

# Open-framework mixed aliphatic dicarboxylates of lanthanum

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## Abstract

A lanthanum mixed dicarboxylate of the formula  $[\text{La}_2(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$  containing metal oxalate layers connected by adipate and oxalate units has been synthesized hydrothermally. Hexagonal channels occur along the *c*-axis of this material. It has been possible to isolate another mixed dicarboxylate of the formula  $[\text{La}_2(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  containing metal succinate layers connected by oxalate units.

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## 1. Introduction

There have been several reports in the literature on the synthesis and characterization of a variety of metal carboxylates, specially those with open-framework structures [1,2]. However, to our knowledge there are very few reports of mixed dicarboxylates of metals. An interesting mixed carboxylate reported recently is that of cobalt oxalato-squarate [3], another example being a chiral mixed carboxylate of Nd exhibiting NLO properties [4]. We have been able to synthesize and characterize a mixed aliphatic dicarboxylate of lanthanum, wherein the oxalate unit is one of the components. The compound has the formula  $[\text{La}_2(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$ , **I**, where (6, 3) lanthanum oxalate layers are linked by adipate and oxalate units. In this article we report the synthesis and structure of this dicarboxylate. We also make a preliminary report on another lanthanum dicarboxylate of the formula,  $[\text{La}_2(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ , **II**.

## 2. Experimental

### 2.1. Synthesis

The lanthanum oxalato-adipate,  $[\text{La}_2(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$ , **I**, was synthesized hydrothermally. In a typical synthesis, 100 mg of  $\text{La}_2\text{O}_3$  was dispersed in 3 ml of deionized water, to which 0.16 ml of concentrated HCl (35%) was added dropwise to obtain a clear solution of  $\text{LaCl}_3$ . To the solution, 5M NaOH solution was added dropwise under constant stirring until the final pH was 7, followed by the addition of 54.7 mg of oxamic acid and 89.7 mg of adipic acid. The final mixture was sealed in a 23 ml PTFE-lined acid digestion bomb and heated at 180 °C for 3 days. The product, comprising of colorless crystals, was vacuum filtered and washed with water. The yield exceeded 80%. The compound was characterized by powder X-ray diffraction (PXRD) which indicated the product to be new material, the PXRD pattern agreed with those generated from single crystal X-ray diffraction data. Elemental analysis of **I** was satisfactory. Calculated: C, 18.95%; H, 0.02%; Found: C, 19.01%; H, 0.023%. By a similar method as employed in **I**, on reacting  $\text{LaCl}_3$  (after adjusting the pH to 7), with succinic and oxamic acid we have obtained a small quan-

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Table 1  
Crystal data and structure refinement parameters for compounds **I** and **II**

Parameters	<b>I</b>	<b>II</b>
Empirical formula	LaC <sub>5</sub> H <sub>2</sub> O <sub>7</sub>	LaC <sub>5</sub> H <sub>10</sub> O <sub>10</sub>
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Fddd
Crystal size (mm)	0.27 × 0.25 × 0.16	0.27 × 0.26 × 0.21
<i>a</i> (Å)	7.0216(3)	9.765
<i>b</i> (Å)	7.1384(2)	15.5827(4)
<i>c</i> (Å)	9.1646(1)	28.3964(8)
$\alpha$ (°)	103.359(2)	90
$\beta$ (°)	108.951(2)	90
$\gamma$ (°)	104.152(2)	90
Volume (Å <sup>3</sup> )	396.40(2)	4320.9(2)
<i>Z</i>	2	16
Formula mass	312.98	369.03
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.622	2.269
$\lambda$ (Mo-K $\alpha$ ) Å	0.71073	0.71073
$\mu$ (mm <sup>-1</sup> )	5.392	3.995
$\Theta$ range (°)	2.50 to 23.26	2.56 to 23.24
Total data collected	1699	4250
Limiting indices	$-7 \leq h \leq 7, -6 \leq k \leq 7, -10 \leq l \leq 9$	$-9 \leq h \leq 10, -17 \leq k \leq 17, -31 \leq l \leq 21$
Unique data	1136	781
Observed data ( $I > 2\sigma(I)$ )	1046	701
Refinement method	Full-matrix least squares on $ F^2 $	Full-matrix least squares on $ F^2 $
$R_{\text{int}}$	0.0217	0.0267
$R$ indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0320, wR_2 = 0.0788$	$R_1 = 0.0303, wR_2 = 0.0807$
$R$ (all data)	$R_1 = 0.0365, wR_2 = 0.0807$	$R_1 = 0.0337, wR_2 = 0.0836$
Goodness of fit	1.062	1.353
No. of variables	126	86
Largest difference map peak and hole $e \text{ \AA}^{-3}$	1.142 and $-1.124$	0.554 and $-1.795$

