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Poly[diethylenetriammonium [aquadi-μ_2-sulfato-sulfatolanthanum(III)]]

Yuan-Rui Wang, Yong-Sheng Hu, Cui-Li Shi, Dan-Ping Li and Ya-Feng Li*

School of Chemical Engineering, Changchun University of Technology, Changchun 130012, People's Republic of China
Correspondence e-mail: fly012345@sohu.com

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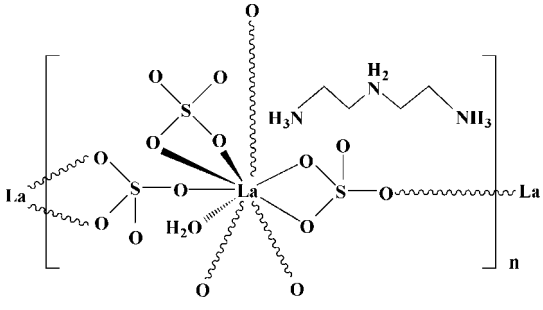
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.021; wR factor = 0.049; data-to-parameter ratio = 15.2.

In the title compound, $\{(C_4H_{16}N_3)[La(SO_4)_3(H_2O)]\}_n$, the La atom adopts an irregular LaO_9 coordination geometry, including one bonded water molecule. The three sulfate groups adopt both monodentate and bidentate coordination to the metal ions. Two of the sulfate groups serve as bridges in the (100) and (010) directions, yielding infinite sheets, whereas the third is pendant to one La^{3+} cation. The protonated organic species interacts with the layers by way of N—H···O hydrogen bonds, and O–H···O hydrogen bonds involving aqua ligands also occur.

Related literature

For related lanthanide sulfate structures, see: Bataille & Louër (2004); Dan *et al.* (2004); Liu *et al.* (2005); Rao *et al.* (2006); Wickleder (2002); Xing *et al.* (2003).



Experimental

Crystal data

$(C_4H_{16}N_3)[La(SO_4)_3(H_2O)]$
M_r = 551.33
Monoclinic, $P2_1$
a = 6.7128 (13) Å
b = 10.442 (2) Å
c = 11.103 (2) Å
β = 93.94 (3)°
V = 776.4 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.23 mm^{-1}
T = 293 K
0.45 × 0.31 × 0.06 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.317, T_{max} = 0.830
7574 measured reflections
3429 independent reflections
3312 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.049
S = 1.17
3429 reflections
225 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}
Absolute structure: Flack (1983), 1552 Friedel pairs
Flack parameter: −0.098 (11)

Table 1
Selected bond lengths (Å).

La1—O1W	2.445 (3)	La1—O8^{i}	2.577 (3)
La1—O1	2.474 (3)	La1—O3	2.580 (3)
La1—O7	2.475 (2)	La1—O9^{ii}	2.583 (3)
La1—O5^{i}	2.510 (3)	La1—O2^{ii}	2.615 (3)
La1—O6	2.542 (3)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1F···O4	0.841 (19)	1.98 (2)	2.775 (5)	157 (4)
O1W—H1G···O11^{iii}	0.850 (18)	2.17 (4)	2.872 (5)	140 (4)
N1—H1A···O8^{ii}	0.89	2.02	2.762 (5)	141
N1—H1B···O9^{ii}	0.89	2.04	2.900 (5)	161
N1—H1C···O6^{i}	0.89	2.07	2.874 (5)	150
N2—H2B···O11	0.90	1.96	2.798 (5)	155
N2—H2A···O2^{iv}	0.90	2.18	3.015 (5)	154
N2—H2A···O4^{iv}	0.90	2.28	2.981 (5)	134
N3—H3A···O5^{v}	0.89	2.18	2.809 (5)	127
N3—H3A···O3^{vi}	0.89	2.25	3.051 (5)	150
N3—H3B···O12^{v}	0.89	1.95	2.834 (5)	174
N3—H3C···O10^{vii}	0.89	2.08	2.784 (5)	135

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2997).

