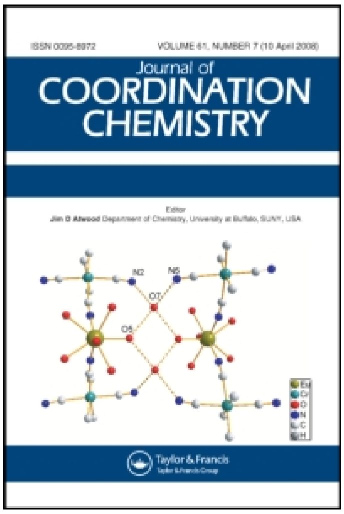

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The first suberato-bridged lanthanide coordination polymer: synthesis, crystal structure and properties of $La_2(H_2O)_2L_3$ (H_2L=HOOC$(CH_2)_6$COOH)

Y. -Q. Zheng[a]; J. Sun[a]; Y. -F. Wang[a]
[a] Municipal Key Laboratory of Solid Materials Chemistry, Institute of Inorganic Chemistry, Ningbo University, Ningbo 315211, P.R. China

To cite this Article Zheng, Y. -Q. , Sun, J. and Wang, Y. -F.(2005) 'The first suberato-bridged lanthanide coordination polymer: synthesis, crystal structure and properties of $La_2(H_2O)_2L_3$ (H_2L=HOOC$(CH_2)_6$COOH)', Journal of Coordination Chemistry, 58: 17, 1551 — 1559

To link to this Article: DOI: 10.1080/00958970500240649

URL: http://dx.doi.org/10.1080/00958970500240649

Journal of Coordination Chemistry
Vol. 58, No. 17, November 2005, 1551–1559

The first suberato-bridged lanthanide coordination polymer: synthesis, crystal structure and properties of $La_2(H_2O)_2L_3$ ($H_2L = HOOC(CH_2)_6COOH$)

Y.-Q. ZHENG*, J. SUN and Y.-F. WANG

Municipal Key Laboratory of Solid Materials Chemistry,
Institute of Inorganic Chemistry, Ningbo University,
Ningbo 315211, P.R. China

(*Received in final form 30 March 2005*)

Reaction of suberic acid ($H_2L = HOOC(CH_2)_6COOH$), $LaCl_3$ and NaOH at 170°C yielded $La_2(H_2O)_2L_3$. The complex is triclinic, space group $P\bar{1}$, with $a = 8.246(1)$, $b = 13.463(2)$, $c = 14.073(2)$ Å, $\alpha = 104.29(1)^\circ$, $\beta = 105.07(1)^\circ$, $\gamma = 93.61(1)^\circ$, $Z = 2$, $V = 1448.4(3)$ Å^3, $R_1 = 0.0324$ and $wR_2 = 0.0723$ for 5319 observed reflections ($I \geq 2\sigma(I)$) of 6597 unique reflections. The crystal structure features infinite lanthanum oxide chains of edge-sharing (LaO_9) mono-capped square antiprisms, in which La atoms are coordinated by nine oxygen atoms of six suberate anions and one water molecule at the cap with d(La–O) = 2.475–2.666 Å. The chains are bridged by the dicarboxylate anions to form a 3D, nonporous framework and interchain hydrogen bonding interactions between the capping water and carboxylate oxygen atoms contribute to the stabilization of the crystal structure. Thermogravimetric and IR properties are presented.

Keywords: Lanthanum(III); Suberato complex; Coordination polymer; Hydrothermal synthesis; Crystal structure

1. Introduction

There is considerable current interest in the rational design and synthesis of metal–organic coordination polymers due to their interesting structures as well as potential applications as smart optoelectronic, magnetic, and porous materials [1–4]. Porous coordination polymers with open frameworks, where guest species can be removed and reintroduced reversibly without collapse of the framework, are of particular interest as heterogeneous catalysts, sensors, storage and separation devices. The past several years have witnessed impressive developments in using

