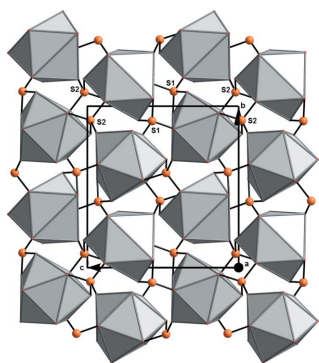# Crystal structure of $NH_4[La(SO_4)_2(H_2O)]$

Meriem Benslimane,[a]* Yasmine Kheira Redjel,[a] Hocine Merazig[a] and Jean-Claude Daran[b]

[a]Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Faculté des Sciences Exactes, Département de Chimie, Université de Constantine 1, 25000 Constantine, Algeria, and [b]Laboratoire de Chimie de Coordination, UPR-CNRS 8241, 05 route de Narbonne, 31077 Toulouse Cedex 4. *Correspondence e-mail: b_meriem80@yahoo.fr

The principal building units in the crystal structure of ammonium aquabis-(sulfato)lanthanate(III) are slightly distorted SO_4 tetrahedra, LaO_9 polyhedra in the form of distorted tricapped trigonal prisms, and NH_4^+ ions. The La^{3+} cation is coordinated by eight O atoms from six different sulfate tetrahedra, two of which are bidentate coordinating and four monodentate, as well as one O atom from a water molecule; each sulfate anion bridges three La^{3+} cations. These bridging modes result in the formation of a three-dimensional anionic $[La(SO_4)_2(H_2O)]^-$ framework that is stabilized by O—H···O hydrogen-bonding interactions. The disordered ammonium cations are situated in the cavities of this framework and are hydrogen-bonded to six surrounding O atoms.

1. Chemical context

Three-dimensional framework materials are characterized by their structural diversity. They are of continuing interest as a result of their technologically important properties and potential applications in catalysis, ion-exchange, adsorption, intercalation, and radioactive waste remediation (Szostak, 1989; Cheetham *et al.*, 1999; Rosi *et al.*, 2003; Ok *et al.*, 2007). Many materials showing such functional features contain structurally versatile cations, in particular heavier metal cations with large coordination spheres. Among many other cations, lanthanide cations have been used widely, since they exhibit high coordination numbers and can show a large topological diversity in the resulting framework structures (Bataille & Louër, 2002; Wickleder, 2002; Yuan *et al.*, 2005). One of the most promising synthetic methods for the preparation of compounds with framework structures is the hydrothermal (or solvothermal) reaction technique (Feng *et al.*, 1997; Natarajan *et al.*, 2000) in which mineralizers such as acids or bases are introduced to increase the solubility and reactivity of the reagents (Laudise, 1959; Laudise & Ballman, 1958). Moreover, organic or inorganic templates are used to direct the topologies of the framework structures and the concomitant physical and chemical properties of the products (Szostak, 1989; Breck, 1974; Barrer, 1982). Thus, we have tried to utilize the hydrothermal technique to react a lanthanide cation (La^{3+}) with sulfuric acid in the presence of NH_4OH and 3-aminobenzoic acid as a template to prepare higher dimensional framework materials. However, in the present case the organic template was not incorporated in the resultant crystal structure of the title compound, $NH_4[La(SO_4)_2(H_2O)]$, which represents a new hydrate form. Other members in the system $NH_4^+/La^{3+}/SO_4^{2-}/(H_2O)$ are two forms of anhydrous $(NH_4)[La(SO_4)_2]$ (Sarukhanyan *et al.*, 1984a; Bénard-