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ ,  $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ ,  $a = 0.0472$  and  $b = 0.9196$  for **I** and  $a = 0.0463$  and  $b = 29.4332$  for **II**.

tity of a lanthanum oxalato-succinate, **II**. We have been able to obtain a preliminary structure of this dicarboxylate as well.

## 2.2. Single-crystal X-ray crystallography

A suitable single crystal of the compound was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyano-acrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a fine-focus, 2.4 kW sealed tube X-ray source (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å) operating at 40 kV and 40 mA. A hemisphere of intensity data was collected at room temperature with  $\omega$  space scans (width of 0.30° and exposure time of 20 s per frame). Pertinent experimental details for the structure determination are presented in Table 1.

The structure was solved by direct methods using SHELXS-86 [5], which readily established the heavy atom position (La) and facilitated the identification of the light atoms (O, C, H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent

Table 2  
Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
La(1)	3449(1)	1476(1)	1426(1)	13(1)
O(1)	5209(9)	2567(8)	4457(7)	24(1)
O(2)	6519(8)	4121(9)	1445(7)	23(1)
O(3)	2389(8)	3500(8)	-0401(6)	20(1)
O(4)	-0263(8)	0915(8)	1438(6)	18(1)
O(5)	2169(12)	-2025(10)	1732(9)	30(2)
O(6)	3417(8)	-0224(8)	-1542(6)	19(1)
O(7)	3654(9)	5090(8)	3077(6)	23(1)
C(1)	1393(12)	-1050(12)	-2273(9)	16(2)
C(2)	4548(12)	5712(13)	4603(9)	17(2)
C(3)	0322(13)	-2209(13)	-4095(10)	23(2)
C(4)	-0378(41)	-0882(21)	-5057(14)	14(1)
C(5)	6202(12)	5171(12)	0544(9)	16(2)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third trace of the orthogonalized tensor  $U_{ij}$ .

reflections was applied using SADABS programme [6]. All the hydrogen positions were initially located in the difference Fourier maps and the hydrogen atoms were placed geometrically and held in the riding mode for the final