---

*Corresponding author. Email: zhengcm@nbu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis
DOI: 10.1080/00958970500240649

benzene di- and polycarboxylic acids as well as aliphatic α,ω-dicarboxylic acids to construct charge–neutral open frameworks [5–12]. These generally do not need counter-ions that would occupy and block the open channels. In comparison with coordination polymers with transition metal dicarboxylate networks, investigation of lanthanide aliphatic α,ω-dicarboxylates is limited [13, 14]. The reported polymers can be classified by two types, one of which exhibits co-bridging of partially and fully deprotonated dicarboxylic acids [14–17]; the other is constructed only by dicarboxylato ligand bridges [14, 18–29]. The principal building blocks are isolated metal oxygen polyhedra, edge-shared metal oxygen bi-polyhedra and edge-shared metal oxygen polyhedron chains. For example, the isolated metal oxygen polyhedra in lutetium succinate $Lu(H_2O)_2(C_4H_4O_4)_{1.5} \cdot 2H_2O$ are interlinked by succinato ligands to generate a 3D open framework with guest H_2O molecules in cavities [22]. The edge-shared metal oxygen bi-polyhedra are bridged by dicarboxylate anions to form 2D open layers in $Gd_2(C_6H_8O_4)_3(H_2O)_4$ [14] and $Eu_2(C_6H_8O_4)_3(H_2O)_4$ [28] as well as 3D microporous networks in $[Ce_2(C_6H_8O_4)_3(H_2O)_4] \cdot 4H_2O(C_6H_{10}O_4)$ [29] and in a series of isostructural adipates represented by $[La_2(C_6H_8O_4)_3(H_2O)_4] \cdot 6H_2O$ [27–29]. Furthermore, edge-shared metal oxygen chains are bridged by dicarboxylate ligands to form 2D open layers [18, 25] and 3D open frameworks [17, 23, 24, 28]. The abovementioned investigations were restricted to the dicarboxylic acids $HOOC–(CH_2)_n–COOH$ with $n \leq 5$ [13] and, to the best of our knowledge, no work with $n \geq 6$ has been reported. As a continuation of our systematic research on α,ω-dicarboxylate complexes [12], we present the synthesis, crystal structure and thermal characterization of a lanthanum suberate $La_2(H_2O)_2 \cdot (C_8H_{12}O_4)_3$, which represents the first example of lanthanide suberato coordination polymers.

2. Experimental

All chemicals of reagent grade were commercially available and used without further purification. C and H microanalyses were performed with a Heraeus Rapid-CHNO instrument. FTIR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer (KBr pellets) in the range 4000–400 cm^{-1}. TG/DTA measurements were carried out from room temperature to 550°C in a flowing nitrogen atmosphere using a Seiko Exstar 6000 TG/DTA6300 instrument with a heating rate of 10°C min^{-1}.

2.1. *Synthesis*

In a typical synthesis, 0.121 g (0.695 mmol) of suberic acid was added to 10 cm^3 of H_2O. Under continuous stirring, NaOH (1.0 M) was then dropwise added until the suberic acid completely dissolved. The resulting solution was mixed with an aqueous solution of 0.290 g $LaCl_3 \cdot nH_2O$ in 17 cm^3 of H_2O and a white flocculent precipitate formed. The mixture was then adjusted to $pH = 7.8$ with NaOH (1.0 M). Subsequently, half of the mixture was transferred to a 23 cm^3 PTFE liner, which was sealed in a stainless autoclave. The reaction was carried out at 170°C for 3 days under autogeneous pressure. After the autoclave was cooled to room temperature, colourless crystals were gathered by filtration. Yield: 31.7% based on initial $LaCl_3 \cdot nH_2O$. Anal. Calcd for

Table 1. Crystal data and structure refinement details.

Compound	$La_2(H_2O)_2(C_8H_{12}O_4)_3$
Empirical formula	$C_{24}H_{40}La_2O_{14}$
Colour/Shape	Colourless, blocky
Size (mm)	$0.53 \times 0.36 \times 0.22$
Formula weight	830.38
Temperature	293 K
Crystal system, space group	triclinic, $P\bar{1}$
a (Å)	8.246(1)
b (Å)	13.463(2)
c (Å)	14.073(2)
α (°)	104.29(1)
β (°)	105.07(1)
γ (°)	93.61(1)
Volume (Å^3), Z	1448.4(3), 2
D_{calcd} (g cm^{-3})	1.904
μ (Mo-$K\alpha$) (cm^{-1})	2.977
$F(000)$	820
Radiation	Graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å)
Scan type	$\vartheta - 2\vartheta$
No. of measured reflections	Total: 7964; unique: 6597 ($R_{\text{int}} = 0.0549$)
Correction	Semi-empirical based on psi-scans
No. of observed reflections [$I \geq 2\sigma(I)$]	5319
No. of variables	379
Goodness-of-fit on F^2	1.231
Final R indices [$I \geq 2\sigma(I)$][a]	$R1 = 0.0324$, $wR2 = 0.0723$
R indices (all data)[a]	$R1 = 0.0464$, $wR2 = 0.0781$
A, B values in weighting scheme[b]	0.0345, 1.23
Extinction coefficient	0.0010(2)
Max. and min. peak in final diff. map	1.61 and -1.72 e Å^{-3}