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supplementary materials

Acta Cryst. (2009). E**65**, m789-m790 [**doi:10.1107/S1600536809022272**]

Poly[diethylenetriammonium [aquadi-μ_2-sulfato-sulfatolanthanum(III)]]

Y.-R. Wang, Y.-S. Hu, C.-L. Shi, D.-P. Li and Y.-F. Li

Comment

Recently, a remarkable plenty of organically templated open-framework rare-earth metal sulfates have been obtained due to sulfate which gives the possibility of high framework dimensionalities and lanthanide with the high coordinated numbers (from 7-fold to 12-fold) according to larger ion diameters of rare-earth elements and in the sequel the complicated topologies (Wickleder, 2002; Rao, *et al.*, 2006). As SO_4 group is able to adopt monodentate (S—O—Ln of -140°) and bidentate (S—O—Ln of -100°) to coordinate the lanthanide elements, the lanthanide sulfates are increasingly expanded with regard to the framework structures. Associated with reported two-dimensional lanthanide sulfates - $[C_2N_2H_{10}]\cdot[Nd_2(SO_4)_4]$(Dan, *et al.*, 2004), $[C_2N_2H_{10}]\cdot[La_2(H_2O)_4\cdot(SO_4)_4]\cdot 2H_2O$ (Xing, *et al.*, 2003), $[C_6H_{14}N_2]_2\cdot[La_2(H_2O)_4\cdot(SO_4)_5]\cdot 5H_2O$ (Bataille, *et al.*, 2004), $[C_2N_2H_{10}]\cdot[Nd_2(H_2O)_2(SO_4)_6]\cdot 4H_2O$ (Liu, *et al.*, 2005) and $[C_6N_2H_{14}]\cdot[C_2N_2H_{10}]\cdot SO_4\cdot[La_2(H_2O)_2\cdot(SO_4)_6]\cdot 4H_2O$ (Dan, *et al.*, 2004), (I) keeps the distinct structure in which bridged μ_2-SO_4 afford one monodentate and one bidentate and grafted SO_4 give the bidentate to the La cations.

The asymmetric unit of (I) comprises of twenty-four non-hydrogen atoms, 17 of which belong to the inorganic framework, including one La cation, three SO_4 groups, one coordination water and one the organic template (four carbon atoms and three nitrogen atoms), as shown in Fig. 1. The two-dimensional layer of (I) is constructed from LaO_9 and SO_4 polyhedra. Three crystallographic independent S atoms, which are tetrahedrally coordinated by four O atoms with the S—O distances 1.458 (12) Å to 1.508 (4) Å, can be divided into two modes: S(1) and S(3) consist of three S—O—La linkages and links two La atoms through one bidentate and one monodentate; S(2) makes two S—O—La linkages as a ligand of one La atom through bidentate. The O—S—O angles are within the expected range for tetrahedral geometry. La ion is 9-coordinated by one monodentate and bidentate of μ_2-$S(1)O_4$ and μ_2-$S(3)O_4$, bidentate of $S(2)O_4$ and one water molecule. The bond distances of La—O vary from 2.445 (4) to 2.617 (25) Å, whereas the angles of O—La—O are between 54.18 (10)° and 149.13 (10)°, which were found in other reported La compounds (Dan, *et al.*, 2004). The bond angles of S—O—La of bidentate coordination range from 99.27 (13)° to 101.15 (16)°, and the S—O—La of monodentate coordination is at 143.04 (13)° and 144.35 (19)°.

As shown in Fig.2, the layer of (I) is accomplished by connect the La by μ_2-$S(1)O_4$ along (100) direction and μ_2-$S(3)O_4$ along (010) direction. The $S(2)O_4$ do not take part in the formation of layer and graft to the La ions by the bidentate coordination. The protonated H_3DETA interact with the layer by the H-bond of N—H···O, which intergrate the Ow—H···O to hold togerther the adjacent layer to the supermolecular network (Fig.3).

Experimental

$La(NO_3)_3\cdot 6H_2O$ (0.30 g, 0.7 mmol) was dissolved in 5 ml deionized water under stirring, and then H_2SO_4 (95%, 0.25 ml, 4.55 mmol) and DETA (0.33 ml, 4 mmol) were added drop-wise to a clear solution with pH = 4.0. After being continuously

stirred for 3 h, the solution with the molar ratio of $La(NO_3)_3{\cdot}6H_2O$: $6.5H_2SO_4$: 4.3DETA: $397H_2O$ was transferred into a 23-ml autoclave and heated at 438 K for 5 days. After cooling to room temperature, colorless rods of (I) were collected by filtration as a single phase (yield 53% based on the La). The atomic ratio of La:S determined by EDX was 1:3, in consistence with the results of structural determination of (I).

Refinement

Water H atoms were located in a difference Fourier map and were refined with O—H = 0.84 (2) Å, H···H = 1.37 (2) Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The remaining H-atoms were placed in calculated positions (C—H = 0.89 Å, N—H = 0.89–0.90 Å) and were included in the refinement as riding with $U_{iso}(H) = 1.2U_{eq}(C, N)$.