Table 3  
Selected bond distances and bond angles in **I**

Moiety	Distance (Å)	Moiety	Distance (Å)
La(1)–O(1)	2.480(5)	La(1)–O(5)	2.553(6)
La(1)–O(2)	2.486(5)	La(1)–O(7)	2.615(5)
La(1)–O(3)	2.506(5)	La(1)–O(4) <sup>b</sup>	2.657(5)
La(1)–O(4)	2.542(5)	La(1)–O(6)	2.701(5)
La(1)–O(6) <sup>a</sup>	2.551(5)	O(3)–C(5) <sup>d</sup>	1.256(9)
O(1)–C(2) <sup>c</sup>	1.262(10)	O(4)–C(1) <sup>b</sup>	1.274(9)
O(2)–C(5)	1.242(9)	O(6)–C(1)	1.267(9)
O(6)–La(1) <sup>a</sup>	2.551(5)	O(4)–La(1) <sup>b</sup>	2.657(5)
O(7)–C(2)	1.247(9)	C(2)–O(1) <sup>c</sup>	1.262(10)
C(1)–O(4) <sup>b</sup>	1.274(9)	C(2)–C(2) <sup>c</sup>	1.520(2)
C(3)–C(4)	1.500(2)	C(4)–C(4) <sup>e</sup>	1.210(3)
C(5)–O(3) <sup>d</sup>	1.256(9)	C(1)–C(3)	1.510(11)
C(5)–C(5) <sup>d</sup>	1.580(2)		
Moiety	Angle (°)	Moiety	Angle (°)
O(1)–La(1)–O(2)	89.7(2)	O(4)–La(1)–O(7)	75.4(2)
O(1)–La(1)–O(3)	130.4(2)	O(6) <sup>a</sup> –La(1)–O(7)	127.1(2)
O(2)–La(1)–O(3)	65.6(2)	O(5)–La(1)–O(7)	130.8(2)
O(1)–La(1)–O(4)	92.6(2)	O(1)–La(1)–O(4) <sup>b</sup>	151.8(2)
O(2)–La(1)–O(4)	141.6(2)	O(2)–La(1)–O(4) <sup>b</sup>	118.5(2)
O(3)–La(1)–O(4)	84.4(2)	O(3)–La(1)–O(4) <sup>b</sup>	68.5(2)
O(1)–La(1)–O(6) <sup>a</sup>	83.7(2)	O(4)–La(1)–O(4) <sup>b</sup>	66.2(2)
O(2)–La(1)–O(6) <sup>a</sup>	67.9(2)	O(6) <sup>a</sup> –La(1)–O(4) <sup>b</sup>	105.4(2)
O(3)–La(1)–O(6) <sup>a</sup>	120.1(2)	O(5)–La(1)–O(4) <sup>b</sup>	74.3(2)
O(4)–La(1)–O(6) <sup>a</sup>	150.4(2)	O(7)–La(1)–O(4) <sup>b</sup>	123.6(2)
O(1)–La(1)–O(5)	81.8(2)	O(1)–La(1)–O(6)	149.6(2)
O(2)–La(1)–O(5)	145.3(2)	O(2)–La(1)–O(6)	78.3(2)
O(3)–La(1)–O(5)	141.8(2)	O(3)–La(1)–O(6)	69.5(2)
O(4)–La(1)–O(5)	72.6(2)	O(4)–La(1)–O(6)	114.2(2)
O(6) <sup>a</sup> –La(1)–O(5)	77.7(2)	O(6) <sup>a</sup> –La(1)–O(6)	66.0(2)
O(1)–La(1)–O(7)	63.3(2)	O(5)–La(1)–O(6)	92.3(2)
O(2)–La(1)–O(7)	71.6(2)	O(7)–La(1)–O(6)	135.2(2)
O(3)–La(1)–O(7)	68.1(2)	O(4) <sup>b</sup> –La(1)–O(6)	48.2(2)
C(2) <sup>c</sup> –O(1)–La(1)	123.2(5)	C(1)–O(6)–La(1) <sup>a</sup>	134.4(5)
C(5)–O(2)–La(1)	120.5(5)	C(1)–O(6)–La(1)	95.5(4)
C(5) <sup>d</sup> –O(3)–La(1)	120.4(5)	C(2)–O(7)–La(1)	118.9(5)
C(1) <sup>b</sup> –O(4)–La(1)	147.9(5)	C(1) <sup>b</sup> –O(4)–La(1) <sup>b</sup>	97.4(4)
La(1)–O(4)–La(1) <sup>b</sup>	113.8(2)	La(1) <sup>a</sup> –O(6)–La(1)	114.0(2)
O(6)–C(1)–O(4) <sup>b</sup>	118.8(7)	O(2)–C(5)–O(3) <sup>d</sup>	126.5(7)
O(6)–C(1)–C(3)	121.2(7)	O(2)–C(5)–C(5) <sup>d</sup>	117.7(8)
O(4) <sup>b</sup> –C(1)–C(3)	120.1(7)	O(3) <sup>d</sup> –C(5)–C(5) <sup>d</sup>	115.7(8)
O(7)–C(2)–O(1) <sup>c</sup>	125.4(8)	O(1) <sup>c</sup> –C(2)–C(2) <sup>c</sup>	117.4(8)
O(7)–C(2)–C(2) <sup>c</sup>	117.2(9)	C(4)–C(3)–C(1)	112.0(8)
C(4) <sup>e</sup> –C(4)–C(3)	135(2)		

Symmetry transformations used to generate equivalent atoms: <sup>a</sup>  $-x + 1, -y, -z$ ; <sup>b</sup>  $-x, -y, -z$ ; <sup>c</sup>  $-x + 1, -y + 1, -z + 1$ ; <sup>d</sup>  $-x + 1, -y + 1, -z$ ; <sup>e</sup>  $-x, -y, -z - 1$ .

refinement. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS [7] package of programs. Details of the

Table 4  
Hydrogen bonding interaction in compound **I**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(5)–H(1)···O(7)	0.93(11)	1.96(11)	2.87(1)	165(10)
Intra O(5)–H(2)···O(3)	0.73(12)	2.14(12)	2.84(1)	162(12)

crystal structure and final refinements of both **I** and **II** are given in Table 1. The atomic coordinates, selected bond lengths and angles in **I** are given in Tables 2 and 3 respectively. The hydrogen bond parameters in **I** are given in Table 4.

