

# Hydrothermal synthesis and structure of $[\text{C}_2\text{N}_2\text{H}_{10}]\text{[La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$ , a new organically templated rare earth sulfate with a layer structure

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Employing ethylenediamine (en) as the template, a new two-dimensional (2D) layered lanthanum sulfate  $[\text{C}_2\text{N}_2\text{H}_{10}]\text{[La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$  has been hydrothermally synthesized for the first time. Its structure, solved by single-crystal X-ray diffraction analysis, comprises a network of  $\text{La}(1)\text{O}_{10}$ ,  $\text{La}(2)\text{O}_8$  polyhedra and  $\text{SO}_4$  tetrahedra forming one-dimensional ladder-like chains. The chains, in turn, are linked *via* oxygen atoms forming macroanionic inorganic zigzag layers. The diprotonated amine molecules and the water molecules are located in the apertures of zigzag layers and interact with the inorganic framework through hydrogen bonding.

## Introduction

A remarkable variety of open-framework organically templated inorganic materials have been reported over the last 10 years.<sup>1</sup> Generally, the inorganic skeleton of the materials is built up from two parts: a metallic cation and an oxo-anion. The metal elements range from main group elements to transition metal elements. And most "oxo-anion part" work has been carried out on the  $[\text{PO}_4]^{3-}$  phosphate anion.<sup>1-9</sup> In addition to phosphates, open framework metal arsenates,<sup>10-12</sup> phosphites,<sup>13-16</sup> selenites,<sup>17,18</sup> germinates<sup>19,20</sup> and carbonates<sup>21</sup> have been reported in the literature. Recently, there has been growing interest in the study of open-framework architectures containing oxo-anions of sulfur. Rao *et al.* synthesized the first members of a family of organically templated open-framework cadmium sulfates by reacting cadmium salts with  $\text{H}_2\text{SO}_4$  in the presence of organic amines or directly with amine sulfates under hydrothermal conditions. These cadmium sulfates include four linarite-like chain structures, one quasi-2D layer compound  $[\text{C}_4\text{N}_2\text{H}_{12}]_4[\text{Cd}_3\text{Cl}_{10}(\text{SO}_4)_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$  formed by strip-like units and one layer cadmium sulfate  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{Cd}_2(\text{H}_2\text{O})_2(\text{SO}_4)_3]$  containing an octahedral-tetrahedral 2D net wherein the sulfate tetrahedron is connected at all four corners.<sup>22,23</sup> Moreover, a layered iron sulfate with a distorted Kagome lattice has been prepared hydrothermally.<sup>24</sup>

Lanthanide elements exhibit interesting topologies and coordination chemistry because of the accessibility of higher coordination numbers, which is not possible with main group elements. There has been intense research activity in the area of lanthanide sulfates due to their application in the separation of rare earth elements. Although a large number of complexes and salts have been described in the literature, structure information of lanthanide sulfates is comparatively limited.<sup>25</sup> The known crystal structures of the rare earth sulfates are mainly restricted to inorganic sulfate hydrates with different water contents<sup>26</sup> and ternary rare earth sulfates with alkaline metal ions or  $\text{NH}_4^+$  as the third component.<sup>26-28</sup> However, to our knowledge, lanthanide sulfates templated by organic amine have not been described in the literature hitherto. In this paper, we report the hydrothermal synthesis and X-ray structural characterization of the first example of 2D layered lanthanum sulfate containing organic templates,  $[\text{C}_2\text{N}_2\text{H}_{10}]\text{[La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$ .

