

## A new three-dimensional neutral framework of lanthanum oxalate: $[\text{La}_2(\text{C}_2\text{O}_4)_3(\text{DMF})(\text{H}_2\text{O})_3]_n$

Jingen Wang, Xihe Huang, Changcang Huang,\* Haiyan Song and Duoping Yang

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: cchuang@fzu.edu.cn

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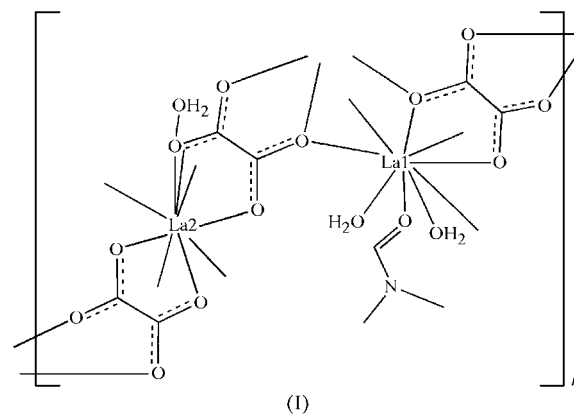
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In the title complex, poly[triaquabis(dimethylformamide)- $\mu_3$ -oxalato- $\mu_2$ -oxalato-dilanthanum(III)],  $[\text{La}_2(\text{C}_2\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_3]_n$ , both La ions are coordinated by nine O atoms, forming slightly distorted tricapped trigonal prisms. The two La ions, the terminal water O atom, and the O and N atoms of the dimethylformamide molecule reside on twofold rotation axes, giving the two La-centered coordination geometries twofold or pseudo-twofold symmetries. The two oxalate ligands, one of which rests on a center of inversion at the mid-point of the C—C bond, adopt different bridging modes, connecting with the La ions to form two types of lanthanide oxalate chains, *i.e.* anionic  $\{[\text{La}(\text{C}_2\text{O}_4)_2(\text{DMF})(\text{H}_2\text{O})_2]^{n-}\}_n$  (DMF is dimethylformamide) and cationic zigzag  $\{[\text{La}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]^{n+}\}_n$ , respectively. Each zigzag cationic chain is linked to four adjacent anionic chains *via* the bridging oxalate anions, and each anionic chain connects with four zigzag cationic chains, constructing a three-dimensional neutral framework.

### Comment

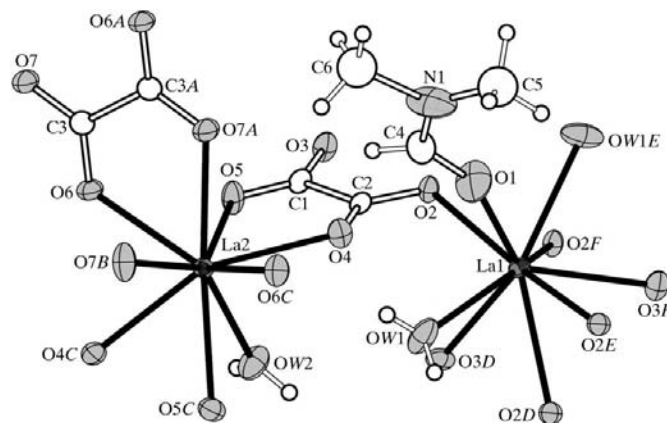
The use of multifunctional organic linker molecules to polymerize metal centers into open-framework materials has led to the development of a rich field of chemistry (Yaghi *et al.*, 1998, 2003; Serre *et al.*, 2004; James, 2003) owing to potential applications in catalysis, separation, gas storage and molecular recognition. Among such novel open-framework materials, lanthanide oxalates are particularly noteworthy. The wide variety of coordination modes of the oxalate anion permits the use of metal–oxalate units as excellent building blocks to construct a great diversity of frameworks ranging from discrete oligomeric entities to one-, two- and three-dimensional networks. Lanthanide oxalates present generally a honeycomb layered structure in which the layers are separated by water or other molecules (Ollendorf & Weigel, 1969; Michaelides *et al.*, 1988; Hansson, 1970, 1973; Trombe & Jaud, 2003). Generally, there are two developed routes to construct three-dimensional open-framework lanthanide oxalates. One

is based on the employment of protonated organic amines, ammonium or alkali metal ions as counter-cations. By this method, some three-dimensional lanthanide–oxalate anionic frameworks, where the cations are suspended in the channels,