### 3. Results and discussion

The asymmetric unit of **I** contains 13 non-hydrogen atoms (Fig. 1a). There is one crystallographically unique La atom, one coordinated water molecule, one oxalate molecule and 1/2 of the adipate unit in the asymmetric unit. The La atom is 9-coordinated by 4 oxygens from two oxalate groups, 4 oxygens of three adipate groups and one water molecule. The central  $-\text{CH}_2$  groups of the adipate moiety are disordered as in many other metal adipates [8] and no effort was made to locate the hydrogens. The carboxylate oxygens of the adipate are three-coordinated with each carboxylate acting as bischelating as well as bis-bridging unit. To our knowledge, such a coordination mode of an adipate group has been observed for the first time in **I** [9]. The bridging of the La centers by the three-coordinated adipate oxygens results in the formation of La–O–La chains parallel to the *a*-axis of the unit cell. The chains get connected by the bischelating oxalate groups to form layer, with a (6, 3) net topology, parallel to the *ab*-plane of the unit cell (Fig. 1b) [10]. The three-dimensional network can be viewed as formed by pillaring of these layers, which are shifted by 1/2 the unit cell length along both the *a*- and *b*-axes of the unit cell and separated by an unit cell length along the *c*-axis of the unit cell, by the oxalate and adipate groups (Fig. 2). In other words, the structure can be described as being formed of La-oxalate dimers which get connected by the bridging adipate oxygens to form (6, 3) layers (Fig. 1b), unlike rare-earth oxalates which form (4, 4) layers with the metal centres connected by the oxalate units [11]. The layers in turn get connected by the out-of-plane oxalate and adipate groups to form the three-dimensional network. Such a connectivity between the layers results in the formation of hexagonal channels down the *c*-axis of the unit cell, with both the pillaring oxalate and adipate groups forming the walls of the channels.

The La–O bond distances in **I** are in the range 2.480(5)–2.701(5) Å (average = 2.566 Å) and the O–La–O bond angles are in the range 48.2(2)–151.8(2)°. Bond Valence Sum (BVS) calculations [12] (La = 3.16) as well as the bond distances are consistent with the +3 oxidation state of La. Within these hexagonal channels, the shortest and the