## Experimental

### Synthesis of $[\text{C}_2\text{N}_2\text{H}_{10}]\text{[La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$

The title compound was synthesized by a hydrothermal reaction of a mixture of  $\text{La}_2\text{O}_3$  (99.9%),  $\text{H}_2\text{SO}_4$  (95–98 wt%) and ethylenediamine (99.0%). In a typical synthesis, solution **I** was prepared by dissolving 0.3 g of  $\text{La}_2\text{O}_3$  into 10.0 mL diluted sulfuric acid (1 mL  $\text{H}_2\text{SO}_4$ /10.0 mL  $\text{H}_2\text{O}$ ) under constant stirring. 0.3 mL en was added to 10.0 mL diluted sulfuric acid (0.3 mL  $\text{H}_2\text{SO}_4$ /10.0 mL  $\text{H}_2\text{O}$ ) under stirring to make solution **II**. Then solution **I** was mixed with solution **II** under constant stirring. The resulting mixture with a molar ratio of  $1.0\text{La}_2\text{O}_3 : 24.4\text{H}_2\text{SO}_4 : 5.0\text{en} : 1100\text{H}_2\text{O}$  was transferred into a 30 mL Teflon-lined stainless-steel autoclave and heated at 373 K for 16 h. The resulting colourless rod-like single crystals were collected by filtration, washed with ethanol and dried at room temperature (yield 70%, with respect to La).

### Powder X-ray diffraction

Data were collected on a Siemens D5005 diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The step size was  $0.02^\circ$  and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer optima 3300 DV ICP spectrometer. The infrared (IR) spectrum was recorded within the  $400\text{--}4000 \text{ cm}^{-1}$  region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses in air with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### X-Ray crystallography

A suitable single crystal of the title compound ( $0.10 \times 0.10 \times 0.08 \text{ mm}$ ) was selected and mounted on a glass fiber. The intensity data was collected on a Siemens Smart CCD diffractometer. The numbers of collected reflections and independent reflections were 5905 and 2916, respectively. Data processing was accomplished with the SAINT processing program.<sup>29</sup> The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using SHELXTL (version 5.1).<sup>30</sup> The lanthanum and sulfur atoms were first located and the carbon, nitrogen and oxygen atoms were found in difference Fourier maps. The hydrogen atoms of the amine molecule were

**Table 1** Crystal data and structure refinement for  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$ 

Empirical formula	$\text{C}_2\text{H}_{22}\text{La}_2\text{N}_2\text{O}_{22}\text{S}_4$
Formula weight	832.28
$T/\text{K}$	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	6.9220(8)
$b/\text{\AA}$	31.639(4)
$c/\text{\AA}$	9.6388(11)
$\beta/^\circ$	105.020(3)
$V/\text{\AA}^3$	2038.8(4)
$Z$	4
$\mu/\text{mm}^{-1}$	4.654
Data/restraints/parameters	2916/12/325
Goodness-of-fit on $F^2$	1.031
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0282$ , $wR_2 = 0.0487$
$R$ indices (all data)	$R_1 = 0.0432$ , $wR_2 = 0.0598$

**Table 2** Selected bond lengths ( $\text{\AA}$ ) for  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$ 

La(1)–O(1)	2.681(5)	S(1)–O(1)	1.487(5)
La(1)–O(2)	2.844(5)	S(1)–O(2)	1.490(5)
La(1)–O(3)#1	2.566(5)	S(1)–O(3)	1.472(5)
La(1)–O(5)	2.699(5)	S(1)–O(4)	1.484(5)
La(1)–O(6)	2.579(5)	S(2)–O(5)	1.480(5)
La(1)–O(7)#2	2.721(5)	S(2)–O(6)	1.477(5)
La(1)–O(8)#2	2.565(5)	S(2)–O(7)	1.468(5)
La(1)–O(9)	2.717(5)	S(2)–O(8)	1.489(5)
La(1)–O(10)	2.539(5)	S(3)–O(9)	1.509(5)
La(1)–O(14)#1	2.491(5)	S(3)–O(10)	1.492(5)
La(2)–O(4)	2.533(5)	S(3)–O(11)	1.456(5)
La(2)–O(9)#3	2.538(5)	S(3)–O(12)	1.446(5)
La(2)–O(13)	2.512(5)	S(4)–O(13)	1.487(5)
La(2)–O(16)#1	2.474(5)	S(4)–O(14)	1.456(5)
La(2)–O(1W)	2.474(6)	S(4)–O(15)	1.468(5)
La(2)–O(2W)	2.552(6)	S(4)–O(16)	1.481(5)
La(2)–O(3W)	2.646(5)	C(1)–N(1)	1.481(10)
La(2)–O(4W)	2.501(6)	C(2)–N(2)	1.488(10)
		C(1)–C(2)	1.520(10)

