

Keywords: crystal structure; hydrous ternary sulfates; hydrothermal synthesis; hydrogen bonding

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Crystal structure of $\text{NH}_4[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]$

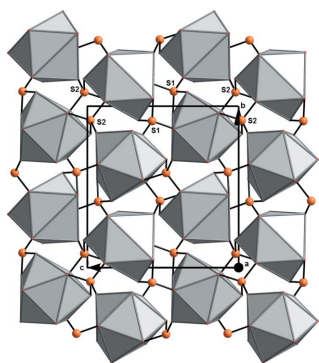
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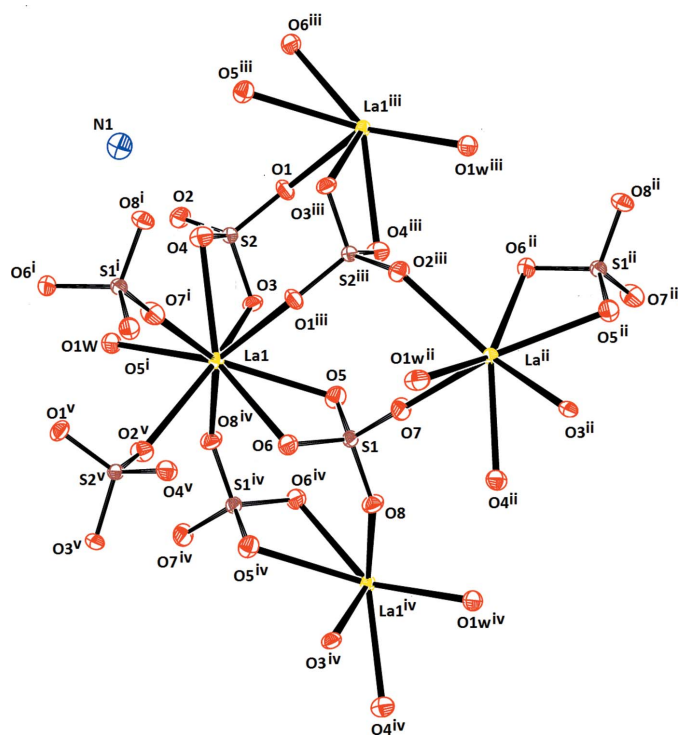
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The principal building units in the crystal structure of ammonium aquabis(sulfato)lanthanate(III) are slightly distorted SO_4 tetrahedra, LaO_9 polyhedra in the form of distorted tricapped trigonal prisms, and NH_4^+ ions. The La^{3+} cation is coordinated 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 $[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]^-$ framework that is stabilized by $\text{O}-\text{H}\cdots\text{O}$ 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, $\text{NH}_4[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]$, which represents a new hydrate form. Other members in the system $\text{NH}_4^+/\text{La}^{3+}/\text{SO}_4^{2-}/(\text{H}_2\text{O})$ are two forms of anhydrous $(\text{NH}_4)[\text{La}(\text{SO}_4)_2]$ (Sarukhanyan *et al.*, 1984a; Bénard-




Figure 1

The principal building units, LaO_9 polyhedra and SO_4 tetrahedra, in the crystal structure of $(\text{NH}_4)[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]$, 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) $x, \frac{3}{2} - y, \frac{1}{2} + z$.]

