. The crystal structure is stabilized by  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen-bond interactions between the coordinated water molecule and the carboxylate O atoms, and also between oxygen atoms of fumaric acid

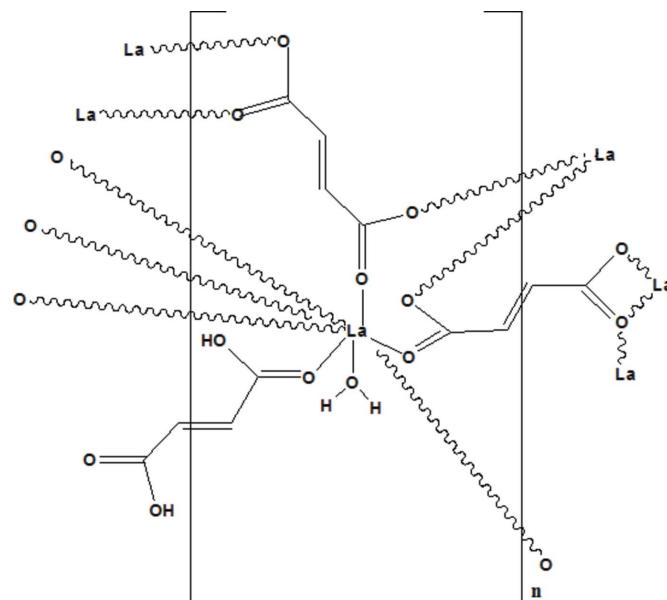
**Keywords:** crystal structure; hydrothermal synthesis; lanthanum(III) coordination polymer; fumaric acid.

**CCDC reference:** 1058359

## 1. Related literature

For general background to metal coordination polymers, see: Fujita *et al.* (1994); Bénard *et al.* (2000); Zhang *et al.* (2000). For structures involving fumarate ligands and transition metals, see: Dalai *et al.* (2002); Xie *et al.* (2003); Devereux *et al.* (2000). For rare earth fumarates, see: Zhang *et al.* (2006); Li &

Zou (2006); Liu *et al.* (2011). For reported La—O distances, see: Dan *et al.* (2005).



## 2. Experimental

### 2.1. Crystal data

$[\text{La}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2]$   
 $M_r = 386.05$   
Monoclinic,  $P2_1/c$   
 $a = 8.4299$  (5) Å  
 $b = 14.6789$  (8) Å  
 $c = 8.8096$  (5) Å  
 $\beta = 103.318$  (3)°

$V = 1060.80$  (11) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 4.07$  mm<sup>-1</sup>  
 $T = 295$  K  
 $0.12 \times 0.11 \times 0.08$  mm

### 2.2. Data collection

Bruker APEXII diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 2002)  
 $T_{\min} = 0.677$ ,  $T_{\max} = 0.796$

17677 measured reflections  
4523 independent reflections  
3901 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.043$   
 $S = 1.02$   
4523 reflections  
171 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 2.06$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.67$  e Å<sup>-3</sup>

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

$D \cdots H \cdots A$	$D \cdots H$	$H \cdots A$	$D \cdots A$	$D \cdots H \cdots A$
$\text{O1W} \cdots \text{H1W} \cdots \text{O8}^{\text{i}}$	0.80 (3)	2.06 (3)	2.7995 (19)	154 (3)
$\text{O1W} \cdots \text{H2W} \cdots \text{O4}^{\text{ii}}$	0.75 (3)	2.17 (3)	2.8913 (18)	163 (3)
$\text{O5} \cdots \text{H5} \cdots \text{O2}^{\text{iii}}$	0.82	1.85	2.655 (2)	167
Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z - \frac{1}{2}$ ; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$				

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *CRYSCAL* (T. Roisnel, local program).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5759).