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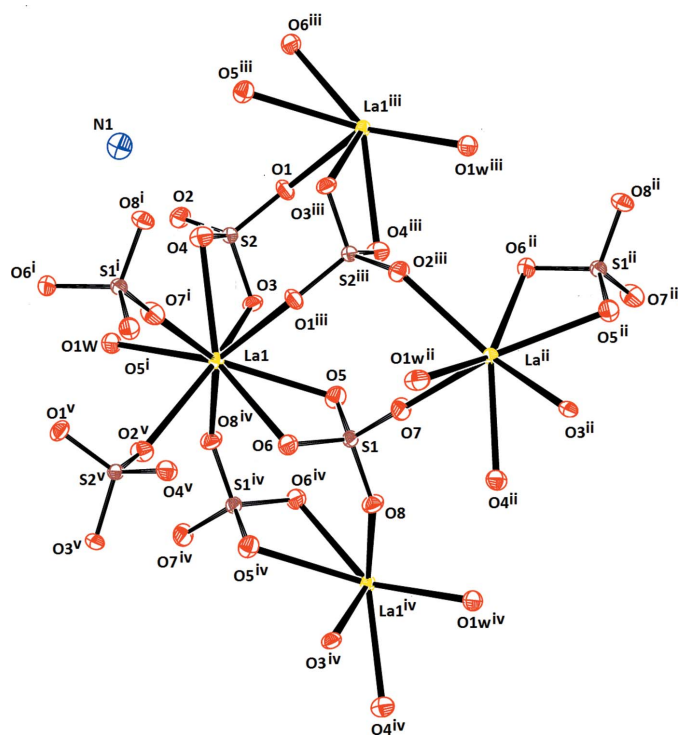
Figure 1
The principal building units, LaO$_9$ polyhedra and SO$_4$ tetrahedra, in the crystal structure of (NH$_4$)[La(SO$_4$)$_2$(H$_2$O)], showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (ii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (iii) $1 - x$, $2 - y$, $-z$; (iv) $2 - x$, $2 - y$, $1 - z$; (v) x, $\frac{3}{2} - y$, $\frac{1}{2} + z$.]

Rocherullé *et al.*, 2001), (NH$_4$)$_5$[La(SO$_4$)$_4$] (Niinisto *et al.*, 1980) and (NH$_4$)[La(SO$_4$)$_2$(H$_2$O)$_4$] (Keppert *et al.*, 1999).

Sulfates with an A^+:Ln^{3+} (A^+ = alkaline ions, Ln^{3+} = lanthanide ions) ratio of 1:1 are one of the best investigated groups among hydrous ternary sulfates. They crystallize either as monohydrates (Blackburn & Gerkin, 1995; Barnes, 1995; Iskhakova *et al.*, 1985a) or tetrahydrates (Eriksson *et al.*, 1974), and in few cases also as dihydrates (Kaučič *et al.*, 1985; Iskhakova & Trunov, 1985). The tetrahydrates are mainly found for the bigger monovalent ions Cs$^+$, NH$_4^+$, and Rb$^+$. For the smaller A^+ ions such as Na$^+$, the monohydrate becomes dominant.

2. Structural commentary

The structure of the title compound comprises LaO$_9$ polyhedra and SO$_4$ tetrahedra as the principal building units (Fig. 1), forming an anionic [La(SO$_4$)$_2$(H$_2$O)]$^-$ framework by sharing common edges and vertices (Fig. 2). The NH$_4^+$ counter-cations are situated in the cavities of this framework.