[a] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

$C_{24}H_{40}La_2O_{14}$ (%): C, 34.71; H, 4.86. Found: C, 34.82; H, 4.77. IR (cm^{-1}): 417m, 497w, 725m, 949w, 1097w, 1198w, 1288s, 1358m, 1423s, 1551vs, 1634w, 2860w, 2932s, 3425m (broad).

2.2. *X-ray crystallography*

A colourless crystal was mounted on a Bruker P4 diffractomerter with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. Lattice parameters were refined from the 2ϑ values (10–25°) of 25 carefully centred reflections. Reflection intensities with $2\vartheta_{\max} = 55°$ were collected at 293 K using the $\vartheta - 2\vartheta$ scan technique. Data were corrected for Lp and absorption effects. SHELXS-97 and SHELXL-97 programs [30, 31] were used for structure solution and refinement. The structure was solved by direct methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms of suberato groups were geometrically generated while the aqua hydrogen atoms were located from successive difference Fourier maps. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares techniques and hydrogen atoms with isotropic displacement parameters. Detailed information on crystal data and structure determination is summarized in table 1. Selected interatomic distances and bond angles are given in table 2.

Table 2. Selected interatomic distances (Å) and bond angles (°).

La(1)–O(1)	2.594(3)	La(1)–O(10)$^{\#3}$	2.500(3)	La(2)–O(6)	2.570(3)
La(1)–O(2)	2.657(3)	La(1)–O(12)$^{\#4}$	2.526(3)	La(2)–O(8)$^{\#6}$	2.496(3)
La(1)–O(4)$^{\#1}$	2.523(3)	La(1)–O(13)	2.549(4)	La(2)–O(9)	2.580(3)
La(1)–O(5)	2.498(3)	La(2)–O(2)	2.500(3)	La(2)–O(10)	2.666(3)
La(1)–O(7)$^{\#2}$	2.643(3)	La(2)–O(3)$^{\#5}$	2.475(3)	La(2)–O(11)$^{\#4}$	2.477(3)
La(1)–O(8)$^{\#2}$	2.628(3)	La(2)–O(5)	2.637(3)	La(2)–O(14)	2.559(4)
O(1)/La(1)/O(2)	49.1(1)	O(5)/La(1)/O(12)$^{\#4}$	93.8(1)	O(3)$^{\#5}$/La(2)/O(10)	70.1(1)
O(1)/La(1)/O(4)$^{\#1}$	145.1(1)	O(5)/La(1)/O(13)	88.6(2)	O(3)$^{\#5}$/La(2)/O(11)$^{\#4}$	83.3(1)
O(1)/La(1)/O(5)	115.4(1)	O(7)$^{\#2}$/La(1)/O(8)$^{\#2}$	49.0(1)	O(3)$^{\#5}$/La(2)/O(14)	136.5(1)
O(1)/La(1)/O(7)$^{\#2}$	81.0(1)	O(7)$^{\#2}$/La(1)/O(10)$^{\#3}$	116.3(1)	O(5)/La(2)/O(6)	49.7(1)
O(1)/La(1)/O(8)$^{\#2}$	75.6(1)	O(7)$^{\#2}$/La(1)/O(12)$^{\#4}$	143.9(1)	O(5)/La(2)/O(8)$^{\#6}$	129.8(1)