Figures

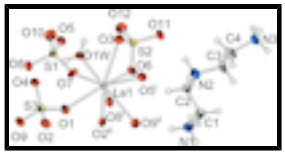

Fig. 1. The asymmetric unit of (I), expanded to show the complete metal coordination and displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 - *x*, 1/2 + *y*, -*z*.]

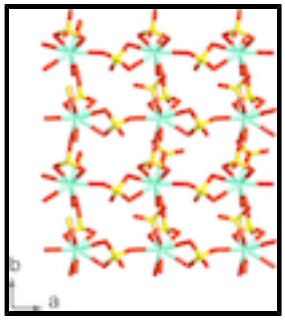

Fig. 2. A stick plot of (I), displaying the layer paralleling *ab* planar formed by link the La with μ_2-S(1)O_4 and μ_2-S(3)O_4.

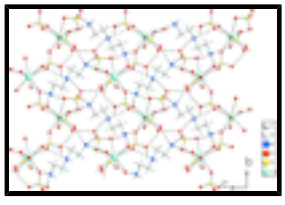

Fig. 3. The ball-stick packing diagram of (I), viewed along (100) direction. The H-bond of N—H···O and OW—H···O hold together adjacent layer.

Poly[diethylenetriammonium [aquadi-μ_2-sulfato-sulfatolanthanum(III)]]

Crystal data

$(C_4H_{16}N_3)[La(SO_4)_3(H_2O)]$	F_{000} = 544
M_r = 551.33	D_x = 2.358 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 2000 reflections
a = 6.7128 (13) Å	θ = 3.0–27.5º
b = 10.442 (2) Å	μ = 3.23 mm^{-1}
c = 11.103 (2) Å	*T* = 293 K

β = 93.94 (3)º	Rod, colourless
V = 776.4 (3) Å^3	0.45 × 0.31 × 0.06 mm
Z = 2	

Data collection

Rigaku R-AXIS RAPID diffractometer	3429 independent reflections
Radiation source: fine-focus sealed tube	3312 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.028
Detector resolution: 10.00 pixels mm^{-1}	θ_{max} = 27.5º
T = 293 K	θ_{min} = 3.0º
ω scans	h = −8→7
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	k = −13→13
T_{min} = 0.317, T_{max} = 0.830	l = −14→14
7574 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.021	$w = 1/[\sigma^2(F_o^2) + (0.0089P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.049	$(\Delta/\sigma)_{max}$ = 0.006
S = 1.17	$\Delta\rho_{max}$ = 0.35 e Å^{-3}
3429 reflections	$\Delta\rho_{min}$ = −0.60 e Å^{-3}
225 parameters	Extinction correction: none
4 restraints	Absolute structure: Flack (1983), 1552 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.098 (11)
Secondary atom site location: difference Fourier map	