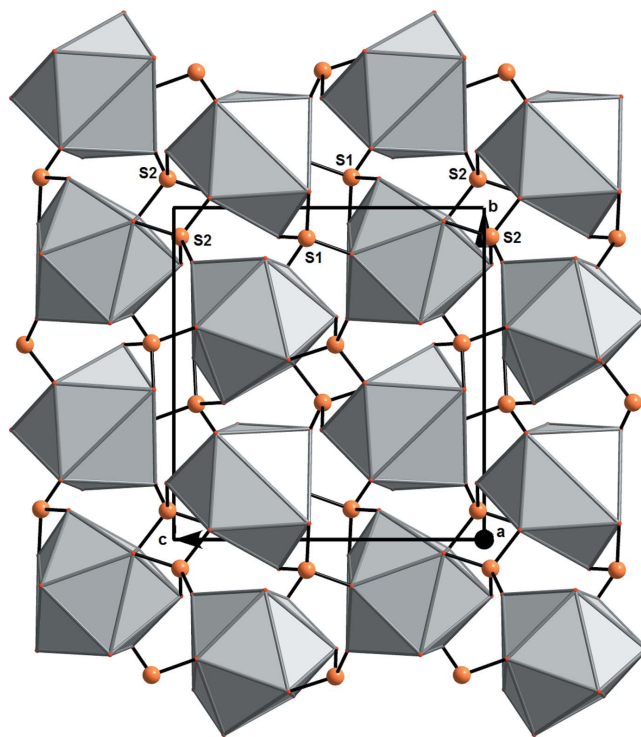
Rocherullé *et al.*, 2001), $(\text{NH}_4)_5[\text{La}(\text{SO}_4)_4]$ (Niinistö *et al.*, 1980) and $(\text{NH}_4)[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$ (Keppert *et al.*, 1999).

Sulfates with an $A^+:\text{Ln}^{3+}$ (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 $[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]^-$ 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 $\text{La}-\text{O}$ 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 $(\text{NH}_4)[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]$, viewed along the a axis.

$\text{O}-\text{La}-\text{O}$ angles, ranging from 53.55 (8) to 145.43 (9)°, are similar to the analogous distances found in $\text{NaLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (Blackburn & Gerkin, 1995). The ninefold coordination of La^{3+} in $\text{NH}_4[\text{La}(\text{SO}_4)_2(\text{H}_2\text{O})]$ 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 $\text{O}-\text{H} \cdots \text{O}$ 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 La₂O₃ (0.1 g, 1 mmol) with 37%wt sulfuric acid and 3-aminobenzoic acid (0.048 g, 1 mmol) in the presence of NH₄OH 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 $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. 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.

Acknowledgements

Technical support (X-ray measurements) from Université Henri Poincaré, Nancy 1, is gratefully acknowledged.

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 × 0.20 × 0.10 |
| Data collection | |
| Diffractometer | Nonius KappaCCD |
| Absorption correction | For a sphere (Dwiggins, 1975) |
| $T_{\text{min}}, T_{\text{max}}$ | 0.419, 0.431 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 2414, 2414, 2362 |
| $(\sin \theta/\lambda)_{\text{max}}$ (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 |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (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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Acta Cryst. (2015). E71, 663-666 [doi:10.1107/S2056989015009457]

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

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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

NH₄[La(SO₄)₂(H₂O)]

$M_r = 367.07$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.4919$ (16) Å

$b = 9.978$ (2) Å

$c = 11.9268$ (19) Å

$\beta = 128.511$ (10)°

$V = 790.7$ (3) Å³

$Z = 4$

$F(000) = 680$

$D_x = 3.083$ Mg m⁻³

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

Cell parameters from 2542 reflections

$\theta = 3\text{--}30.5^\circ$

$\mu = 5.96$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.30 \times 0.20 \times 0.10 \times 0.10$ (radius) mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm⁻¹

CCD scans

Absorption correction: for a sphere

(Dwiggins, 1975)

$T_{\min} = 0.419$, $T_{\max} = 0.431$

2414 measured reflections

2414 independent reflections

2362 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$

$\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -12 \rightarrow 0$

$k = -14 \rightarrow 0$

$l = -12 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.081$

$S = 1.26$

2414 reflections

124 parameters

3 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

$$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 2.7376P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.81 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.48 \text{ e } \text{\AA}^{-3}$$