O(1)/La(1)/O(10)$^{\#3}$	72.7(1)	O(7)$^{\#2}$/La(1)/O(13)	140.9(1)	O(5)/La(2)/O(9)	140.8(1)
O(1)/La(1)/O(12)$^{\#4}$	75.1(1)	O(8)$^{\#2}$/La(1)/O(10)$^{\#3}$	68.4(1)	O(5)/La(2)/O(10)	141.3(1)
O(1)/La(1)/O(13)	137.9(2)	O(8)$^{\#2}$/La(1)/O(12)$^{\#4}$	143.2(1)	O(5)/La(2)/O(11)$^{\#4}$	73.4(1)
O(2)/La(1)/O(4)$^{\#1}$	139.8(1)	O(8)$^{\#2}$/La(1)/O(13)	124.3(1)	O(5)/La(2)/O(14)	105.0(1)
O(2)/La(1)/O(5)	67.4(1)	O(10)$^{\#3}$/La(1)/O(12)$^{\#4}$	82.0(1)	O(6)/La(2)/O(8)$^{\#6}$	81.9(1)
O(2)/La(1)/O(7)$^{\#2}$	75.8(1)	O(10)$^{\#3}$/La(1)/O(13)	81.1(2)	O(6)/La(2)/O(9)	158.7(1)
O(2)/La(1)/O(8)$^{\#2}$	107.2(1)	O(12)$^{\#4}$/La(1)/O(13)	68.9(2)	O(6)/La(2)/O(10)	140.1(1)
O(2)/La(1)/O(10)$^{\#3}$	118.9(1)	O(2)/La(2)/O(3)$^{\#6}$	147.1(1)	O(6)/La(2)/O(11)$^{\#4}$	121.3(1)
O(2)/La(1)/O(12)$^{\#4}$	68.1(1)	O(2)/La(2)/O(5)	67.7(1)	O(6)/La(2)/O(14)	76.6(1)
O(2)/La(1)/O(13)	128.5(1)	O(2)/La(2)/O(6)	92.9(1)	O(8)$^{\#6}$/La(2)/O(9)	89.1(1)
O(4)$^{\#1}$/La(1)/O(5)	79.1(1)	O(2)/La(2)/O(8)$^{\#6}$	137.1(1)	O(8)$^{\#6}$/La(2)/O(10)	67.8(1)
O(4)$^{\#1}$/La(1)/O(7)$^{\#2}$	73.3(1)	O(2)/La(2)/O(9)	80.6(1)	O(8)$^{\#6}$/La(2)/O(11)$^{\#4}$	142.3(1)
O(4)$^{\#1}$/La(1)/O(8)$^{\#2}$	69.8(1)	O(2)/La(2)/O(10)	49.4(1)	O(8)$^{\#6}$/La(2)/O(14)	69.6(1)
O(4)$^{\#1}$/La(1)/O(10)$^{\#3}$	97.8(1)	O(2)/La(2)/O(11)$^{\#4}$	75.6(1)	O(9)/La(2)/O(10)	49.4(1)
O(4)$^{\#1}$/La(1)/O(12)$^{\#4}$	138.1(1)	O(2)/La(2)/O(14)	67.7(1)	O(9)/La(2)/O(11)$^{\#4}$	76.9(1)
O(4)$^{\#1}$/La(1)/O(13)	69.7(2)	O(3)$^{\#5}$/La(2)/O(5)	82.4(1)	O(9)/La(2)/O(14)	82.3(1)
O(5)/La(1)/O(7)$^{\#2}$	72.44(9)	O(3)$^{\#5}$/La(2)/O(6)	76.8(1)	O(10)/La(2)/O(11)$^{\#4}$	76.7(1)
O(5)/La(1)/O(8)$^{\#2}$	118.85(9)	O(3)$^{\#5}$/La(2)/O(8)$^{\#6}$	73.1(1)	O(10)/La(2)/O(14)	113.7(1)
O(5)/La(1)/O(10)$^{\#3}$	169.7(1)	O(3)$^{\#5}$/La(2)/O(9)	119.0(1)	O(11)$^{\#4}$/La(2)/O(14)	140.1(1)

Hydrogen bonding contacts

D–H	d(D–H)	d(H···A)	∠(D–H···A)	d(D–H···A)	A
O(13)–H(13)A	0.62	2.37	139	2.858	O(11)$^{\#9}$
O(13)–H(13)B	0.76	2.16	162	2.892	O(3)
O(14)–H(14)A	0.71	2.27	147	2.893	O(7)
O(14)–H(14)B	0.79	2.28	145	2.966	O(1)

Symmetry codes used are: $\#1 = x, y, z+1$; $\#2 = -x+1, -y+2, z+2$; $\#3 = x-1, y, z$; $\#4 = -x+1, -y+1, -z$; $\#5 = x+1, y, z+1$; $\#6 = -x+2, -y+2, -z+2$; $\#7 = x, y, z-1$; $\#8 = x-1, y, z$; $\#9 = x+1, y, z$ (identical with figure 1).