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## supporting information

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## Hydrothermal synthesis and crystal structure of a new lanthanum(III) coordination polymer with fumaric acid

**Hayet Anana, Chahrazed Trifa, Sofiane Bouacida, Chaouki Boudaren and Hocine Merazig**

### S1. Comment

Coordination polymers of metal cations with organic multifunctional ligands have been received increasing interest, for these coordination polymers have one-, two-, three dimensional structures as well as potential applications as catalysts, magnetic and porous materials (Fujita *et al.*, 1994; Bénard *et al.*, 2000; Zhang *et al.*, 2000). Multi-carboxyle ligands are useful to construct unique architectures of metal-coordination polymers. The synthesis of novel lanthanide polymers and studies on luminescent, electric and magnetic properties of the compounds are of interest. Some metal coordination polymers using fumaric acid as ligand have been reported in the literature containing transition metals Cu (Dalai *et al.*, 2002), Zn (Xie *et al.*, 2003), and Mn (Devereux *et al.*, 2000). A series of rare earth fumarate complexes have also been reported (Zhang *et al.*, 2006; Li & Zou., 2006; Liu *et al.*, 2011). Hydrothermal synthesis has some advantages over conventional methods for the formation of a polymer framework with higher dimensions. Fumaric acid was used to synthesize a new lanthanum (III) coordination polymer,  $[\text{La}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2]_n$ , (I), by using hydrothermal synthesis method and the crystal structure is reported in the present article.

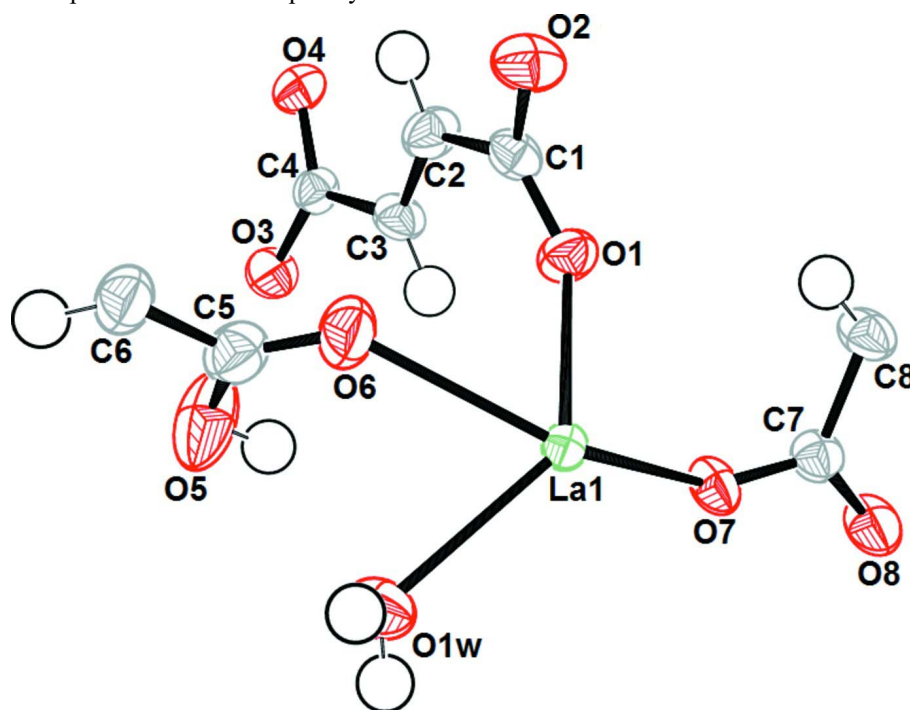
The structure of the asymmetric unit of the title complex is shown in Fig. 1. It comprises a  $\text{La}^{\text{III}}$  cation, 1.5 fumarate dianions ( $\text{L}^{2-}$ ), 0.5 fumaric acid ( $\text{H}_2\text{L}$ ) and one water ligand. Overall there are three types of  $\text{La}-\text{O}$  bridging modes in (I), the fumarate dianion exhibits full monodentate and  $\mu_2$ -oxo-bridged chelating