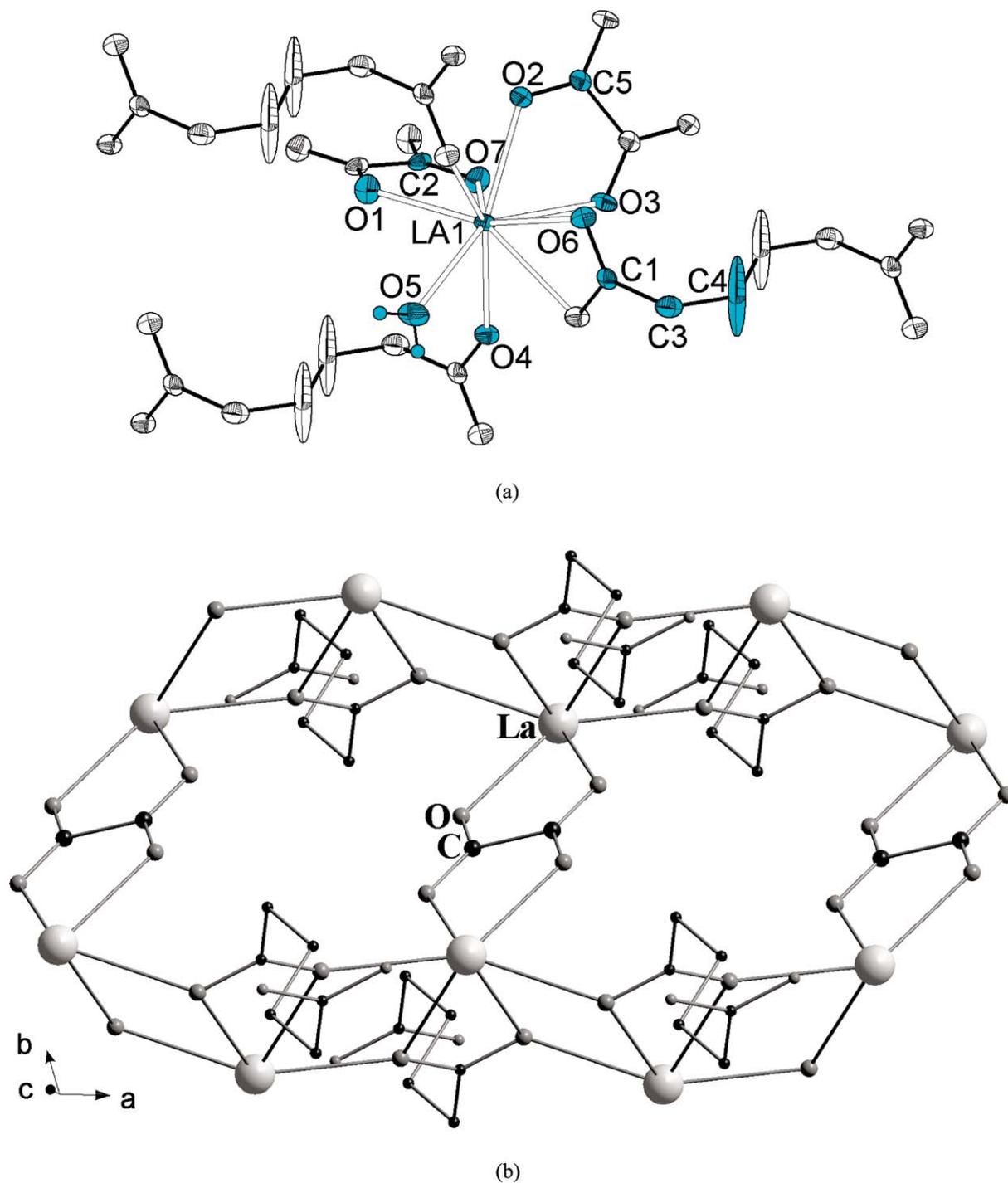


Fig. 1. (a) ORTEP plot of  $[\text{La}_2(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$ , **I**. The asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. (b) The (6, 3) layers parallel to the  $ab$ -plane of the unit cell, formed by joining of the La–O–La chains running parallel to the  $a$ -axis of the unit cell by the bischelating oxalate molecules.

longest opposite La–La distances are 8.089 and 10.76 Å respectively. The La–La separation between the adjacent layers down the  $c$ -axis is 9.167 Å.

We have been able to isolate one or two crystals of another 3-dimensional mixed dicarboxylate of the formula  $[\text{La}_2(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ , **II**, wherein two adjacent lanthanum-succinate layers parallel to the  $ab$ -plane

of the unit cell (Fig. 3a) and containing La–O–La chains running parallel to the  $b$ -axis of the unit cell, get connected by the pillaring oxalate units, thus completing the 3-dimensional framework structure of **II** (Fig. 3b). Two adjacent lanthanum-succinate layers are separated by 1/2 the unit cell length along the  $c$ -axis and are related by a mirror image with a 90° rotation. Such a connectivity between