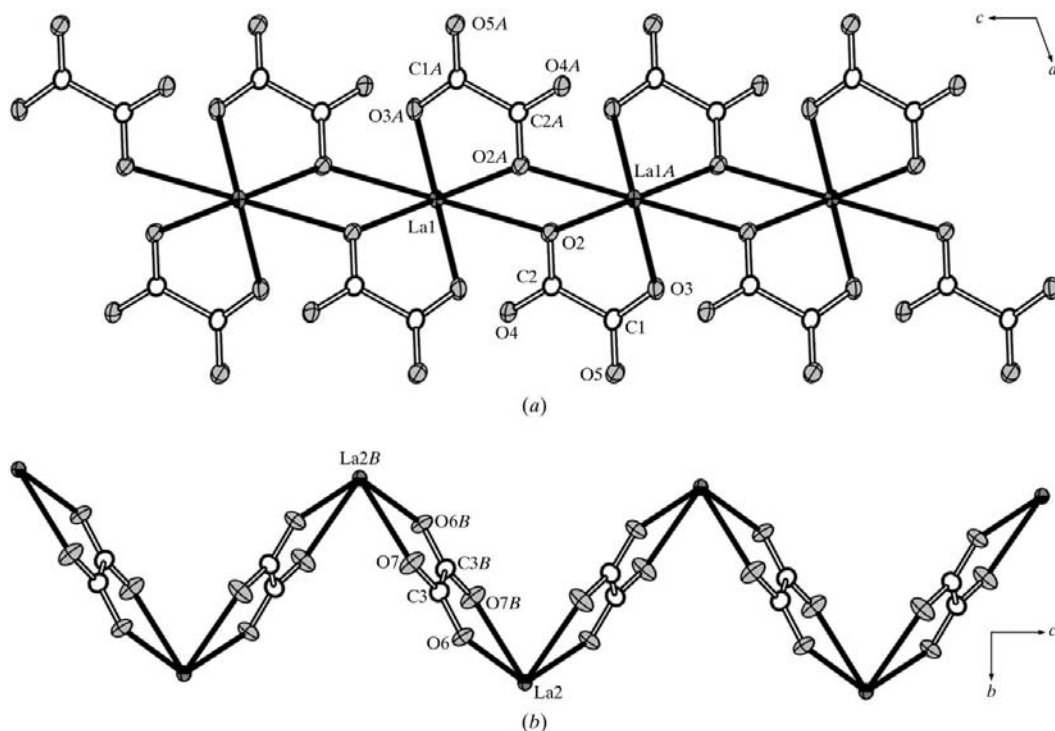


have been prepared (Chapelet-Arab *et al.*, 2005*a,b*; Vaidhyathan *et al.*, 2002; Mohanu *et al.*, 2006). The other method involves combining a second ligand and/or alkali metal ion into the framework, by which route several three-dimensional neutral frameworks have been created (Romero *et al.*, 1996, 1997; Yuan *et al.*, 2004; Zhang *et al.*, 2007). Interestingly, only one example of a three-dimensional neutral framework constructed by lanthanide centers and oxalate anions alone,  $[\{\text{Er}(\text{H}_2\text{O})_3\}_2(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$  (II), has been reported to date (Camara *et al.*, 2003). In view of the limited number of lanthanide oxalates with three-dimensional neutral frameworks, we have attempted to synthesize new examples by introducing bulky solvent molecules to replace the coordinated water molecules under solvothermal conditions. A new DMF–lanthanum oxalate,  $[\text{La}_2(\text{C}_2\text{O}_4)_3(\text{DMF})(\text{H}_2\text{O})_3]_n$  (DMF is dimethylformamide), (I), has been obtained and its structure is reported here.

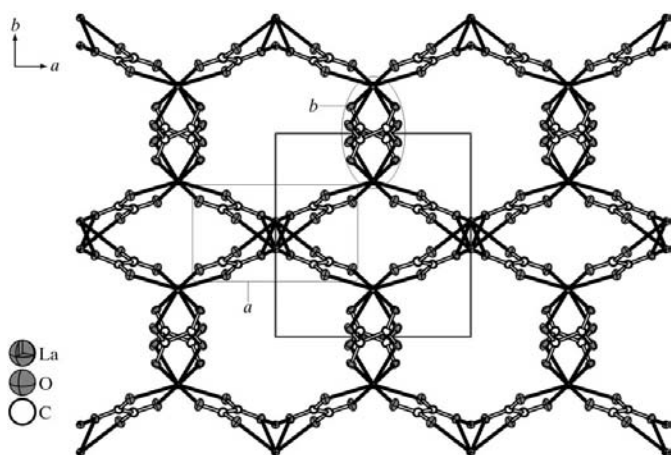
There are two crystallographically independent  $\text{La}^{3+}$  ions, two unique oxalate ligands, one DMF molecule and two