3. Results and discussion

3.1. *Synthesis and IR spectrum*

Hydrothermal reaction of $LaCl_3 \cdot nH_2O$, suberic acid and NaOH in H_2O at pH = 7.8 yielded $La_2(H_2O)_2(C_8H_{12}O_4)_3$ at 170°C. The IR spectrum displays two strong sharp bands at 1551 and 1423 cm^{-1}, respectively, due to the asymmetric and symmetric $-CO_2$ stretching vibrations of the carboxylate groups. A broad band centred at 3425 cm^{-1} and a weak absorption at 1634 cm^{-1} could be attributed to the aqua ligands and absorptions at 2932 and 2860 result from the CH_2 groups of the dicarboxylate anions.

3.2. *Thermal analyses*

TG-DTA curves show a first weight loss of 4.7% over 100–250°C with an endothermic processes centred at 193°C, corresponding to the complete dehydration of $La_2(H_2O)_2(C_8H_{12}O_4)_3$ (Calcd 4.3% for two moles of H_2O). Since the TG curve indicates no significant variation in weight on heating upto 340°C, a weak endothermic peak at 327°C suggests that the initially formed anhydrous lanthanum suberate undergoes rearrangement. Significant weight loss of 57.9% at 340–550°C with three endothermic peaks at 360, 400 and 490°C, respectively, is very close to the calculated value of 56.4% for liberation of three moles of suberic anhydride per formula unit. The white residue was identified as La_2O_3 by powder X-ray diffraction.

3.3. *X-ray structure*

The asymmetric unit consists of two La^{3+} cations (La(1) and La(2)), three suberate anions (L(1), L(2) and L(3)) and two water molecules. As shown in figure 1, both La atoms are similarly sited in significantly distorted, mono-capped, square antiprisms (LaO_9), bonded to nine oxygen atoms from six suberate anions and one water molecule at the cap. (LaO_9) coordination polyhedra are edge-shared through two carboxylate oxygen atoms (O(2) and O(5); O(8) and O(10)) of different suberate anions to generate infinite lanthanum oxide chains extending in the [1 0 0] direction (figure 2). The resulting chains are further connected by the dicarboxylate anions to form a 3D framework, which could be described as inorganic layers of lanthanum oxide chains pillared by organic spacers (figure 2). In contrast to reported lanthanide dicarboxylates with porous 3D frameworks [13, 23, 29], the suberato ligands in this case are so arranged that no apparent porosity can be observed. The structure is stabilized by interchain hydrogen bonding interactions between the coordinated water and carboxylate oxygen atoms with $d(O \cdots O) = 2.858–2.966$ Å (figure 2, table 2). La–O bond distances lie in the range 2.475–2.666 Å and are comparable with those observed in a lanthanum adipate $[La_2(C_6H_8O_4)_3(H_2O)_4] \cdot 6H_2O$, where the edge-shared dinuclear (La_2O_{16}) units of the (LaO_9) polyhedra are interconnected by adipato ligands to form a 3D porous framework with lattice H_2O molecules in tunnels [27]. To the best of our knowledge, the present complex is the first suberato-bridged lanthanide coordination polymer. The structure is similar to a very recently reported Eu adipate compound $[Eu_2(C_6H_8O_4)_3(H_2O)] \cdot H_2O$, where alternating ($EuO_8$) and ($EuO_9$) polyhedra are edge-shared to create 1D chains, which complete a 3D framework through bridging adipato ligands [28].