The La^{3+} cation is coordinated by eight O atoms from six different sulfate tetrahedra. Two tetrahedra are in a bidentate coordination mode and four tetrahedra are in a monodentate mode. The distorted tricapped trigonal–prismatic coordination sphere is completed by one O atom from a water molecule. The La—O bond lengths, ranging from 2.472 (3) to 2.637 (3) Å with 2.496 (3) Å to the water molecule, and the
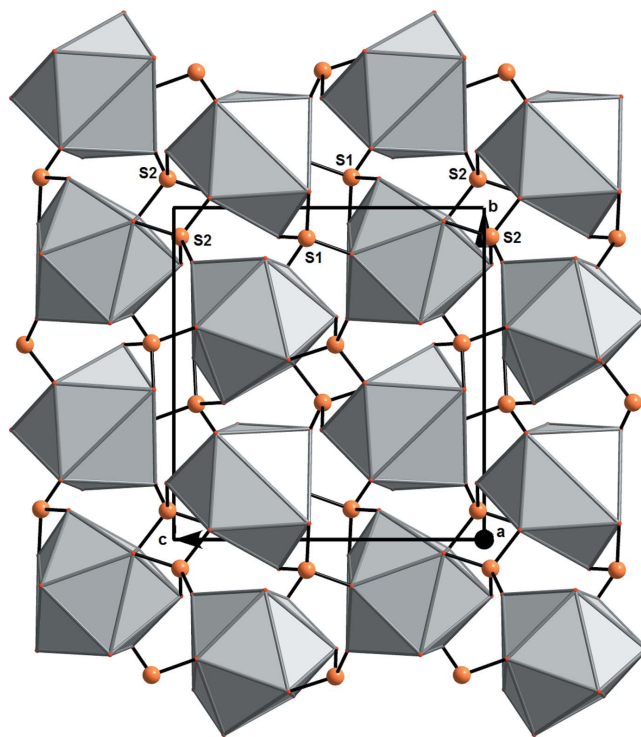
Figure 2
The connection of LaO$_9$ polyhedra and SO$_4$ tetrahedra in the crystal structure of (NH$_4$)[La(SO$_4$)$_2$(H$_2$O)], viewed along the *a* axis.

O—La—O angles, ranging from 53.55 (8) to 145.43 (9)°, are similar to the analogous distances found in NaLa(SO$_4$)$_2$·H$_2$O (Blackburn & Gerkin, 1995). The ninefold coordination of La^{3+} in NH$_4$[La(SO$_4$)$_2$(H$_2$O)] is typical for the majority of monohydrated alkali rare earth sulfate complexes and of rare earth complexes in general. For early members of the rare earth sulfate series, the coordination number of nine is realized, *e.g.* for Ce, Pr, La and Nd (Blackburn & Gerkin, 1994, 1995; Iskhakova *et al.*, 1985b, 1988). For later members of the sulfate series, such as Gd (Sarukhanyan *et al.*, 1984b), the coordination number decreases to eight, presumably in association with the lanthanide contraction. There are two sulfur atoms (S1, S2) in the asymmetric unit of the title compound, both with very similar S—O bond lengths in the ranges 1.465 (3)–1.488 (3) and 1.468 (3)–1.490 (3) Å, respectively. The range of O—S—O bond angles, 106.04 (16)–110.89 (19)° for S1 and 104.70 (16)–111.52 (17)° for S2, reflect the distortion of the two sulfate tetrahedra. Each SO$_4$ anion bridges three La^{3+} cations (Fig. 2).

3. Supramolecular features

The bridging modes of the O atoms result in the formation of a three-dimensional anionic framework, stabilized by O—H···O hydrogen-bonding interactions between the aqua ligand and the two SO$_4$ tetrahedra (Table 1) whereby each sulfate tetrahedron establishes one hydrogen bond with the water molecule *via* the oxygen atom (O6 and O3) corresponding to the longest S—O bonds. The N atoms are situated in the cavities of this framework. Although the H atoms of the

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H11$\cdots$O3^i	0.84 (5)	1.94 (5)	2.717 (5)	153 (5)
O1W—H21$\cdots$O6^{ii}	0.85 (3)	1.95 (3)	2.778 (4)	168 (5)
N1$\cdots$O1^{iii}			2.942 (5)	
N1$\cdots$O6^{ii}			3.036 (5)	
N1$\cdots$O3^{iv}			2.914 (5)	
N1$\cdots$O8^v			2.943 (5)	
N1$\cdots$O5^{vi}			2.865 (5)	
N1$\cdots$O4			2.866 (5)	

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

ammonium cation could not be located, the N$\cdots$O distances between 2.865 (5) and 3.036 (5) Å strongly suggest N—H$\cdots$O hydrogen bonds of medium strength (Table 1). It appears most likely that the number of O atoms (six) in the vicinity of the N atom is the reason for the disorder of the ammonium cation.