**Figure 1**  
The coordination around the two  $\text{La}^{\text{III}}$  ions in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (A)  $1 - x, -y, 1 - z$ ; (B)  $x, -y, \frac{1}{2} + z$ ; (C)  $1 - x, y, \frac{3}{2} - z$ ; (D)  $x, 1 - y, \frac{1}{2} + z$ ; (E)  $-x, y, \frac{3}{2} - z$ ; (F)  $-x, 1 - y, 1 - z$ .]


**Figure 2**

A view of (a) the anionic chain of  $\{[\text{La}(\text{H}_2\text{O})_2(\text{DMF})(\text{C}_2\text{O}_4)_2]^{n-}\}_n$  and (b) the zigzag cationic chain of  $\{[\text{La}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)]^{n+}\}_n$  in (I). The water and DMF molecules have been omitted for clarity. [Symmetry codes: (a)  $-x, 1-y, 1-z$ ; (b)  $1-x, -y, 1-z$ .]


**Figure 3**

A packing diagram for (I), viewed down the  $c$  axis. The water and DMF molecules have been omitted for clarity.

independent water molecules in the asymmetric unit (Fig. 1). Both the La centers, located on twofold rotation axes, are nine-coordinated by O atoms, forming slightly distorted tricapped trigonal prisms, with the La–O distances ranging from 2.418 (4) to 2.658 (4) Å (Table 1). There is a distinct dissimilarity between the two oxalate ligands, both in their crystallographic positions and in their coordination modes. One oxalate ligand (containing C1 and C2, denoted ox1), adopting a  $(\kappa^2)-(\kappa^2-\kappa^1-\mu_2)-\mu_3$  bridging mode, sits in a general position. The other oxalate ligand (containing C3, denoted

ox2), adopting a  $(\kappa^2)-(\kappa^2)-\mu_2$  bridging mode, straddles an inversion center across the C–C bond.

The La1 center is coordinated by two ox1 ligands through atoms O2 and O3 in chelating mode, two water molecules (OW1), one DMF molecule and two O2 atoms from other ox1 anions, which act as  $\mu_2$ -bridging atoms. Each La1 oxalate unit connects with two adjacent equivalent units by sharing the two  $\mu_2$ -bridging O2 atoms, forming an edge-shared  $\{[\text{La}(\text{H}_2\text{O})_2(\text{DMF})(\text{C}_2\text{O}_4)_2]^{n-}\}_n$  anionic chain along the  $c$  axis (Fig. 2a). Such an arrangement of the anionic chain has not been observed in previously reported lanthanide oxalates. The nine O atoms of the La2 coordination environment belong to two ox2 ligands (atoms O6 and O7), two ox1 ligands (atoms O4 and O5) from the neighboring  $\{[\text{La}(\text{H}_2\text{O})_2(\text{DMF})(\text{C}_2\text{O}_4)_2]^{n-}\}_n$  anionic chain, and one water molecule (OW2). The  $\{\text{La}_2(\text{H}_2\text{O})\}$  units and ox2 ligands connect with each other alternately, resulting in a zigzag cationic  $\{[\text{La}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)]^{n+}\}_n$  chain (Fig. 2b), along the  $c$  axis, which is identical to that of  $[\text{Gd}(\text{C}_2\text{O}_4)\{\text{MeNH}(\text{CH}_2\text{CO}_2)(\text{CH}_2\text{PO}_3\text{H})\} \cdot 0.5\text{H}_2\text{O}]$  (Song & Mao, 2005). Each zigzag cationic chain is linked to four adjacent anionic chains *via* the bridging ox1 anions, and each anionic chain connects with four zigzag cationic chains, constructing a three-dimensional neutral framework (Fig. 3). There is a noticeable difference between (I) and (II). In (II), the oxalate ligand adopts a  $(\kappa^2)-(\kappa^2)-\mu_2$  bridging mode and each  $\text{Er}^{\text{III}}$  ion connects to three oxalate anions, resulting in the three-dimensional neutral framework. Furthermore, extended hydrogen bonds are found between the oxalate O atoms and the terminal water molecules (Table 2).