patterns, respectively, whereas the fumaric acid shows a double monodentate coordination mode. The  $\text{La}^{\text{III}}$  cation is sited within a distorted tricapped trigonal prism defined by nine O atoms derived from seven different bridging ligands and a coordinated water molecule. One of the carboxylate groups, derived from  $\text{L}^{2-}$ , is chelating, and the remaining six carboxylates coordinate in a monodentate mode. The average  $\text{La}-\text{O}$  bond distance of  $\text{LaO}_8(\text{H}_2\text{O})$  polyhedra is 2.56 Å; the shortest  $\text{La}-\text{O}$  separation is 2.4510 (12) Å, resulting from the  $\text{La1}-\text{O1}$  bond of a bridging carboxylate, and the longest is 2.7696 (12) Å for  $\text{La1}-\text{O7}$  from the edge-sharing  $\text{La}-\text{O}$  bond. Other distances of  $\text{La}-\text{O}(\text{fum})$  vary in the range of 2.4963 (12)–2.6117 (13) Å, comparable to the usual  $\text{La}-\text{O}(\text{carboxylate})$  bonds reported (Dan *et al.*, 2005). The  $\text{LaO}_8(\text{H}_2\text{O})$  coordination polyhedra are edge-shared through one monodentate carboxylate O atoms (O7) and two bidentate carboxylate groups (O3—C4—O4 and O1—C1—O2) to generate infinite lanthanum-oxygen chains (Fig. 2). The adjacent lanthanum (III) centres have a general separation of 4.739 Å. Furthermore, the one-dimensional infinite chains are linked together with monodentate fumarate ligands to form a two-dimensional layered parallel to the crystallographic (100) (Fig.2), and the shortest interlayer distance of  $\text{La}\cdots\text{La}$  is 8.430 Å (calculated between the two lanthanum atom centres). This type of organic-inorganic layered structure has been reported of the lanthanide fumarates:  $[\text{Ln}_2(\text{fum})_3(\text{H}_2\text{fum})(\text{H}_2\text{O})_2]$  (Ln: Ce or Nd) (Zhang *et al.*, 2006). Finally, the two-dimensional layered structure is further constructed into a three-dimensional open framework by the ligands (Fig.3). The crystal is stabilized by hydrogen bond interactions between the coordinated water and carboxylate O atoms.