4. Synthesis and crystallization

The title compound was obtained during the attempted preparation of a complex resulting from the hydrothermal reaction of La$_2$O$_3$ (0.1 g, 1 mmol) with 37%wt sulfuric acid and 3-aminobenzoic acid (0.048 g, 1 mmol) in the presence of NH$_4$OH in 10 ml water. The mixture was kept in a 23 ml Teflon-lined steel autoclave at 433 K for 3 d. After this treatment, the autoclave was cooled slowly to room temperature. Slow evaporation of the solvent at room temperature led to the formation of prismatic colourless crystals of the title compound.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The oxygen-bound hydrogen atoms were located in a difference Fourier map and were refined with restraints of the O—H bond length [0.85 (1) Å] and H$\cdots$H distances (1.39 Å) and with $U_{iso}(H) = 1.5U_{eq}(O)$. The ammonium hydrogen atoms could not be located reliably by difference Fourier methods. Several disorder models considering the hydrogen-bonding environment (see Table 1) failed, eventually leading to the exclusion of the ammonium hydrogen atoms from the refinement. The maximum and minimum peaks in the final difference Fourier map are 0.93 and 0.72 Å, respectively, from atom La1.

Diffraction data were collected some time ago, and merged in the corresponding crystal class. Unfortunately, the original measurement data got lost; experiments to repeat the crystal growth were unsuccessful. Therefore the crystal structure was finally solved and refined with the merged data set.

Table 2
Experimental details.

Crystal data	
Chemical formula	NH$_4$[La(SO$_4$)$_2$(H$_2$O)]
M_r	367.07
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.4919 (16), 9.978 (2), 11.9268 (19)
β (°)	128.511 (10)
V (Å^3)	790.7 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.96
Crystal size (mm)	$0.30 \times 0.20 \times 0.10$
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	For a sphere (Dwiggins, 1975)
T_{min}, T_{max}	0.419, 0.431
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	2414, 2414, 2362
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.081, 1.26
No. of reflections	2414
No. of parameters	124
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.81, −1.48

Computer programs: *COLLECT* (Nonius, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 1999).

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Crystal structure of NH₄[La(SO₄)₂(H₂O)]

Meriem Benslimane, Yasmine Kheira Redjel, Hocine Merazig and Jean-Claude Daran

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Ammonium aquabis(sulfato)lanthanate(III)