Of the three crystallographically distinct suberate anions, two dicarboxylate anions, L(1) and L(3), exhibit similar coordination modes, being bound to four La atoms with one terminal carboxylate group bidentately bridging two metal atoms in *syn-anti* fashion and the other end chelating one metal atom with a chelating oxygen atom bonded to an additional metal atom (figure 1). The third suberate anion L(2) bridges four La atoms in such a way that every carboxylate chelates one La atom with one oxygen additionally coordinating a second metal atom (figure 1). Such coordination of suberate anions has not been reported in the literature. For example, suberate anions in $\{[Mn(phen)_2(H_2O)]_2(C_8H_{12}O_4)\}\{[Mn(phen)_2(C_8H_{12}O_4)]_2L \cdot 4H_2O$ [32], $Ni(H_2O)_4(C_8H_{12}O_4)$ [33] and $Cd(H_2O)_2(C_8H_{12}O_4)$ [34] bismonodentately bridge metal atoms into 1D polymeric chains. In $[Cu_2(phen)_2(C_8H_{12}O_4)_2] \cdot 3H_2O$, the carboxylate group of the tridentate suberate anion monoatomically coordinates one Cu atom or bridges two metal atoms [35]. Suberate anions in $Co(H_2O)_2(C_8H_{12}O_4)$ link three Co atoms with the carboxylate groups chelating one metal atom and bisatomically bridging two metal atoms [36]. The bisbidentate suberate anions in $Zn(C_8H_{12}O_4)$ interlink