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
La1	0.53138 (2)	0.36394 (2)	0.180431 (16)	0.00943 (6)
S1	−0.00721 (14)	0.31013 (9)	0.24266 (10)	0.0156 (2)
S2	0.42405 (15)	0.58541 (9)	0.36244 (10)	0.0176 (2)
S3	0.42773 (14)	0.02938 (9)	0.06143 (10)	0.0167 (2)
O1	0.4541 (4)	0.1705 (3)	0.0573 (3)	0.0236 (7)
O2	0.6123 (4)	−0.0363 (3)	0.0235 (3)	0.0234 (7)
O3	0.4904 (4)	0.4531 (3)	0.3940 (3)	0.0241 (7)
O4	0.3862 (5)	−0.0119 (3)	0.1833 (3)	0.0287 (7)
O5	−0.1328 (4)	0.4210 (3)	0.2793 (3)	0.0226 (6)
O6	0.4374 (4)	0.5935 (3)	0.2274 (3)	0.0220 (7)
O7	0.1623 (3)	0.3571 (4)	0.1758 (2)	0.0233 (6)
O8	−0.1464 (4)	0.2337 (3)	0.1610 (3)	0.0217 (7)
O9	0.2667 (4)	−0.0115 (3)	−0.0290 (3)	0.0226 (7)
O10	0.0654 (5)	0.2351 (3)	0.3473 (3)	0.0333 (8)
O11	0.5666 (5)	0.6790 (3)	0.4210 (3)	0.0285 (7)
O12	0.2219 (4)	0.6107 (3)	0.3958 (3)	0.0320 (8)
O1W	0.5151 (5)	0.1920 (3)	0.3288 (3)	0.0242 (7)
H1F	0.478 (6)	0.119 (3)	0.303 (4)	0.029*
H1G	0.554 (7)	0.188 (4)	0.403 (2)	0.029*
N1	1.0903 (5)	0.6434 (3)	0.0681 (4)	0.0267 (8)
H1A	1.1667	0.6620	0.0081	0.032*
H1B	0.9960	0.5881	0.0422	0.032*
H1C	1.1651	0.6089	0.1290	0.032*
N2	0.7510 (5)	0.8376 (3)	0.2587 (4)	0.0270 (10)
H2A	0.6714	0.8687	0.1970	0.032*
H2B	0.6714	0.8081	0.3145	0.032*
N3	1.0998 (5)	1.0100 (3)	0.4815 (4)	0.0265 (9)
H3A	1.1893	0.9822	0.5384	0.032*
H3B	0.9983	1.0464	0.5159	0.032*
H3C	1.1567	1.0671	0.4352	0.032*
C1	0.9941 (7)	0.7643 (4)	0.1105 (5)	0.0280 (10)
H1D	0.9115	0.8028	0.0451	0.034*
H1E	1.0952	0.8257	0.1387	0.034*
C2	0.8674 (6)	0.7262 (4)	0.2127 (4)	0.0221 (9)
H2C	0.7749	0.6595	0.1847	0.027*
H2D	0.9532	0.6915	0.2786	0.027*
C3	0.8728 (7)	0.9459 (4)	0.3132 (5)	0.0293 (11)
H3D	0.9384	0.9900	0.2500	0.035*
H3E	0.7849	1.0066	0.3492	0.035*
C4	1.0257 (7)	0.9011 (4)	0.4067 (5)	0.0339 (12)
H4A	0.9679	0.8373	0.4573	0.041*
H4B	1.1359	0.8618	0.3682	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00845 (8)	0.00909 (8)	0.01059 (9)	−0.00017 (11)	−0.00037 (6)	−0.00017 (12)
S1	0.0125 (4)	0.0176 (4)	0.0165 (5)	−0.0001 (4)	−0.0004 (4)	0.0015 (4)
S2	0.0180 (5)	0.0177 (5)	0.0169 (5)	−0.0002 (4)	0.0002 (4)	−0.0024 (4)
S3	0.0182 (5)	0.0156 (4)	0.0161 (5)	−0.0013 (4)	0.0002 (4)	−0.0022 (4)
O1	0.0310 (17)	0.0163 (14)	0.0238 (18)	−0.0007 (13)	0.0034 (14)	−0.0025 (12)
O2	0.0223 (16)	0.0224 (14)	0.0253 (18)	0.0088 (12)	0.0006 (13)	−0.0037 (13)
O3	0.0279 (17)	0.0219 (14)	0.0226 (18)	0.0050 (13)	0.0023 (14)	0.0011 (13)
O4	0.0431 (19)	0.0273 (16)	0.0161 (18)	−0.0080 (15)	0.0038 (14)	−0.0004 (13)
O5	0.0148 (14)	0.0283 (14)	0.0247 (17)	0.0027 (13)	0.0012 (13)	−0.0069 (13)
O6	0.0255 (16)	0.0225 (14)	0.0175 (17)	0.0009 (13)	−0.0028 (13)	−0.0019 (12)
O7	0.0146 (11)	0.0317 (14)	0.0243 (14)	0.0013 (18)	0.0053 (10)	0.010 (2)
O8	0.0191 (14)	0.0188 (14)	0.0268 (18)	−0.0017 (12)	−0.0004 (13)	−0.0053 (12)
O9	0.0210 (15)	0.0258 (15)	0.0204 (18)	0.0016 (13)	−0.0035 (12)	−0.0051 (13)
O10	0.0318 (18)	0.0370 (18)	0.030 (2)	0.0032 (16)	−0.0058 (15)	0.0145 (15)
O11	0.0305 (17)	0.0313 (16)	0.0228 (18)	−0.0111 (14)	−0.0037 (14)	−0.0056 (14)
O12	0.0224 (15)	0.0356 (17)	0.039 (2)	0.0066 (14)	0.0108 (15)	−0.0046 (16)
O1W	0.0368 (17)	0.0208 (15)	0.0153 (17)	−0.0009 (15)	0.0034 (14)	0.0021 (13)
N1	0.0235 (19)	0.033 (2)	0.024 (2)	−0.0013 (17)	0.0031 (16)	0.0009 (17)
N2	0.0222 (16)	0.027 (3)	0.031 (2)	0.0017 (15)	−0.0033 (15)	−0.0011 (16)
N3	0.030 (2)	0.0243 (18)	0.024 (2)	−0.0041 (17)	−0.0034 (17)	0.0005 (16)
C1	0.028 (2)	0.026 (2)	0.030 (3)	−0.0006 (19)	0.000 (2)	0.004 (2)
C2	0.023 (2)	0.020 (2)	0.024 (2)	0.0011 (17)	0.0016 (18)	0.0003 (18)
C3	0.035 (3)	0.0159 (19)	0.036 (3)	−0.0007 (19)	−0.008 (2)	−0.0034 (19)
C4	0.050 (3)	0.022 (2)	0.028 (3)	0.007 (2)	−0.011 (2)	−0.0010 (18)