Crystal data

$NH_4[La(SO_4)_2(H_2O)]$	$F(000) = 680$
$M_r = 367.07$	$D_x = 3.083$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2542 reflections
$a = 8.4919$ (16) Å	$\theta = 3$–30.5°
$b = 9.978$ (2) Å	$\mu = 5.96$ mm^{-1}
$c = 11.9268$ (19) Å	$T = 100$ K
$\beta = 128.511$ (10)°	Prism, colourless
$V = 790.7$ (3) Å^3	$0.30 \times 0.20 \times 0.10 \times 0.10$ (radius) mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2414 measured reflections
Radiation source: fine-focus sealed tube	2414 independent reflections
Graphite monochromator	2362 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{int} = 0.0000$
CCD scans	$\theta_{max} = 30.5°$, $\theta_{min} = 3.0°$
Absorption correction: for a sphere (Dwiggins, 1975)	$h = -12 \rightarrow 0$
	$k = -14 \rightarrow 0$
$T_{min} = 0.419$, $T_{max} = 0.431$	$l = -12 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.027$	
$wR(F^2) = 0.081$	
$S = 1.26$	Hydrogen site location: inferred from neighbouring sites
2414 reflections	H atoms treated by a mixture of independent and constrained refinement
124 parameters	
3 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 2.7376P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.81$ e Å^{-3}
$\Delta\rho_{min} = -1.48$ e Å^{-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 (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
La1	0.71683 (3)	0.839390 (18)	0.248314 (19)	0.01052 (8)
S1	0.74128 (12)	1.09162 (8)	0.42791 (8)	0.01163 (15)
S2	0.70608 (12)	0.91270 (8)	−0.02026 (8)	0.01129 (15)
O1	0.6085 (4)	1.0290 (3)	−0.1156 (3)	0.0179 (5)
O2	0.8105 (5)	0.8337 (3)	−0.0602 (3)	0.0189 (5)
O3	0.8535 (4)	0.9585 (3)	0.1310 (3)	0.0156 (5)
O8	0.9057 (4)	1.1402 (3)	0.5727 (3)	0.0182 (5)
O4	0.5597 (4)	0.8301 (3)	−0.0221 (3)	0.0188 (5)
O7	0.5667 (4)	1.1797 (3)	0.3641 (3)	0.0229 (6)
O6	0.6873 (4)	0.9516 (3)	0.4347 (3)	0.0185 (5)
O5	0.8062 (4)	1.0870 (3)	0.3387 (3)	0.0192 (5)
O1W	0.8711 (5)	0.6537 (3)	0.2059 (3)	0.0241 (6)
H11	0.982 (5)	0.615 (6)	0.266 (4)	0.036*
H21	0.820 (8)	0.632 (6)	0.121 (2)	0.036*
N1	0.2567 (6)	0.6458 (4)	−0.2302 (4)	0.0244 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.01098 (11)	0.00981 (11)	0.01113 (11)	−0.00037 (5)	0.00706 (9)	−0.00028 (5)
S1	0.0106 (3)	0.0110 (3)	0.0114 (3)	0.0009 (3)	0.0059 (3)	−0.0005 (3)
S2	0.0118 (3)	0.0111 (3)	0.0101 (3)	0.0008 (3)	0.0064 (3)	0.0000 (2)
O1	0.0212 (12)	0.0144 (11)	0.0173 (11)	0.0055 (10)	0.0116 (10)	0.0056 (9)
O2	0.0214 (13)	0.0207 (14)	0.0180 (13)	0.0035 (10)	0.0140 (12)	−0.0013 (9)
O3	0.0158 (11)	0.0162 (11)	0.0111 (10)	−0.0037 (9)	0.0066 (9)	−0.0028 (9)
O8	0.0141 (12)	0.0206 (12)	0.0141 (12)	−0.0009 (10)	0.0059 (10)	−0.0041 (10)
O4	0.0181 (13)	0.0212 (13)	0.0174 (12)	−0.0061 (9)	0.0111 (11)	−0.0018 (9)
O7	0.0139 (12)	0.0207 (13)	0.0217 (13)	0.0068 (10)	0.0049 (11)	−0.0025 (10)
O6	0.0240 (13)	0.0145 (11)	0.0174 (12)	−0.0029 (10)	0.0130 (11)	−0.0002 (9)
O5	0.0246 (13)	0.0181 (12)	0.0211 (12)	−0.0020 (10)	0.0174 (11)	−0.0016 (10)
O1W	0.0289 (16)	0.0220 (14)	0.0177 (13)	0.0126 (11)	0.0127 (12)	0.0010 (10)
N1	0.0248 (16)	0.0252 (18)	0.0296 (18)	−0.0037 (13)	0.0201 (15)	−0.0006 (13)

Geometric parameters (Å, º)