## S2. Experimental

All chemicals were purchased from commercial sources and used as received without further purification. The title compound, was synthesized by using a hydrothermal method. Typically mixtures of fumaric acid (1 mmol, 0.116 g), lanthanum (III) chloride pentahydrate (0.5 mmol, 0.185 g) were suspended in H<sub>2</sub>O (*ca* 10 ml). The mixture was then placed in a Teflon lined autoclave, sealed and heated to 413 K for 2 days. The reactor was cooled to room temperature over a period of 1 h. The light brown crystals suitable for X-ray diffraction were filtered, washed with water and dried in air.

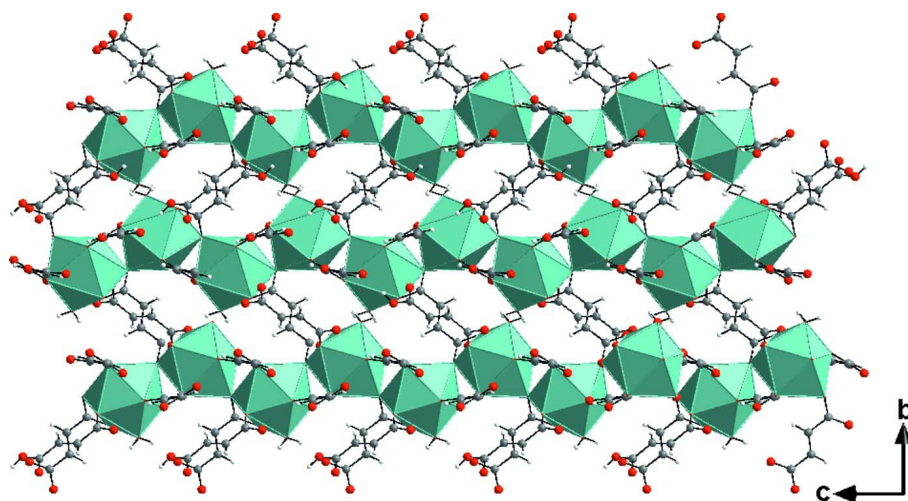
## S3. Refinement

All non-H atoms were refined with anisotropic atomic displacement parameters. The remaining H atoms were located in difference Fourier maps but introduced in calculated positions and treated as riding on their parent atom (C and O atoms) with C—H = 0.93 Å and O—H = 0.82 Å with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C}, \text{O})$ . H atoms of the water molecule were located in difference Fourier maps and refined isotropically.