Geometric parameters (Å, °)

La1—O1W	2.445 (3)	N1—C1	1.508 (6)
La1—O1	2.474 (3)	N1—H1A	0.8900
La1—O7	2.475 (2)	N1—H1B	0.8900
La1—O5^{i}	2.510 (3)	N1—H1C	0.8900
La1—O6	2.542 (3)	N2—C3	1.498 (5)
La1—O8^{i}	2.577 (3)	N2—C2	1.510 (5)
La1—O3	2.580 (3)	N2—H2A	0.9000
La1—O9^{ii}	2.583 (3)	N2—H2B	0.9000
La1—O2^{ii}	2.615 (3)	N3—C4	1.474 (5)
S1—O10	1.457 (3)	N3—H3A	0.8900
S1—O7	1.484 (3)	N3—H3B	0.8900
S1—O8	1.488 (3)	N3—H3C	0.8900
S1—O5	1.504 (3)	C1—C2	1.517 (6)
S2—O12	1.455 (3)	C1—H1D	0.9700
S2—O11	1.486 (3)	C1—H1E	0.9700
S2—O3	1.486 (3)	C2—H2C	0.9700
S2—O6	1.511 (3)	C2—H2D	0.9700

S3—O4	1.465 (3)	C3—C4	1.485 (6)
S3—O1	1.485 (3)	C3—H3D	0.9700
S3—O9	1.486 (3)	C3—H3E	0.9700
S3—O2	1.501 (3)	C4—H4A	0.9700
O1W—H1F	0.841 (19)	C4—H4B	0.9700
O1W—H1G	0.850 (18)		
O1W—La1—O1	75.84 (11)	S3—O1—La1	144.5 (2)
O1W—La1—O7	84.36 (11)	S3—O2—La1^{iii}	99.36 (14)
O1—La1—O7	78.07 (11)	S2—O3—La1	99.67 (16)
O1W—La1—O5^{i}	87.70 (11)	S1—O5—La1^{iv}	101.69 (14)
O1—La1—O5^{i}	125.67 (9)	S2—O6—La1	100.57 (14)
O7—La1—O5^{i}	152.06 (10)	S1—O7—La1	143.12 (17)
O1W—La1—O6	122.10 (10)	S1—O8—La1^{iv}	99.29 (14)
O1—La1—O6	146.90 (10)	S3—O9—La1^{iii}	101.23 (14)
O7—La1—O6	76.67 (11)	La1—O1W—H1F	117 (3)
O5^{i}—La1—O6	85.11 (9)	La1—O1W—H1G	132 (3)
O1W—La1—O8^{i}	75.26 (11)	H1F—O1W—H1G	110 (3)
O1—La1—O8^{i}	70.62 (9)	C1—N1—H1A	109.5
O7—La1—O8^{i}	145.87 (10)	C1—N1—H1B	109.5
O5^{i}—La1—O8^{i}	55.10 (9)	H1A—N1—H1B	109.5
O6—La1—O8^{i}	137.43 (9)	C1—N1—H1C	109.5
O1W—La1—O3	68.48 (10)	H1A—N1—H1C	109.5
O1—La1—O3	140.45 (10)	H1B—N1—H1C	109.5
O7—La1—O3	81.93 (10)	C3—N2—C2	115.9 (3)
O5^{i}—La1—O3	70.24 (10)	C3—N2—H2A	108.3
O6—La1—O3	55.07 (9)	C2—N2—H2A	108.3
O8^{i}—La1—O3	114.26 (10)	C3—N2—H2B	108.3
O1W—La1—O9^{ii}	149.15 (10)	C2—N2—H2B	108.3
O1—La1—O9^{ii}	98.68 (10)	H2A—N2—H2B	107.4
O7—La1—O9^{ii}	124.77 (10)	C4—N3—H3A	109.5
O5^{i}—La1—O9^{ii}	70.70 (10)	C4—N3—H3B	109.5
O6—La1—O9^{ii}	78.89 (10)	H3A—N3—H3B	109.5
O8^{i}—La1—O9^{ii}	74.33 (10)	C4—N3—H3C	109.5
O3—La1—O9^{ii}	120.71 (10)	H3A—N3—H3C	109.5
O1W—La1—O2^{ii}	147.69 (10)	H3B—N3—H3C	109.5
O1—La1—O2^{ii}	78.24 (10)	N1—C1—C2	106.8 (4)
O7—La1—O2^{ii}	71.61 (9)	N1—C1—H1D	110.4
O5^{i}—La1—O2^{ii}	123.41 (9)	C2—C1—H1D	110.4
O6—La1—O2^{ii}	73.73 (10)	N1—C1—H1E	110.4
O8^{i}—La1—O2^{ii}	113.54 (10)	C2—C1—H1E	110.4
O3—La1—O2^{ii}	126.54 (10)	H1D—C1—H1E	108.6
O9^{ii}—La1—O2^{ii}	54.16 (9)	N2—C2—C1	112.4 (3)
O10—S1—O7	110.52 (18)	N2—C2—H2C	109.1