La1—O7ⁱ	2.472 (3)	S1—O8	1.471 (3)
La1—O1W	2.496 (3)	S1—O5	1.472 (3)
La1—O8ⁱⁱ	2.521 (3)	S1—O6	1.488 (3)
La1—O1ⁱⁱⁱ	2.533 (3)	S2—O1	1.468 (3)
La1—O2ⁱᵛ	2.563 (3)	S2—O2	1.470 (3)
La1—O3	2.596 (3)	S2—O4	1.480 (3)
La1—O5	2.612 (3)	S2—O3	1.490 (3)
La1—O4	2.614 (3)	O1W—H11	0.845 (10)
La1—O6	2.637 (3)	O1W—H21	0.844 (10)
S1—O7	1.465 (3)		
O7ⁱ—La1—O1W	82.44 (12)	O7ⁱ—La1—O6	99.16 (10)
O7ⁱ—La1—O8ⁱⁱ	143.78 (10)	O1W—La1—O6	145.43 (9)
O1W—La1—O8ⁱⁱ	71.36 (10)	O8ⁱⁱ—La1—O6	89.43 (9)
O7ⁱ—La1—O1ⁱⁱⁱ	71.36 (10)	O1ⁱⁱⁱ—La1—O6	70.57 (9)
O1W—La1—O1ⁱⁱⁱ	139.83 (10)	O2ⁱᵛ—La1—O6	71.00 (9)
O8ⁱⁱ—La1—O1ⁱⁱⁱ	143.55 (9)	O3—La1—O6	124.69 (8)
O7ⁱ—La1—O2ⁱᵛ	72.90 (10)	O5—La1—O6	53.55 (8)
O1W—La1—O2ⁱᵛ	76.67 (10)	O4—La1—O6	144.28 (9)
O8ⁱⁱ—La1—O2ⁱᵛ	76.96 (10)	O7—S1—O8	109.04 (17)
O1ⁱⁱⁱ—La1—O2ⁱᵛ	121.24 (9)	O7—S1—O5	110.89 (19)
O7ⁱ—La1—O3	127.89 (10)	O8—S1—O5	110.49 (17)
O1W—La1—O3	76.32 (10)	O7—S1—O6	110.19 (18)
O8ⁱⁱ—La1—O3	70.11 (9)	O8—S1—O6	110.17 (16)
O1ⁱⁱⁱ—La1—O3	96.07 (9)	O5—S1—O6	106.04 (16)
O2ⁱᵛ—La1—O3	142.55 (9)	O7—S1—La1	119.80 (13)
O7ⁱ—La1—O5	140.16 (10)	O8—S1—La1	131.15 (12)
O1W—La1—O5	137.02 (11)	O5—S1—La1	52.71 (11)
O8ⁱⁱ—La1—O5	71.62 (9)	O6—S1—La1	53.78 (11)
O1ⁱⁱⁱ—La1—O5	72.00 (9)	O1—S2—O2	109.67 (16)
O2ⁱᵛ—La1—O5	114.84 (9)	O1—S2—O4	111.40 (17)
O3—La1—O5	71.17 (8)	O2—S2—O4	111.52 (17)
O7ⁱ—La1—O4	74.43 (10)	O1—S2—O3	109.85 (16)
O1W—La1—O4	69.69 (10)	O2—S2—O3	109.59 (17)
O8ⁱⁱ—La1—O4	116.81 (9)	O4—S2—O3	104.70 (16)
O1ⁱⁱⁱ—La1—O4	74.17 (9)	La1—O1W—H11	128 (4)
O2ⁱᵛ—La1—O4	135.44 (9)	La1—O1W—H21	119 (4)
O3—La1—O4	53.65 (8)	H11—O1W—H21	112 (3)
O5—La1—O4	109.69 (9)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11···O3ᵛ	0.84 (5)	1.94 (5)	2.717 (5)	153 (5)
O1*W*—H21···O6ᵛⁱ	0.85 (3)	1.95 (3)	2.778 (4)	168 (5)

N1···O1^{vii}	2.942 (5)
N1···O6^{vi}	3.036 (5)
N1···O3^{viii}	2.914 (5)
N1···O8^{i}	2.943 (5)
N1···O5^{iii}	2.865 (5)
N1···O4	2.866 (5)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (iii) −*x*+1, −*y*+2, −*z*; (v) −*x*+2, *y*−1/2, −*z*+1/2; (vi) *x*, −*y*+3/2, *z*−1/2; (vii) −*x*+1, *y*−1/2, −*z*−1/2; (viii) *x*−1, −*y*+3/2, *z*−1/2.