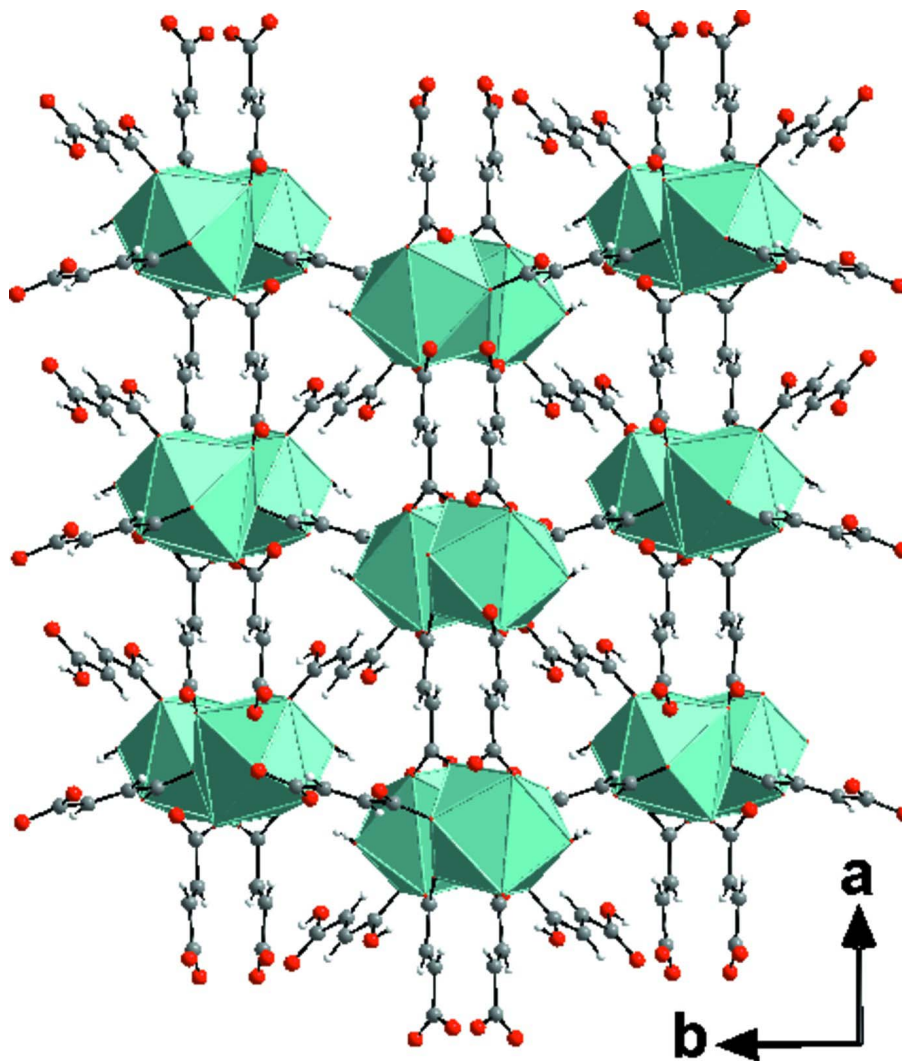
**Figure 1**

An ORTEP-3 (Farrugia, 2012) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**

A packing diagram of (I), showing the two-dimensional layered framework structure.



**Figure 3**

A packing diagram of (I), showing the three-dimensional open-framework structure.

**Poly[di aquatris( $\mu_4$ -but-2-enedioato)( $\mu_2$ -but-2-enedioic acid)dilanthanum(III)]**

*Crystal data*

$[\text{La}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2]$

$M_r = 386.05$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 8.4299\ (5)\ \text{\AA}$

$b = 14.6789\ (8)\ \text{\AA}$

$c = 8.8096\ (5)\ \text{\AA}$

$\beta = 103.318\ (3)^\circ$

$V = 1060.80\ (11)\ \text{\AA}^3$

$Z = 4$

$F(000) = 736$

$D_x = 2.417\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 7844 reflections

$\theta = 2.8\text{--}34.5^\circ$

$\mu = 4.07\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Prism, brown

$0.12 \times 0.11 \times 0.08\ \text{mm}$



*Data collection*

Bruker APEXII  
diffractometer  
Graphite monochromator  
CCD rotation images, thin slices scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2002)  
 $T_{\min} = 0.677$ ,  $T_{\max} = 0.796$   
17677 measured reflections