O10—S1—O8	111.06 (19)	C1—C2—H2C	109.1
O7—S1—O8	110.06 (18)	N2—C2—H2D	109.1
O10—S1—O5	111.2 (2)	C1—C2—H2D	109.1
O7—S1—O5	110.1 (2)	H2C—C2—H2D	107.9
O8—S1—O5	103.72 (16)	C4—C3—N2	112.1 (3)
O12—S2—O11	110.7 (2)	C4—C3—H3D	109.2
O12—S2—O3	112.23 (19)	N2—C3—H3D	109.2
O11—S2—O3	109.55 (19)	C4—C3—H3E	109.2
O12—S2—O6	111.26 (19)	N2—C3—H3E	109.2
O11—S2—O6	108.49 (18)	H3D—C3—H3E	107.9
O3—S2—O6	104.40 (17)	N3—C4—C3	109.9 (4)
O4—S3—O1	110.57 (18)	N3—C4—H4A	109.7
O4—S3—O9	111.30 (18)	C3—C4—H4A	109.7
O1—S3—O9	110.28 (18)	N3—C4—H4B	109.7
O4—S3—O2	109.77 (19)	C3—C4—H4B	109.7
O1—S3—O2	109.99 (18)	H4A—C4—H4B	108.2
O9—S3—O2	104.78 (17)		
O4—S3—O1—La1	20.4 (4)	O11—S2—O6—La1	121.73 (16)
O4—S3—O1—La1	20.4 (4)	O3—S2—O6—La1	4.98 (17)
O9—S3—O1—La1	144.0 (3)	O1W—La1—O6—S2	11.55 (19)
O2—S3—O1—La1	−101.0 (3)	O1—La1—O6—S2	127.22 (17)
La1^{iii}—S3—O1—La1	−159.2 (2)	O7—La1—O6—S2	86.02 (15)
O1W—La1—O1—S3	−4.8 (3)	O5^{i}—La1—O6—S2	−72.65 (15)
O7—La1—O1—S3	−91.9 (3)	O8^{i}—La1—O6—S2	−92.26 (18)
O5^{i}—La1—O1—S3	71.8 (3)	O3—La1—O6—S2	−3.38 (12)
O6—La1—O1—S3	−132.8 (3)	O9^{ii}—La1—O6—S2	−143.91 (15)
O8^{i}—La1—O1—S3	74.3 (3)	O2^{ii}—La1—O6—S2	160.44 (16)
O3—La1—O1—S3	−30.7 (4)	S1^{i}—La1—O6—S2	−79.21 (14)
O9^{ii}—La1—O1—S3	144.2 (3)	S3^{ii}—La1—O6—S2	−170.95 (15)
O2^{ii}—La1—O1—S3	−165.3 (3)	O10—S1—O7—La1	−4.0 (4)
S1^{i}—La1—O1—S3	71.8 (3)	O8—S1—O7—La1	−127.0 (3)
S2—La1—O1—S3	−76.5 (4)	O5—S1—O7—La1	119.3 (4)
S3^{ii}—La1—O1—S3	169.9 (3)	La1^{iv}—S1—O7—La1	174.6 (2)
O4—S3—O2—La1^{iii}	125.92 (15)	O1W—La1—O7—S1	16.6 (4)
O4—S3—O2—La1^{iii}	125.92 (15)	O1—La1—O7—S1	93.2 (4)
O1—S3—O2—La1^{iii}	−112.21 (16)	O5^{i}—La1—O7—S1	−57.7 (5)
O9—S3—O2—La1^{iii}	6.31 (17)	O6—La1—O7—S1	−108.3 (4)
O12—S2—O3—La1	115.73 (19)	O8^{i}—La1—O7—S1	69.6 (4)
O11—S2—O3—La1	−120.90 (17)	O3—La1—O7—S1	−52.4 (4)
O11—S2—O3—La1	−120.90 (17)	O9^{ii}—La1—O7—S1	−174.4 (3)
O6—S2—O3—La1	−4.89 (17)	O2^{ii}—La1—O7—S1	174.7 (4)
O1W—La1—O3—S2	−163.00 (19)	S1^{i}—La1—O7—S1	15.3 (6)
O1—La1—O3—S2	−135.94 (15)	S2—La1—O7—S1	−79.7 (4)
O7—La1—O3—S2	−75.91 (16)	S3^{ii}—La1—O7—S1	−178.3 (4)

