

# Topological aspects of lanthanide–adipate–aqua compounds: Close packed and open framework structures



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## ARTICLE INFO

### Article history:

Received 22 January 2013

Received in revised form

8 April 2013

Accepted 14 April 2013

Available online 22 April 2013

### Keywords:

Lanthanide

Adipate

Close packed framework structure

Open framework structure

## ABSTRACT

A search in the Cambridge Structural Database (CSD) for lanthanide complexes with adipate  $[\text{OOC}(\text{CH}_2)_4\text{COO}]^{2-}$  and aqua ligands retrieved a fair number of compounds. To this dataset a new lanthanum metal–organic framework,  $\{[\text{La}_2(\text{adip})_3(\text{H}_2\text{O})_2]\}$  (**1**) (adipH<sub>2</sub>=adipic acid), synthesised and structurally characterized in these labs, was included. The crystal structures of these coordination polymers, of general formulation  $[\text{Ln}_2(\text{adip})_3(\text{H}_2\text{O})_x]$ , exhibit a variety of topologies and dimensionality, which were clustered in different classes and described in detail. It was explored that the majority of these evidences the presence of metal chains or dinuclear Ln<sub>2</sub> entities (separated in both cases by 4.0–4.8 Å), where lanthanide ions are differently connected by carboxylate groups with chelating or oxygen-bridging mode. The different amount of coordinated water molecules appear to affect the solid state networks. Moreover the crystal packing of these compounds shows peculiar aspects and examples were reported in the literature where the long alkyl chain of adipate connectors give rise to interpenetrated structures, or to porous material where lattice water or neutral larger molecules are clathrated.

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## 1. Introduction

The design and synthesis of metal–organic frameworks (MOFs) has become a promising area of research, not only for their intriguing architectures and topologies [1] but also for their application in different areas like gas storage, [2] catalysis, [3] magnetism, [4] ion exchange, [5] electrical conductivity, [6] chemical sensing, luminescence [7] etc. Rare earth MOFs are of special interest due to their unique optical, electrical and magnetic properties originating from the metal ions. [8] Such complexes are also applied as device components for optical communication, [9] medical diagnostics. [7] It is well-known that lanthanide ions possess high electron affinity and prefer to bind hard donor atoms. So, the flexible dicarboxylate ligands are effective for the construction of lanthanide coordination polymers [10]. The high coordination number of lanthanides, compared to transition metal ions, influences the formation of frameworks with versatile design. [11–14] Lanthanide contraction may also influence the metal coordination number which in turn affects the overall network structure. [15–18] Therefore, rational design and synthesis of coordination polymers of rare earth metal ions with desired geometries is still a

challenge. In this paper we report the hydrothermal synthesis and X-ray single crystal structure of a novel La(III)-adipate coordination polymer  $\{[\text{La}_2(\text{adip})_3(\text{H}_2\text{O})_2]\}$ , (adipH<sub>2</sub>=adipic acid) that joins the broad library of analogous compounds retrieved from the literature. A brief review summarizing the different topologies of the structurally characterized rare earth adipate compounds is also reported.

## 2. Experimental

### 2.1. Materials and instrumentation

Lanthanum chloride hydrate was purchased from SIGMA-ALDRICH Inc. and adipic acid from Merck. Both the chemicals were used without any further purification. IR spectrum of the complex was recorded in the range 4000–400 cm<sup>-1</sup> in a JASCO FT IR-6200 applying ATR technique.

### 2.2. Synthesis of complex **1**

LaCl<sub>3</sub>·7H<sub>2</sub>O (185.7 mg, 0.5 mmol) and adipic acid (36.5 mg, 0.25 mmol) were poured in a beaker containing in 10 mL of deionized water. Triethyl amine (0.14 mL, 1 mmol) was added dropwise into the solution with constant stirring. The resulting transparent solution was transferred into a 25 mL teflon lined solvothermal bomb and heated at 160 °C for 3 days. Grey colored mixture was

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obtained after cooling the bomb to room temperature. The solid was filtered off and the clear solution was kept in a desiccator for crystallization. Colourless needle shaped crystals, formed after seven days, were isolated by decanting the supernatant liquid followed by washing with deionized water–ethanol solvent mixture. Yield: 60%. Elemental analysis calc. for  $C_{18}H_{28}La_2O_{14}$  (746.22): C 28.97%, H 3.78%; found C 28.95%, H 3.79%.