4523 independent reflections  
3901 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\max} = 34.6^\circ$ ,  $\theta_{\min} = 2.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -23 \rightarrow 22$   
 $l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.043$   
 $S = 1.02$   
4523 reflections  
171 parameters  
0 restraints  
Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map  
Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 0.4033P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 2.06 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.91794 (19)	0.17630 (11)	0.3525 (2)	0.0094 (3)
C2	1.09547 (19)	0.16975 (12)	0.3538 (2)	0.0116 (3)
H2	1.1677	0.1528	0.4461	0.014*
C3	1.1551 (2)	0.18705 (11)	0.22925 (19)	0.0104 (3)
H3	1.0842	0.2006	0.1344	0.012*
C4	1.33672 (18)	0.18480 (11)	0.24064 (19)	0.0091 (3)
C5	0.9759 (2)	0.43916 (12)	0.3056 (2)	0.0136 (3)
C6	1.0339 (2)	0.50146 (12)	0.4385 (2)	0.0137 (3)
H6	1.1173	0.5426	0.4366	0.016*
C7	0.53342 (19)	0.10280 (11)	-0.12552 (19)	0.0100 (3)
C8	0.5242 (2)	0.04320 (11)	0.0094 (2)	0.0115 (3)
H8	0.5533	0.0672	0.1098	0.014*
O1	0.81442 (14)	0.18896 (8)	0.22694 (15)	0.0121 (2)
O2	0.88376 (15)	0.16822 (9)	0.48504 (15)	0.0135 (2)
O1W	0.68340 (16)	0.47790 (9)	0.02557 (17)	0.0140 (2)
O3	1.38637 (14)	0.22346 (9)	0.13278 (15)	0.0128 (2)

O4	1.42800 (14)	0.14400 (8)	0.35629 (14)	0.0113 (2)
O5	1.05314 (17)	0.44700 (11)	0.19286 (17)	0.0232 (3)
H5	1.0152	0.4107	0.1232	0.035*
O6	0.86412 (16)	0.38537 (9)	0.30246 (15)	0.0165 (3)
O7	0.59366 (15)	0.18252 (8)	−0.09912 (15)	0.0106 (2)
O8	0.48750 (15)	0.07304 (9)	−0.26313 (14)	0.0145 (2)
La1	0.631512 (10)	0.309568 (6)	0.097101 (10)	0.00675 (3)
H1W	0.656 (3)	0.4969 (19)	−0.062 (4)	0.030 (7)*
H2W	0.651 (3)	0.513 (2)	0.071 (4)	0.036 (8)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0093 (6)	0.0092 (7)	0.0107 (7)	0.0008 (5)	0.0044 (5)	0.0017 (5)
C2	0.0082 (6)	0.0166 (8)	0.0099 (7)	0.0000 (5)	0.0019 (5)	0.0009 (6)
C3	0.0115 (6)	0.0117 (7)	0.0090 (6)	−0.0008 (5)	0.0045 (5)	0.0017 (6)
C4	0.0075 (6)	0.0111 (7)	0.0088 (6)	−0.0007 (5)	0.0021 (5)	−0.0002 (5)
C5	0.0131 (7)	0.0166 (8)	0.0108 (7)	−0.0010 (6)	0.0021 (6)	−0.0006 (6)
C6	0.0142 (7)	0.0153 (8)	0.0113 (7)	−0.0037 (6)	0.0021 (6)	−0.0020 (6)
C7	0.0113 (6)	0.0107 (7)	0.0088 (7)	−0.0007 (5)	0.0036 (5)	−0.0001 (5)
C8	0.0170 (7)	0.0099 (7)	0.0085 (7)	−0.0018 (6)	0.0046 (6)	0.0000 (5)
O1	0.0097 (5)	0.0139 (6)	0.0117 (5)	0.0015 (4)	0.0005 (4)	0.0016 (5)
O2	0.0118 (5)	0.0187 (6)	0.0117 (6)	0.0027 (4)	0.0063 (4)	0.0031 (5)
O1W	0.0171 (6)	0.0110 (6)	0.0141 (6)	0.0019 (4)	0.0040 (5)	0.0016 (5)
O3	0.0105 (5)	0.0175 (6)	0.0113 (6)	−0.0030 (4)	0.0043 (4)	0.0025 (5)
O4	0.0095 (5)	0.0133 (6)	0.0102 (5)	0.0009 (4)	0.0006 (4)	0.0002 (4)
O5	0.0213 (7)	0.0347 (8)	0.0161 (6)	−0.0129 (6)	0.0094 (5)	−0.0119 (6)
O6	0.0180 (6)	0.0191 (7)	0.0118 (6)	−0.0075 (5)	0.0024 (5)	−0.0026 (5)
O7	0.0138 (5)	0.0082 (5)	0.0108 (5)	−0.0019 (4)	0.0051 (4)	−0.0010 (4)
O8	0.0218 (6)	0.0138 (6)	0.0086 (5)	−0.0061 (5)	0.0051 (5)	−0.0017 (5)
La1	0.00657 (4)	0.00743 (4)	0.00650 (4)	−0.00024 (3)	0.00204 (3)	−0.00044 (3)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—O1	1.255 (2)	C8—H8	0.93
C1—O2	1.271 (2)	O1W—H1W	0.80 (3)
C1—C2	1.497 (2)	O1W—H2W	0.75 (3)
C2—C3	1.332 (2)	O3—La1 <sup>iv</sup>	2.5032 (11)
C2—H2	0.93	O4—La1 <sup>v</sup>	2.4963 (12)
C3—C4	1.512 (2)	O5—H5	0.82
C3—H3	0.93	La1—C7 <sup>vi</sup>	3.0398 (15)
C4—O3	1.2583 (19)	O6—La1	2.5926 (13)
C4—O4	1.276 (2)	O7—La1	2.5127 (12)
C5—O6	1.225 (2)	O1—La1	2.4510 (12)
C5—O5	1.312 (2)	O1W—La1	2.6117 (13)
C5—C6	1.477 (2)	O2—La1 <sup>vi</sup>	2.5631 (11)
C6—C6 <sup>i</sup>	1.338 (3)	O7—La1 <sup>ii</sup>	2.7696 (12)
C6—H6	0.93	O8—La1 <sup>ii</sup>	2.5784 (12)