O5^{i}—La1—O3—S2	101.50 (16)	O10—S1—O8—La1^{iv}	115.43 (17)
O6—La1—O3—S2	3.43 (12)	O7—S1—O8—La1^{iv}	−121.86 (17)
O8^{i}—La1—O3—S2	135.54 (13)	O5—S1—O8—La1^{iv}	−4.05 (18)
O9^{ii}—La1—O3—S2	49.94 (18)	O4—S3—O9—La1^{iii}	−125.00 (16)
O2^{ii}—La1—O3—S2	−16.0 (2)	O4—S3—O9—La1^{iii}	−125.00 (16)
S1^{i}—La1—O3—S2	119.34 (14)	O1—S3—O9—La1^{iii}	111.89 (16)
S3^{ii}—La1—O3—S2	18.23 (18)	O2—S3—O9—La1^{iii}	−6.43 (18)
O1—S3—O4—O4	0.00 (18)	O12—S2—O11—O11	0.0 (3)
O9—S3—O4—O4	0.00 (10)	O3—S2—O11—O11	0.0 (3)
O2—S3—O4—O4	0.00 (13)	O6—S2—O11—O11	0.0 (4)
La1^{iii}—S3—O4—O4	0.00 (5)	La1—S2—O11—O11	0.0 (4)
O10—S1—O5—La1^{iv}	−115.22 (18)	C3—N2—C2—C1	−62.8 (5)
O7—S1—O5—La1^{iv}	121.94 (14)	N1—C1—C2—N2	−176.3 (3)
O8—S1—O5—La1^{iv}	4.19 (18)	C2—N2—C3—C4	−51.4 (6)
O12—S2—O6—La1	−116.29 (17)	N2—C3—C4—N3	−163.4 (4)
O11—S2—O6—La1	121.73 (16)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1F···O4	0.841 (19)	1.98 (2)	2.775 (5)	157 (4)
O1W—H1G···O11^{v}	0.850 (18)	2.17 (4)	2.872 (5)	140 (4)
N1—H1A···O8^{ii}	0.89	2.02	2.762 (5)	141
N1—H1B···O9^{ii}	0.89	2.04	2.900 (5)	161
N1—H1C···O6^{i}	0.89	2.07	2.874 (5)	150
N2—H2B···O11	0.90	1.96	2.798 (5)	155
N2—H2A···O2^{vi}	0.90	2.18	3.015 (5)	154
N2—H2A···O4^{vi}	0.90	2.28	2.981 (5)	134
N3—H3A···O5^{vii}	0.89	2.18	2.809 (5)	127
N3—H3A···O3^{viii}	0.89	2.25	3.051 (5)	150
N3—H3B···O12^{vii}	0.89	1.95	2.834 (5)	174
N3—H3C···O10^{ix}	0.89	2.08	2.784 (5)	135