IR ( $cm^{-1}$ ): 850s, 943w, 1030w, 1126w, 1295w, 1319w, 1342w, 1398s, 1434m, 1458m, 1519s, 1538s, 1554s, 1604s, 1651m, 1685m, 1691m, 1704s, 1747w, 1776w, 1796w, 3000–3200 broad, 3502w, 3524w, 3546w, 3566w, 3591w, 3613m, 3652m, 3674m, 3691w, 3720m, 3750s, 3799m, 3824m, 3841m, 3863m, 3897m, 3922w, 3946w, 3978w.

### 2.3. X-ray crystallography

Diffraction data of complex **1** were collected at room temperature (293(2) K) on a Nonius DIP-1030H system with Mo-K radiation ( $\lambda=0.71073$  Å). Cell refinement, indexing and scaling of the data sets were carried out using Denzo and Scalepack [19]. The structure was solved by direct methods and subsequent Fourier analyses [20] and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections [20]. H atoms of the water molecules were not located. All the calculations were performed by using the WinGX System of programs, Ver 1.80.05 [21]. Figures of packing diagrams were carried out with Diamond Crystal Ver 3.1. [22]

Crystallographic data of **1**:  $C_{18}H_{28}La_2O_{14}$ ,  $M=746.22$ , triclinic, space group  $\bar{1}P$ ,  $a=8.265(4)$ ,  $b=11.851(4)$ ,  $c=13.410(4)$  Å,  $\alpha=108.01(4)$ ,  $\beta=93.94(6)$ ,  $\gamma=107.89(4)^\circ$ ,  $V=1169.1(7)$  Å<sup>3</sup>,  $Z=2$ ,  $D_c=2.120$  g/cm<sup>3</sup>,  $\mu(MoK\alpha)=3.675$  mm<sup>-1</sup>,  $F(000)=724$ ,  $\theta$  range = 1.62–25.68°. Final  $R_1=0.0668$ ,  $wR_2=0.1546$ ,  $S=0.862$  for 307 parameters and 41868 reflections, 4249 unique [ $R(int)=0.0790$ ], of which 1859 with  $I > 2\sigma(I)$ , max positive and negative peaks in  $\Delta F$  map 1.858,  $-1.756$  e./Å<sup>3</sup>.

## 3. Results and discussion

### 3.1. Description of crystal structure of $[La_2(adip)_3(H_2O)_2]$ (**1**)

The X-ray structural analysis of **1** shows that the asymmetric unit comprises two La(III) ions, three adipate anions and two aqua ligands (Fig. 1).

Each of the metal ions is bound to nine oxygen atoms of two chelating bidentate adipates, four monodentate adipate oxygens and one water molecule. The bond lengths and angles, listed in

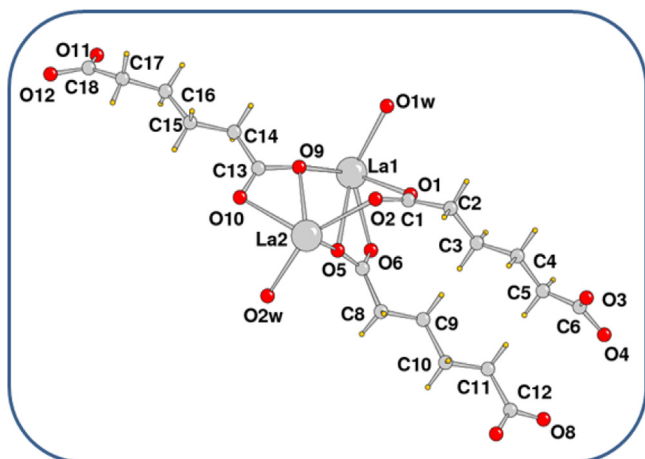


Fig. 1. Crystallographic independent unit of complex **1**.

Table 1, indicate that the La<sub>1</sub>–O distances range from 2.495(11) to 2.702(10) Å with an average bond length of 2.577 Å; similarly, La<sub>2</sub>–O bond lengths vary from 2.450(12) to 2.669(10) Å (mean 2.546 Å). The crystal packing consists of edge-shared of LaO<sub>8</sub>(H<sub>2</sub>O) polyhedra that form one dimensional chains along the (1 0 0) direction (Fig. 2), where the metal ions are at an alternate distance of 4.196 and 4.165 Å with intermetallic La–La–La angle of 162.65°. These chains are then cross-linked through adipate backbones to form a 3-D framework (Fig. 3). Two adipate chains connect the lanthanum centers with carboxylate coordination modes  $\mu_2-\eta^1:\eta^1$  and  $\mu_2-\eta^2:\eta^1$  (see Scheme 1a), while one adipate has both carboxylates  $\mu_2-\eta^2:\eta^1$  coordinated (Scheme 1b). In all cases the chelating O–La–O' angles are closely comparable (*ca.* 50°).