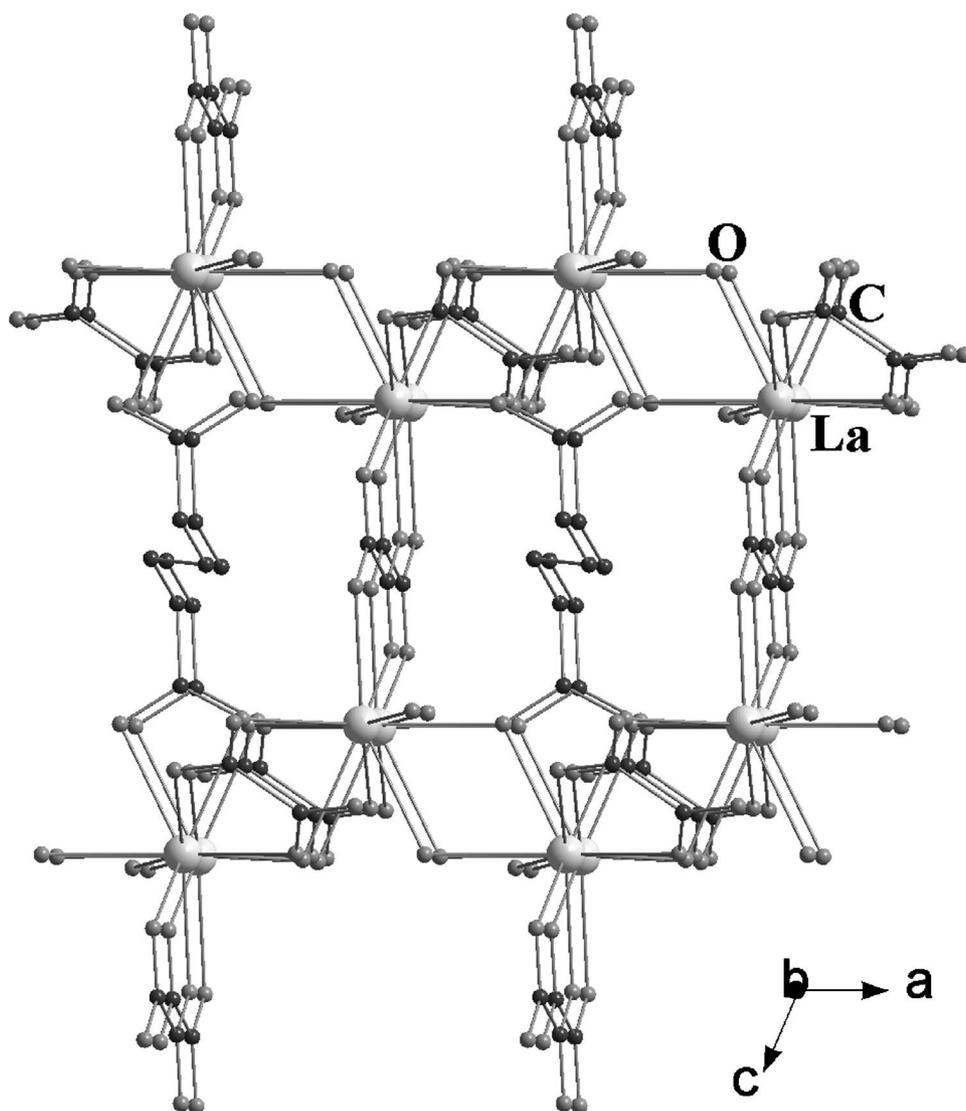


Fig. 2. A view of the three-dimensional structure of **I** down the *b*-axis of the unit cell. Note the three-coordinating oxygens of the adipate molecule, each carboxylate group of the adipate molecule acts as both bischelating and bisbridging to the La centres.

these lanthanum-succinate layers by the oxalate units gives rise to a network of interconnected 6-membered channels in between the lanthanum-succinate layers. These channels are occupied by the interstitial water molecules, which forms hydrogen bonds with the coordinated water molecules and the 2-coordinated oxygens of the succinate groups, thereby rendering additional stability to the structure (Fig. 3b). BVS calculations [12] ( $La = 3.07$ ) and charge balance considerations are consistent with the assumption of the terminal oxygen being coordinated water in **II**. We have not yet been able to isolate sufficient quantity of the compound **II** for full characterization.

The supplementary material has been sent to Cambridge crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as supplementary material No. CCDC 257632 and CCDC 257633 and can be obtained by contacting the CCDC.

#### 4. Conclusions

In conclusion, we have been successful in synthesizing a mixed dicarboxylate involving oxalate and adipate units with a 3-dimensional open-framework structure. The dicarboxylate, containing metal oxalate layers, forms hexagonal channels along the *c*-axis of the unit cell wherein the two carboxylate groups form the walls of the channels. Another dicarboxylate, with lanthanum-succinate layers connected by oxalate units, has also been identified.