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

Fig. 1

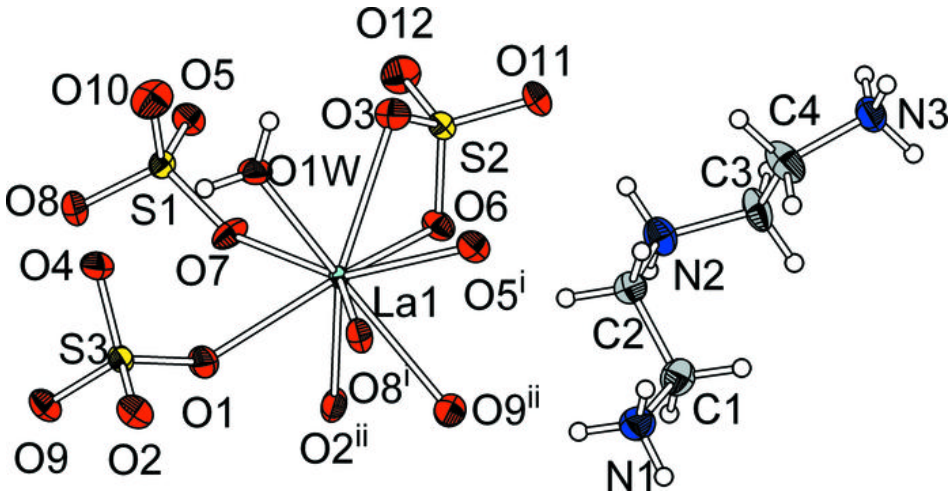
O12
O11
O10
O5
O3
S2
O1W
C4
N3
C3
O8
S1
O6
O4
O7
La1
O5i
N2
C2
S3
O8i
O1
O9ii
C1
O9
O2
O2ii
N1

Fig. 2

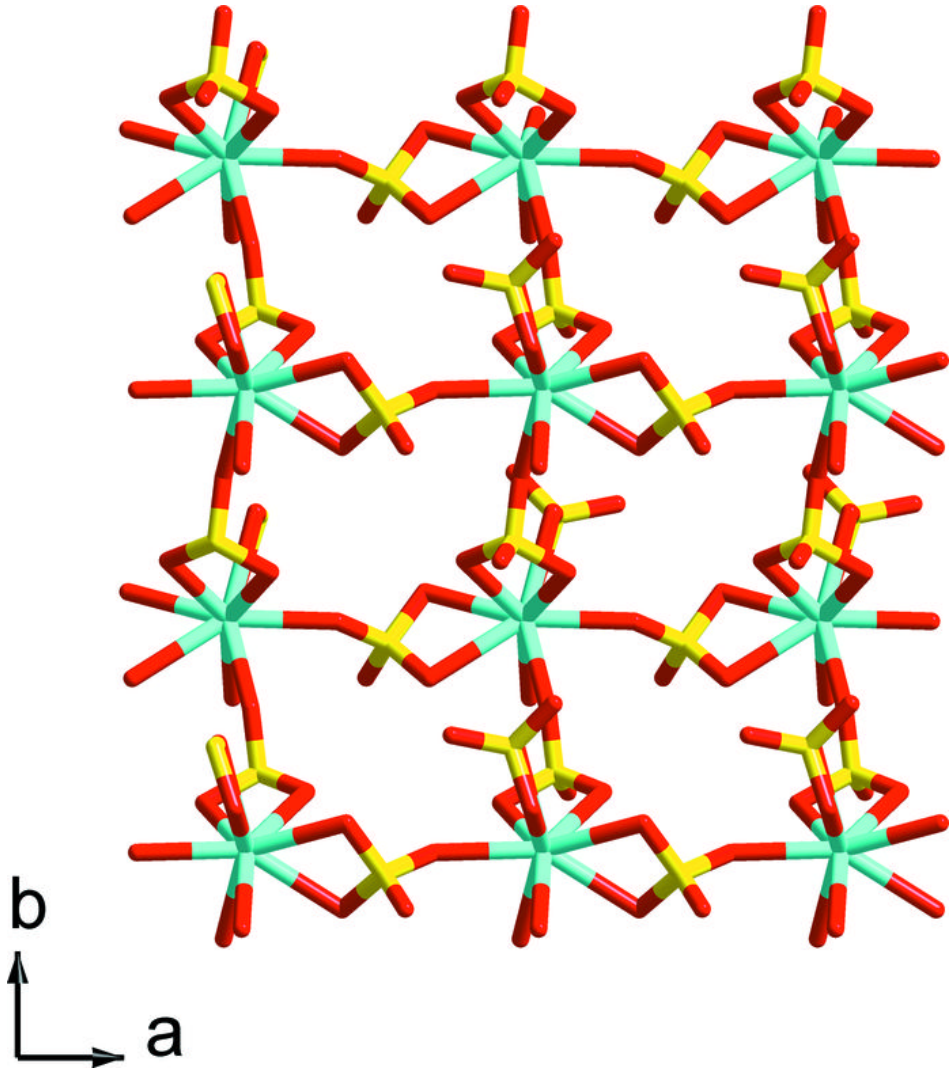

Fig. 3