Lanthanum adipate complexes of different stoichiometry, namely  $[La_2(adip)_3(H_2O)_4] \cdot (adipH) \cdot 4H_2O$  [23] and  $[La_2(adip)_3(H_2O)_4] \cdot 6H_2O$ , [24,25] have been already reported in the literature. Since these compounds give origin to metal–organic frameworks (MOFs) with porous properties, it appears worthwhile to examine the crystal structures of these and of analogous structures built by rare earth ions with adipic acid, the account of which is reported hereinafter.

### 3.2. Crystal structures of adipate lanthanide compounds

A search in the Cambridge Structural Database [26] of structures containing only lanthanide ions (*Ln*), adipic acid (*adipH*<sub>2</sub>) and water molecules retrieved 28 structures. These can be clustered in different classes according to the increasing number of aqua ligands in their formulation, namely  $[Eu_2(adip)_3(H_2O)] \cdot H_2O$ ,  $[Ln_2(adip)_3(H_2O)_2] \cdot x(H_2O)$ ,  $[Ln_2(adip)_3(H_2O)_4] \cdot xH_2O$ , and  $[Ln_2(adip)_3(H_2O)_4] \cdot (adipH) \cdot 4(H_2O)$ . Table 2 reports for each class, the space group, the

Table 1  
Selected coordination bond lengths (Å) and angles (°) for **1**.

La(1)–O(1)	2.495(11)	La(2)–O(2)	2.458(13)
La(1)–O(4) <sup>a</sup>	2.514(12)	La(2)–O(3) <sup>f</sup>	2.567(11)
La(1)–O(5)	2.702(10)	La(2)–O(4) <sup>f</sup>	2.669(10)
La(1)–O(6)	2.574(11)	La(2)–O(5)	2.495(11)
La(1)–O(7) <sup>b</sup>	2.537(12)	La(2)–O(8) <sup>d</sup>	2.450(12)
La(1)–O(9)	2.511(11)	La(2)–O(9)	2.641(10)
La(1)–O(11) <sup>c</sup>	2.627(11)	La(2)–O(10)	2.561(12)
La(1)–O(12) <sup>c</sup>	2.666(11)	La(2)–O(12) <sup>e</sup>	2.492(12)
La(1)–O(1w)	2.566(11)	La(2)–O(2w)	2.584(11)
O(3) <sup>f</sup> –La(2)–O(4) <sup>f</sup>	49.8(4)	O(10)–La(2)–O(9)	50.2(4)
O(6)–La(1)–O(5)	49.6(3)	O(11) <sup>c</sup> –La(1)–O(12) <sup>c</sup>	49.8(3)

Symmetry codes:

- <sup>a</sup>  $-x, -y, -z$ .
- <sup>b</sup>  $x, y+1, z$ .
- <sup>c</sup>  $-x+1, -y+2, -z+1$ .
- <sup>d</sup>  $x+1, y+1, z$ .
- <sup>e</sup>  $-x+2, -y+2, -z+1$ .
- <sup>f</sup>  $-x+1, -y, -z$ .

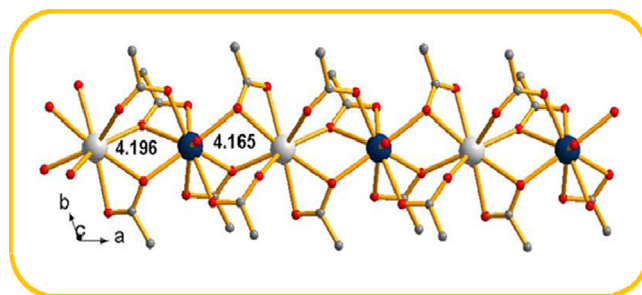


Fig. 2. The lanthanum array (La<sub>1</sub> blue, La<sub>2</sub> grey spheres) along axis-*a* with indication of the metal–metal distances (Å). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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