Symmetry transformations used to generate equivalent atoms: #1  $x + 1, y, z$ ; #2  $x, -y + 3/2, z + 1/2$ ; #3  $x - 1, y, z$ .

placed geometrically (N–H, 0.89; C–H, 0.97  $\text{\AA}$ ) and the hydrogen atoms of the water were located by difference Fourier map. All non-hydrogen atoms were refined anisotropically. Further details of the X-ray structural analysis are given in Table 1 and selected bond lengths are listed in Table 2.

CCDC reference number 196729.

See <http://www.rsc.org/suppdata/dt/b2/b211076h/> for crystallographic data in CIF or other electronic format.

## Results and discussion

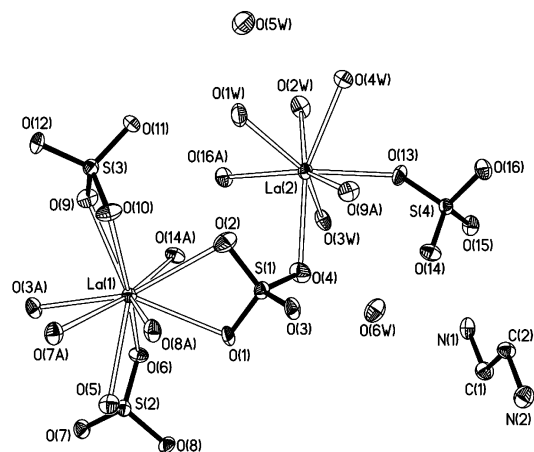
The ICP analysis for the compound gives a La : S ratio of 1 : 2, whereas the elemental analysis shows that the C, H, and N contents are 3.10, 2.64, and 3.45 wt%, respectively, corresponding well to the values (2.90, 2.65 and 3.36 wt%) on the basis of the single crystal structure formula.

The IR spectrum of the compound shows the typical sharp peaks for ethylenediamine in the region 1400–1600  $\text{cm}^{-1}$ , and characteristic bands due to the sulfate ion in the 1120 and 610  $\text{cm}^{-1}$  regions. Absorption at 810  $\text{cm}^{-1}$  can be attributed to La–O vibration. A band around 3500  $\text{cm}^{-1}$  is due to the presence of water.

Thermogravimetric analysis shows that the weight loss of the compound is *ca.* 12.80% from 100 to 340  $^\circ\text{C}$  corresponding to the loss of lattice and coordinated water molecules (calc. 12.98%). There are two periods of sharp weight loss in the range 350 to 900  $^\circ\text{C}$  (obs. = 36.40%, calc. = 38.20%) due to the loss of amine molecules and  $\text{SO}_3$ . The structure collapses and converts into an amorphous phase after calcinations at 500  $^\circ\text{C}$

for 2 h. The powder X-ray diffraction pattern of the sample heated at 900  $^\circ\text{C}$  corresponds to  $\text{La}_2\text{O}_2(\text{SO}_4)$  (JCPDS file card No. 16–0501), indicating destruction of the framework structure upon loss of the amine.