C7—O8	1.263 (2)	La1—O4 <sup>vii</sup>	2.4963 (12)
C7—O7	1.2755 (19)	La1—O3 <sup>viii</sup>	2.5032 (11)
C7—C8	1.492 (2)	La1—O2 <sup>ii</sup>	2.5631 (11)
C7—La1 <sup>ii</sup>	3.0398 (15)	La1—O8 <sup>vi</sup>	2.5784 (12)
C8—C8 <sup>iii</sup>	1.331 (3)	La1—O7 <sup>vi</sup>	2.7696 (12)
O1—C1—O2	124.39 (15)	O1—La1—O7	75.61 (4)
O1—C1—C2	120.47 (14)	O4 <sup>vii</sup> —La1—O7	70.40 (4)
O2—C1—C2	115.14 (15)	O3 <sup>viii</sup> —La1—O7	74.57 (4)
C3—C2—C1	123.19 (16)	O1—La1—O2 <sup>ii</sup>	77.47 (4)
C3—C2—H2	118.4	O4 <sup>vii</sup> —La1—O2 <sup>ii</sup>	96.12 (4)
C1—C2—H2	118.4	O3 <sup>viii</sup> —La1—O2 <sup>ii</sup>	153.47 (4)
C2—C3—C4	120.64 (15)	O7—La1—O2 <sup>ii</sup>	79.32 (4)
C2—C3—H3	119.7	O1—La1—O8 <sup>vi</sup>	125.08 (4)
C4—C3—H3	119.7	O4 <sup>vii</sup> —La1—O8 <sup>vi</sup>	85.20 (4)
O3—C4—O4	124.78 (14)	O3 <sup>viii</sup> —La1—O8 <sup>vi</sup>	77.55 (4)
O3—C4—C3	116.62 (14)	O7—La1—O8 <sup>vi</sup>	145.63 (4)
O4—C4—C3	118.60 (13)	O2 <sup>ii</sup> —La1—O8 <sup>vi</sup>	128.50 (4)
O6—C5—O5	123.56 (17)	O1—La1—O6	72.00 (4)
O6—C5—C6	121.97 (15)	O4 <sup>vii</sup> —La1—O6	137.48 (4)
O5—C5—C6	114.46 (15)	O3 <sup>viii</sup> —La1—O6	129.99 (4)
C6 <sup>i</sup> —C6—C5	119.8 (2)	O7—La1—O6	138.97 (4)
C6 <sup>i</sup> —C6—H6	120.1	O2 <sup>ii</sup> —La1—O6	69.69 (4)
C5—C6—H6	120.1	O8 <sup>vi</sup> —La1—O6	75.14 (4)
O8—C7—O7	120.91 (15)	O1—La1—O1W	132.35 (4)
O8—C7—C8	120.09 (15)	O4 <sup>vii</sup> —La1—O1W	69.95 (4)
O7—C7—C8	118.95 (15)	O3 <sup>viii</sup> —La1—O1W	134.19 (4)
O8—C7—La1 <sup>ii</sup>	56.95 (8)	O7—La1—O1W	122.55 (4)
O7—C7—La1 <sup>ii</sup>	65.65 (8)	O2 <sup>ii</sup> —La1—O1W	65.59 (4)
C8—C7—La1 <sup>ii</sup>	164.17 (11)	O8 <sup>vi</sup> —La1—O1W	66.82 (4)
C8 <sup>iii</sup> —C8—C7	122.0 (2)	O6—La1—O1W	67.70 (4)
C8 <sup>iii</sup> —C8—H8	119	O1—La1—O7 <sup>vi</sup>	77.26 (4)
C7—C8—H8	119	O4 <sup>vii</sup> —La1—O7 <sup>vi</sup>	126.88 (4)
C1—O1—La1	138.87 (11)	O3 <sup>viii</sup> —La1—O7 <sup>vi</sup>	67.52 (4)
C1—O2—La1 <sup>vi</sup>	136.53 (11)	O7—La1—O7 <sup>vi</sup>	132.16 (3)
La1—O1W—H1W	122 (2)	O2 <sup>ii</sup> —La1—O7 <sup>vi</sup>	131.09 (4)
La1—O1W—H2W	116 (2)	O8 <sup>vi</sup> —La1—O7 <sup>vi</sup>	48.61 (4)
H1W—O1W—H2W	102 (3)	O6—La1—O7 <sup>vi</sup>	62.92 (4)
C4—O3—La1 <sup>iv</sup>	138.62 (11)	O1W—La1—O7 <sup>vi</sup>	104.86 (4)
C4—O4—La1 <sup>v</sup>	136.10 (11)	O1—La1—C7 <sup>vi</sup>	100.89 (4)
C5—O5—H5	109.5	O4 <sup>vii</sup> —La1—C7 <sup>vi</sup>	107.86 (4)
C5—O6—La1	138.30 (12)	O3 <sup>viii</sup> —La1—C7 <sup>vi</sup>	74.18 (4)
C7—O7—La1	142.04 (10)	O7—La1—C7 <sup>vi</sup>	148.44 (4)
C7—O7—La1 <sup>ii</sup>	89.54 (9)	O2 <sup>ii</sup> —La1—C7 <sup>vi</sup>	131.24 (4)
La1—O7—La1 <sup>ii</sup>	127.52 (4)	O8 <sup>vi</sup> —La1—C7 <sup>vi</sup>	24.23 (4)
C7—O8—La1 <sup>ii</sup>	98.82 (10)	O6—La1—C7 <sup>vi</sup>	63.86 (4)
O1—La1—O4 <sup>vii</sup>	146.01 (4)	O1W—La1—C7 <sup>vi</sup>	83.41 (4)
O1—La1—O3 <sup>viii</sup>	91.46 (4)	O7 <sup>vi</sup> —La1—C7 <sup>vi</sup>	24.81 (4)