Experimental

A mixture of lanthanum nitrate hexahydrate [La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O], oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), dimethylamine (C<sub>2</sub>H<sub>6</sub>NH), dimethylformamide and ethanol (molar ratio 1:1:2.5:130:500) was placed in a 15 ml Teflon-lined steel bomb and heated at 368 K for 96 h under autogenous pressure. Upon cooling to room temperature, colorless crystals of (I) were filtered off, washed with distilled water and dried in air.

Crystal data

[La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(C<sub>3</sub>H<sub>7</sub>NO)(H<sub>2</sub>O)<sub>3</sub>] V = 872.4 (3) Å<sup>3</sup>  
 M<sub>r</sub> = 669.02 Z = 2  
 Monoclinic, P2<sub>1</sub>/c Mo Kα radiation  
 a = 10.392 (2) Å μ = 4.92 mm<sup>-1</sup>  
 b = 10.224 (2) Å T = 298 (2) K  
 c = 8.7073 (17) Å 0.20 × 0.19 × 0.18 mm  
 β = 109.43 (3)°

Data collection

Rigaku R-AXIS RAPID 2008 independent reflections  
 diffractometer 1779 reflections with I > 2σ(I)  
 8351 measured reflections R<sub>int</sub> = 0.046

Refinement

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.026 H atoms treated by a mixture of  
 wR(F<sup>2</sup>) = 0.058 independent and constrained  
 S = 1.06 refinement  
 2008 reflections Δρ<sub>max</sub> = 1.52 e Å<sup>-3</sup>  
 143 parameters Δρ<sub>min</sub> = -1.10 e Å<sup>-3</sup>  
 2 restraints

Table 1

Selected geometric parameters (Å, °).

La1—O1	2.418 (5)	La2—O4	2.516 (3)
La1—O3 <sup>i</sup>	2.553 (3)	La2—O6	2.518 (3)
La1—OW1	2.591 (3)	La2—O7 <sup>ii</sup>	2.532 (3)
La1—O2 <sup>i</sup>	2.621 (2)	La2—O5	2.644 (3)
La1—O2	2.624 (2)	La2—OW2	2.657 (4)
O1—La1—O3 <sup>i</sup>	126.96 (7)	O2 <sup>i</sup> —La1—O2	132.11 (8)
O3 <sup>i</sup> —La1—OW1	71.14 (11)	O6—La2—O7 <sup>ii</sup>	64.28 (9)
OW1 <sup>iii</sup> —La1—OW1	139.49 (17)	O6—La2—O7 <sup>v</sup>	76.39 (9)
O1—La1—O2 <sup>iv</sup>	130.39 (6)	O4—La2—O5 <sup>vi</sup>	103.31 (9)
O3 <sup>iv</sup> —La1—O2 <sup>iv</sup>	61.59 (8)	O4—La2—O5	63.66 (8)
O1—La1—O2	83.28 (6)	O4—La2—OW2	73.57 (7)
O3 <sup>i</sup> —La1—O2	70.93 (8)	O6—La2—OW2	114.86 (6)
OW1—La1—O2	101.42 (9)	O5—La2—OW2	67.83 (7)

Symmetry codes: (i) x, -y + 1, z + ½; (ii) -x + 1, -y, -z + 1; (iii) -x, y, -z + ¾; (iv) -x, -y + 1, -z + 1; (v) x, -y, z + ½; (vi) -x + 1, y, -z + ¾.

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
OW1—H1W1...O3 <sup>vii</sup>	0.818 (10)	1.931 (18)	2.721 (4)	162 (5)
OW1—H2W1...O6 <sup>vi</sup>	0.818 (10)	2.15 (2)	2.940 (4)	164 (6)
OW2—H1W2...O5 <sup>viii</sup>	0.818 (10)	2.148 (11)	2.966 (4)	178 (5)

Symmetry codes: (vi) -x + 1, y, -z + ¾; (vii) x, y, z + 1; (viii) -x + 1, -y + 1, -z + 1.

The C and H atoms of the DMF ligand are disordered over two twofold axis symmetry-related positions, and the DMF H atoms were refined in the rigid-model approximation with C—H distance constraints of 0.96 Å. H atoms of the coordinated water molecules were located in difference Fourier maps and refined with restraints on the O—H bond lengths and the H—O—H angle.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: RAPID-AUTO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1993); software used to prepare material for publication: SHELXL97-2 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3099). Services for accessing these data are described at the back of the journal.

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