The asymmetric unit contains 32 non-hydrogen atoms as shown in Fig. 1 (selected bond lengths are collected in Table 2), 26 of which belong to the framework, 4 to the organic cation and 2 to the free water molecule. There are two crystallographically distinct La atoms and four distinct S atoms. Of the two lanthanum atoms, La(1) is ten-coordinated by O atoms from the six sulfate groups. La(2), on the other hand, is eight-coordinated by four O atoms from four sulfates (S1, S3,  $2 \times$  S4) and four O atoms from water ligands  $[\text{La}(2)\text{O}_4(\text{H}_2\text{O})_4]$ . The average values of La–O bond lengths  $\{d_{\text{av}}[\text{La}(1)\text{–O}] = 2.640 \text{ \AA}$ ,  $d_{\text{av}}[\text{La}(2)\text{–O}] = 2.514 \text{ \AA}$  and  $d_{\text{av}}[\text{La}(2)\text{–O}_w] = 2.543 \text{ \AA}\}$ , are in good agreement with those reported earlier.<sup>25</sup> All four S atoms form the centers of tetrahedral sulfate groups. The S–O bond distance in the  $\text{SO}_4$  tetrahedron are in the range 1.446(5) to 1.509(5)  $\text{\AA}$   $\{[\text{S}(1)\text{–O}]_{\text{av}} = 1.483(5) \text{ \AA}$ ,  $[\text{S}(2)\text{–O}]_{\text{av}} = 1.479(5) \text{ \AA}$ ,  $[\text{S}(3)\text{–O}]_{\text{av}} = 1.476(5) \text{ \AA}$  and  $[\text{S}(4)\text{–O}]_{\text{av}} = 1.473(5) \text{ \AA}\}$ , with the O–S–O bond angles in the range 103.2(3)–112.2(3) $^\circ$ ,  $\{[\text{O}\text{–S}(1)\text{–O}]_{\text{av}} = 109.5(3)^\circ$ ,  $[\text{O}\text{–S}(2)\text{–O}]_{\text{av}} = 109.5(3)^\circ$ ,  $[\text{O}\text{–S}(3)\text{–O}]_{\text{av}} = 109.5(3)^\circ$  and  $[\text{O}\text{–S}(4)\text{–O}]_{\text{av}} = 109.5(3)^\circ\}$ . Of the four different S atoms, S(1) makes four S–O–La bonds *via* the bridging oxygen atoms with two crystallographically unique La(1) atoms and one La(2) atom. The S(2) $\text{O}_4$  tetrahedron shares edges with two La(1)O polyhedra neighbors. The S(4) atom is tetrahedrally coordinated to four oxygens, of which three share vertices with one La(1) polyhedron and two La(2) polyhedra, the remaining is terminal S–O groups. S(3) makes three S–O–La linkages to neighboring La(1) and La(2) atoms *via* one two-coordinated oxygen atom (La–O–S bridge), O(10), and one three-coordinated oxygen atom  $[\text{S}\text{–}(\mu_3\text{O})\text{–La}_2$  bridge), O(9), and the other two oxygen-atom vertices are “unsaturated” O atoms. These three different types of S–O bonds show their expected differences in bond lengths:  $d_{\text{av}}[\text{S}\text{–O}] = 1.480 \text{ \AA}$ ,  $d_{\text{av}}[\text{S}\text{=O}] = 1.456 \text{ \AA}$ , the longest S–O bond  $[d_{\text{Ls,O}}(\text{S}\text{–O}) = 1.509 \text{ \AA}]$  in the  $\text{SO}_4$  tetrahedron are associated with the three-coordinated oxygen atoms.

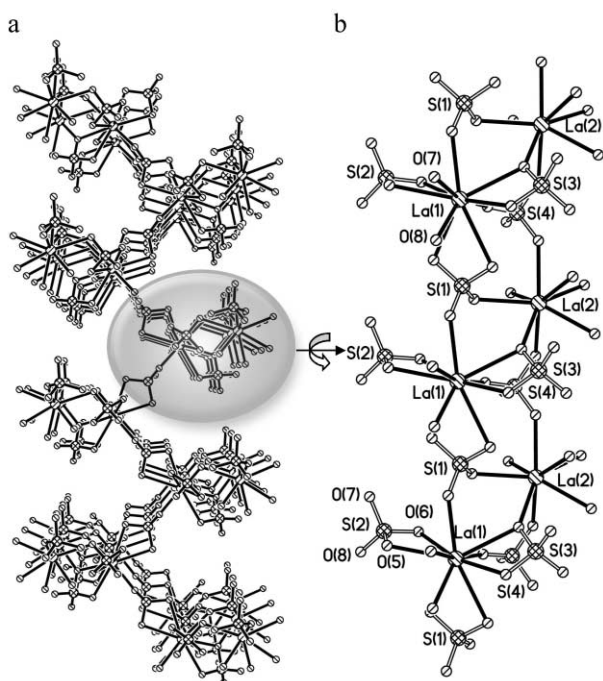
**Fig. 1** ORTEP<sup>31</sup> view of the  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$  structure showing the atom labeling scheme (50% thermal ellipsoids).