O4 <sup>vii</sup> —La1—O3 <sup>viii</sup>	79.57 (4)		
O1—C1—C2—C3	8.0 (3)	C1—O1—La1—O6	22.16 (15)
O2—C1—C2—C3	−171.99 (16)	C1—O1—La1—O1W	55.44 (17)
C1—C2—C3—C4	176.25 (15)	C1—O1—La1—O7 <sup>vi</sup>	−43.17 (16)
C2—C3—C4—O3	−162.53 (16)	C1—O1—La1—C7 <sup>vi</sup>	−35.55 (16)
C2—C3—C4—O4	18.0 (2)	C7—O7—La1—O1	70.34 (18)
O6—C5—C6—C6 <sup>i</sup>	1.5 (3)	La1 <sup>ii</sup> —O7—La1—O1	−124.25 (6)
O5—C5—C6—C6 <sup>i</sup>	−178.9 (2)	C7—O7—La1—O4 <sup>vii</sup>	−109.49 (18)
O8—C7—C8—C8 <sup>iii</sup>	3.3 (3)	La1 <sup>ii</sup> —O7—La1—O4 <sup>vii</sup>	55.92 (6)
O7—C7—C8—C8 <sup>iii</sup>	−174.2 (2)	C7—O7—La1—O3 <sup>viii</sup>	−25.29 (17)
La1 <sup>ii</sup> —C7—C8—C8 <sup>iii</sup>	−71.3 (5)	La1 <sup>ii</sup> —O7—La1—O3 <sup>viii</sup>	140.12 (7)
O2—C1—O1—La1	70.6 (2)	C7—O7—La1—O2 <sup>ii</sup>	150.00 (18)
C2—C1—O1—La1	−109.40 (17)	La1 <sup>ii</sup> —O7—La1—O2 <sup>ii</sup>	−44.59 (6)
O1—C1—O2—La1 <sup>vi</sup>	−9.9 (3)	C7—O7—La1—O8 <sup>vi</sup>	−62.2 (2)
C2—C1—O2—La1 <sup>vi</sup>	170.08 (11)	La1 <sup>ii</sup> —O7—La1—O8 <sup>vi</sup>	103.23 (7)
O4—C4—O3—La1 <sup>iv</sup>	−33.2 (3)	C7—O7—La1—O6	109.01 (17)
C3—C4—O3—La1 <sup>iv</sup>	147.30 (13)	La1 <sup>ii</sup> —O7—La1—O6	−85.58 (8)
O3—C4—O4—La1 <sup>v</sup>	72.1 (2)	C7—O7—La1—O1W	−158.26 (17)
C3—C4—O4—La1 <sup>v</sup>	−108.47 (15)	La1 <sup>ii</sup> —O7—La1—O1W	7.15 (8)
O5—C5—O6—La1	−30.8 (3)	C7—O7—La1—O7 <sup>vi</sup>	13.0 (2)
C6—C5—O6—La1	148.76 (14)	La1 <sup>ii</sup> —O7—La1—O7 <sup>vi</sup>	178.394 (15)
O8—C7—O7—La1	154.08 (13)	C7—O7—La1—C7 <sup>vi</sup>	−17.1 (2)
C8—C7—O7—La1	−28.5 (3)	La1 <sup>ii</sup> —O7—La1—C7 <sup>vi</sup>	148.33 (6)
La1 <sup>ii</sup> —C7—O7—La1	168.47 (17)	C5—O6—La1—O1	117.06 (19)
O8—C7—O7—La1 <sup>ii</sup>	−14.40 (15)	C5—O6—La1—O4 <sup>vii</sup>	−42.3 (2)
C8—C7—O7—La1 <sup>ii</sup>	163.03 (13)	C5—O6—La1—O3 <sup>viii</sup>	−166.68 (17)
O7—C7—O8—La1 <sup>ii</sup>	15.68 (17)	C5—O6—La1—O7	77.5 (2)
C8—C7—O8—La1 <sup>ii</sup>	−161.72 (12)	C5—O6—La1—O2 <sup>ii</sup>	34.12 (18)
C1—O1—La1—O4 <sup>vii</sup>	176.91 (14)	C5—O6—La1—O8 <sup>vi</sup>	−107.59 (19)
C1—O1—La1—O3 <sup>viii</sup>	−109.72 (16)	C5—O6—La1—O1W	−36.94 (18)
C1—O1—La1—O7	176.62 (16)	C5—O6—La1—O7 <sup>vi</sup>	−158.3 (2)
C1—O1—La1—O2 <sup>ii</sup>	94.61 (16)	C5—O6—La1—C7 <sup>vi</sup>	−130.57 (19)
C1—O1—La1—O8 <sup>vi</sup>	−33.94 (17)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W $\cdots$ O8 <sup>ix</sup>	0.80 (3)	2.06 (3)	2.7995 (19)	154 (3)
O1W—H2W $\cdots$ O4 <sup>x</sup>	0.75 (3)	2.17 (3)	2.8913 (18)	163 (3)
O5—H5 $\cdots$ O2 <sup>ii</sup>	0.82	1.85	2.655 (2)	167

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