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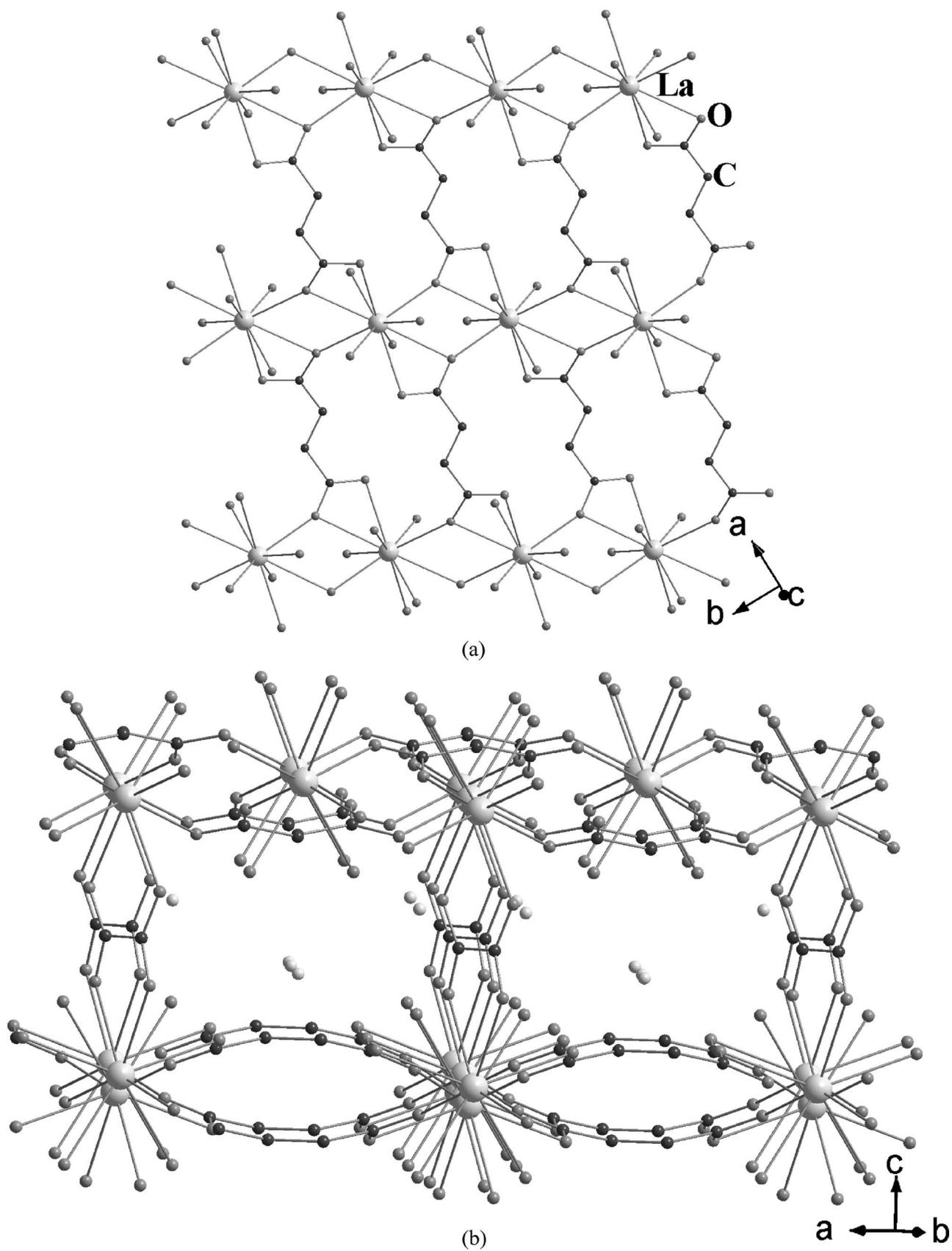


Fig. 3. (a) The lanthanum-succinate layers parallel to the  $ab$ -plane of the unit cell, formed by joining of the La–O–La chains running parallel to the  $b$ -axis of the unit cell by the chelating-bridging succinate molecules. (b) The three-dimensional structure of **II** formed by joining of the layers by the pillaring oxalates, which results in the formation of the network of interconnected channels in between the layers. Note the different orientations of the two adjacent layers.

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