The framework structure is made from the linkage of LaO polyhedra and  $\text{SO}_4$  tetrahedra by sharing both the vertices and the edges. The connectivity between these units form zigzag layers, which are anionic. The inorganic layer can be viewed as being built up of four-membered rings  $[\text{–La}(1)\text{–S}(4)\text{–La}(2)\text{–S}(1)\text{–}]$  formed by two LaO polyhedra and two  $\text{SO}_4$  tetrahedra linked through vertices, with S(2) $\text{O}_4$  and S(3) $\text{O}_4$  tetrahedra grafted from the La(1), La(2) center respectively. The connectivity between the edge-sharing four-membered rings results in a ladder-type arrangement along the  $a$  axis [Fig. 2(b)]. The ladder-like chains are connected *via* two bridging atoms O(7)

**Table 3** Hydrogen bonds for  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$ 

D–H ⋯ A	$d(\text{D–H})/\text{\AA}$	$d(\text{H} \cdots \text{A})/\text{\AA}$	$d(\text{D} \cdots \text{A})/\text{\AA}$	$\angle(\text{DHA})^\circ$
N(1)–H(1C) ⋯ O(2)#1	0.89	2.11	2.926(8)	151.3
N(1)–H(1C) ⋯ O(10)#1	0.89	2.46	3.064(8)	125.8
N(1)–H(1D) ⋯ O(12)#2	0.89	1.87	2.737(8)	165.2
N(1)–H(1E) ⋯ O(6W)	0.89	2.06	2.859(8)	148.3
N(2)–H(2C) ⋯ O(1)#3	0.89	2.20	2.896(8)	134.7
N(2)–H(2C) ⋯ O(7)#4	0.89	2.54	3.073(8)	119.3
N(2)–H(2D) ⋯ O(5)#5	0.89	2.32	3.138(8)	151.8
N(2)–H(2E) ⋯ O(8)#3	0.89	2.09	2.962(8)	165.3
O(1W)–H(1WA) ⋯ O(5W)	0.88(5)	1.90(6)	2.740(8)	161(10)
O(1W)–H(1WB) ⋯ O(11)	0.87(5)	1.86(6)	2.674(7)	154(10)
O(2W)–H(2WA) ⋯ O(13)#6	0.85(5)	2.02(7)	2.783(7)	149(10)
O(2W)–H(2WB) ⋯ O(4W)	0.83(5)	2.13(9)	2.749(8)	132(10)
O(2W)–H(2WB) ⋯ O(3W)#6	0.83(5)	2.38(10)	2.837(8)	116(9)
O(3W)–H(3WA) ⋯ O(2W)#6	0.87(5)	2.02(6)	2.837(8)	156(10)
O(3W)–H(3WB) ⋯ O(15)#7	0.85(5)	2.05(6)	2.868(7)	161(10)
O(4W)–H(4WA) ⋯ O(5W)#8	0.88(5)	1.87(6)	2.722(8)	163(10)
O(4W)–H(4WB) ⋯ O(11)#9	0.85(5)	1.98(5)	2.815(8)	166(10)
O(5W)–H(5WA) ⋯ O(15)#10	0.84(5)	2.06(6)	2.862(8)	159(11)
O(5W)–H(5WB) ⋯ O(16)#8	0.84(5)	2.18(7)	2.931(8)	149(10)
O(5W)–H(5WB) ⋯ O(2W)#9	0.84(5)	2.47(9)	3.070(8)	130(10)
O(6W)–H(6WA) ⋯ O(3W)	0.95(5)	1.86(5)	2.814(9)	173(9)
O(6W)–H(6WB) ⋯ O(10)#1	0.85(5)	2.10(6)	2.923(7)	161(10)