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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| 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 (\AA^2)

| | 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 (\AA , $^\circ$)

| | | | |
|---|-------------|---------------------------|-------------|
| La1—O7 ⁱ | 2.472 (3) | S1—O8 | 1.471 (3) |
| La1—O1W | 2.496 (3) | S1—O5 | 1.472 (3) |
| La1—O8 ⁱⁱ | 2.521 (3) | S1—O6 | 1.488 (3) |
| La1—O1 ⁱⁱⁱ | 2.533 (3) | S2—O1 | 1.468 (3) |
| La1—O2 ^{iv} | 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) | | |
| O7 ⁱ —La1—O1W | 82.44 (12) | O7 ⁱ —La1—O6 | 99.16 (10) |
| O7 ⁱ —La1—O8 ⁱⁱ | 143.78 (10) | O1W—La1—O6 | 145.43 (9) |
| O1W—La1—O8 ⁱⁱ | 71.36 (10) | O8 ⁱⁱ —La1—O6 | 89.43 (9) |
| O7 ⁱ —La1—O1 ⁱⁱⁱ | 71.36 (10) | O1 ⁱⁱⁱ —La1—O6 | 70.57 (9) |
| O1W—La1—O1 ⁱⁱⁱ | 139.83 (10) | O2 ^{iv} —La1—O6 | 71.00 (9) |
| O8 ⁱⁱ —La1—O1 ⁱⁱⁱ | 143.55 (9) | O3—La1—O6 | 124.69 (8) |
| O7 ⁱ —La1—O2 ^{iv} | 72.90 (10) | O5—La1—O6 | 53.55 (8) |
| O1W—La1—O2 ^{iv} | 76.67 (10) | O4—La1—O6 | 144.28 (9) |
| O8 ⁱⁱ —La1—O2 ^{iv} | 76.96 (10) | O7—S1—O8 | 109.04 (17) |
| O1 ⁱⁱⁱ —La1—O2 ^{iv} | 121.24 (9) | O7—S1—O5 | 110.89 (19) |
| O7 ⁱ —La1—O3 | 127.89 (10) | O8—S1—O5 | 110.49 (17) |
| O1W—La1—O3 | 76.32 (10) | O7—S1—O6 | 110.19 (18) |
| O8 ⁱⁱ —La1—O3 | 70.11 (9) | O8—S1—O6 | 110.17 (16) |
| O1 ⁱⁱⁱ —La1—O3 | 96.07 (9) | O5—S1—O6 | 106.04 (16) |
| O2 ^{iv} —La1—O3 | 142.55 (9) | O7—S1—La1 | 119.80 (13) |
| O7 ⁱ —La1—O5 | 140.16 (10) | O8—S1—La1 | 131.15 (12) |
| O1W—La1—O5 | 137.02 (11) | O5—S1—La1 | 52.71 (11) |
| O8 ⁱⁱ —La1—O5 | 71.62 (9) | O6—S1—La1 | 53.78 (11) |
| O1 ⁱⁱⁱ —La1—O5 | 72.00 (9) | O1—S2—O2 | 109.67 (16) |
| O2 ^{iv} —La1—O5 | 114.84 (9) | O1—S2—O4 | 111.40 (17) |
| O3—La1—O5 | 71.17 (8) | O2—S2—O4 | 111.52 (17) |
| O7 ⁱ —La1—O4 | 74.43 (10) | O1—S2—O3 | 109.85 (16) |
| O1W—La1—O4 | 69.69 (10) | O2—S2—O3 | 109.59 (17) |
| O8 ⁱⁱ —La1—O4 | 116.81 (9) | O4—S2—O3 | 104.70 (16) |
| O1 ⁱⁱⁱ —La1—O4 | 74.17 (9) | La1—O1W—H11 | 128 (4) |
| O2 ^{iv} —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 (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| O1W—H11 \cdots O3 ^v | 0.84 (5) | 1.94 (5) | 2.717 (5) | 153 (5) |
| O1W—H21 \cdots O6 ^{vi} | 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) $x-1, -y+3/2, z-1/2$.