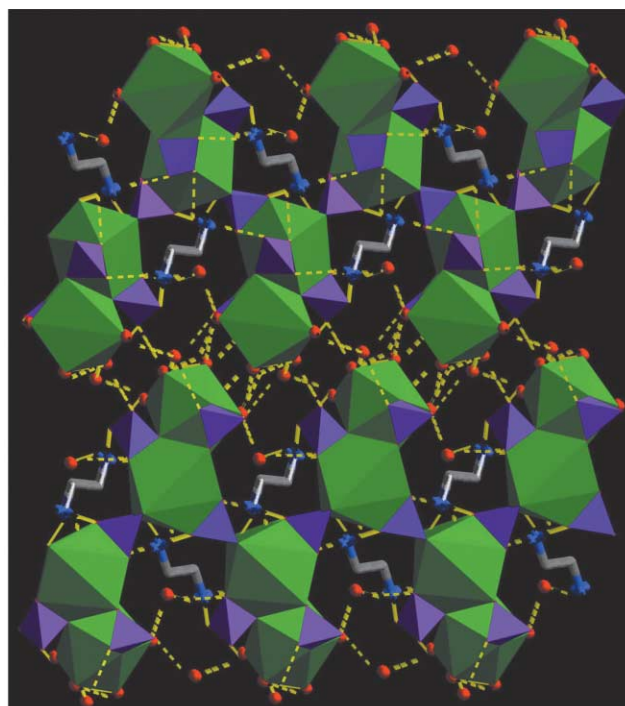
Symmetry transformations used to generate equivalent atoms: #1  $x - 1, y, z - 1$ ; #2  $x - 2, y, z - 1$ ; #3  $x - 1, y, z$ ; #4  $x - 2, y, z$ ; #5  $x - 2, -y + 3/2, z - 1/2$ ; #6  $-x - 1, -y + 1, -z$ ; #7  $x + 1, y, z$ ; #8  $-x - 1, -y + 1, z - 1/2$ ; #9  $-x, -y + 1, -z + 1$ ; #10  $x + 1, y, z + 1$ .



**Fig. 2** (a) The inorganic zigzag layer structure of  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$  viewed along the  $[100]$  direction; (b) Four-membered ring ladders involving edge-sharing between the sulfate tetrahedron and lanthanum polyhedron, seen along the  $a$  axis.

and O(8) from S(2)O<sub>4</sub> tetrahedron forming infinite 2D layers in the  $bc$  plane, as shown in Fig. 2(a).

The inorganic layers are anionic and the empirical formula of the layer is  $[\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]^{2-}$ , the negative charge of which is achieved by incorporation of doubly protonated ethylenediamine. The ethylenediamine cations and water molecules are located in the apertures of zigzag layers. Like many other open-framework structures, the lanthanum sulfate structure possesses a large number of hydrogen bond interactions involving the hydrogen atoms attached to the amine and free water molecule with framework oxygen atoms. There are also hydrogen-bond interactions between the amine molecule and the free water molecule [ $\text{N}(1) \cdots \text{O}(6\text{W}) = 2.859(8) \text{\AA}$ ]. In addition, strong inter-layer interactions through O–H ⋯ O hydrogen bonding



**Fig. 3** Structure of  $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{H}_2\text{O})_4(\text{SO}_4)_4]\cdot 2\text{H}_2\text{O}$  in the  $bc$  plane. Note that both the water and amine molecules occupy the apertures of zigzag layers. Lanthanum polyhedra: green, sulfate tetrahedra: purple, O<sub>w</sub>: red, N: blue. Yellow dotted lines represent the various hydrogen bond interactions. H atoms have been omitted for clarity.

are also observed. These multipoint hydrogen bond interactions help in the formation and stability of the 2-D layer structure shown in Fig. 3. The complete list of hydrogen bond interactions observed in the title compound is presented in Table 3.

In summary, we have successfully synthesized a new organically templated lanthanum sulfate with a layered structure under hydrothermal conditions. Its layer structure is constructed by the fusion of four-membered ring ladders involving edge sharing between the sulfate tetrahedron and lanthanum polyhedron. The protonated diamine molecules and free water molecules are located in the apertures of zigzag layers. H-bonds, which are believed to be responsible for stabilizing the layered structure,

are prevalent in the compound. We are continuing the exploratory synthesis of a new lanthanum sulfate by variation of template agent and crystallization conditions.

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