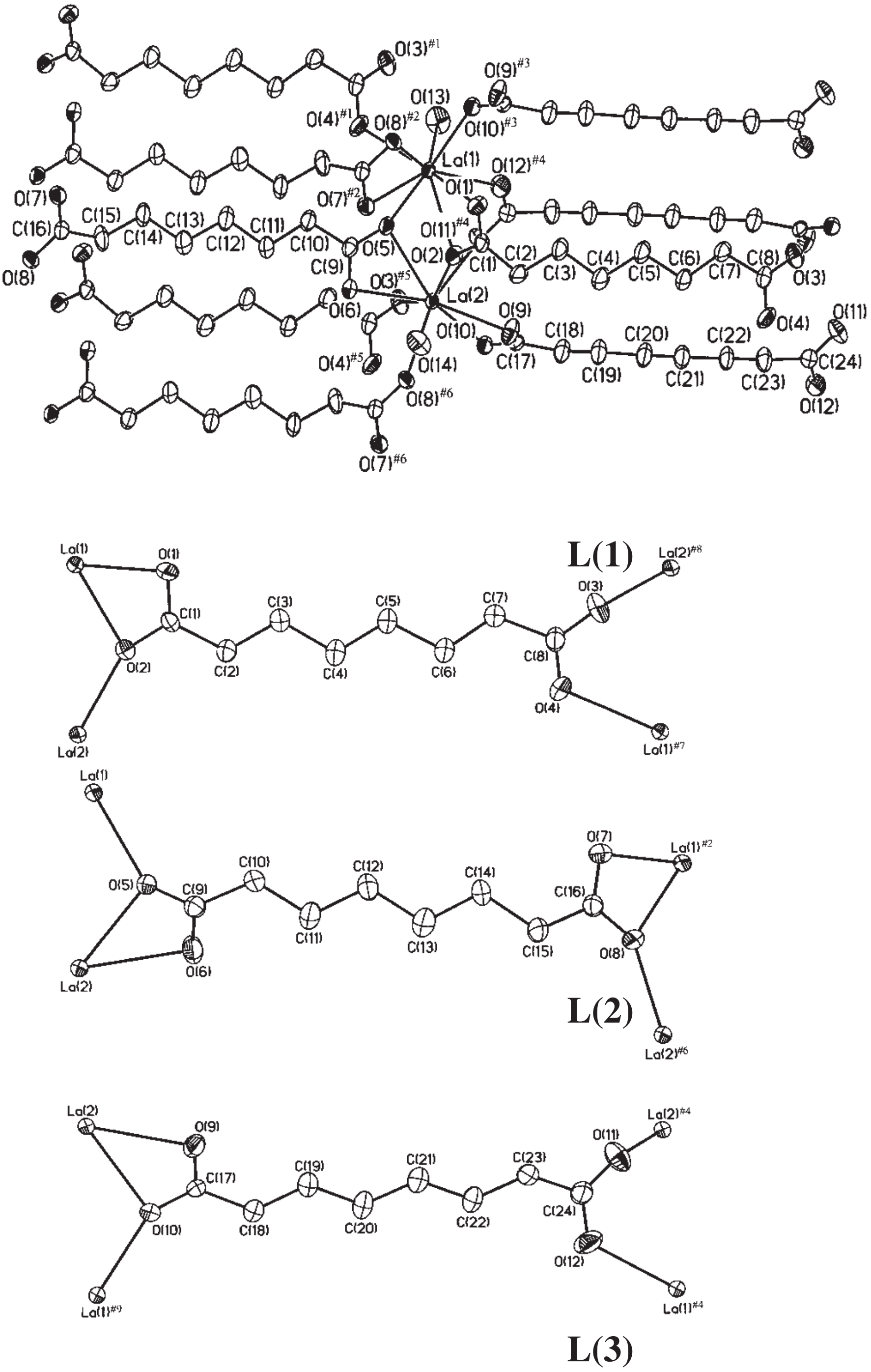

Figure 1. The coordination environments of the lanthanum atoms and the bridging modes of suberate anions along with the atomic labelling scheme for the complex. Displacement ellipsoids are drawn at the 45% probability level (for symmetry codes see table 2).

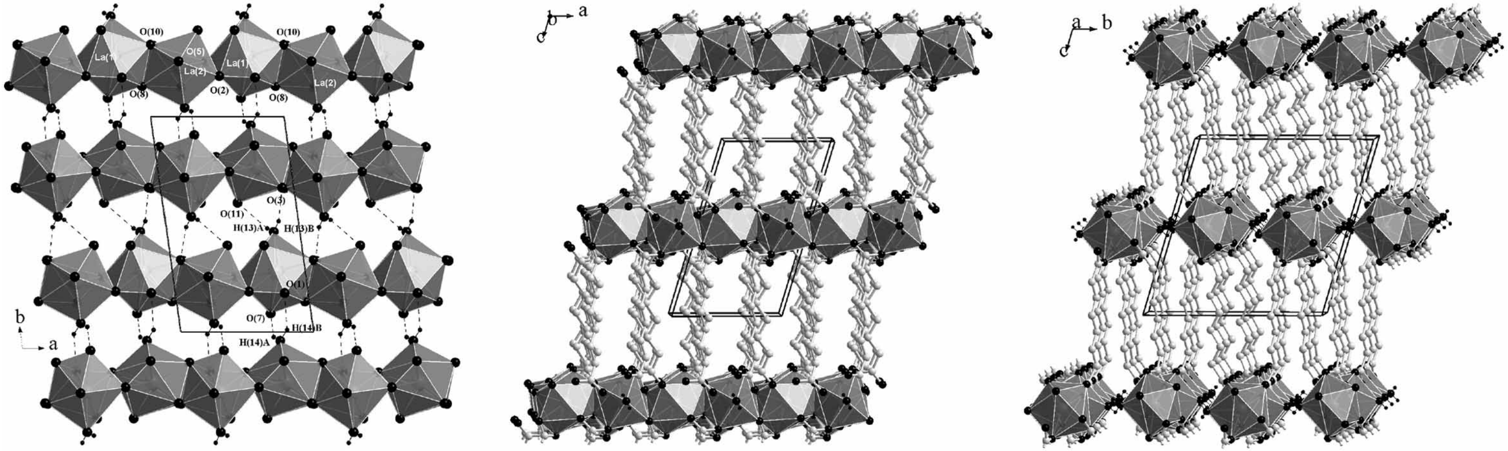

Figure 2. The edge-shared lanthanum oxide chains with hydrogen bonds indicated as dashed lines and perspective views of crystal structure of **1**.

metal atoms to afford a 3D network [37]. As far as the suberate anions in $Mn_2(H_2O)(C_8H_{12}O_4)_2$ are concerned, three carboxylate oxygen atoms each coordinate one Mn atom and the fourth bridges two metal atoms [12a].

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with Cambridge Crystallographic Data Centre as supplementary publication CCDC 267523. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, or email: deposit@ccdc.cam.ac.uk).

Acknowledgements

The project was supported by the State Basic Research Project of China scheme (2003CCA00800), the Zhejiang Provincial Natural Science Foundation (Z203067) and the Ningbo Municipal Science Foundation (2003A62011, 2003A61014, 2003A62026).

References

[1] L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko. *J. Am. Chem. Soc.*, **125**, 3062 (2003) and references therein.
[2] S.R. Batten. *Curr. Op. Solid State Mater. Sci.*, **5**, 107 (2001).
[3] O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002).
[4] G.R. Desiraju. *J. Mol. Struct.*, **656**, 5 (2003).
[5] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi. *Science*, **295**, 469 (2002).
[6] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi. *Nature*, **402**, 276 (1999).
[7] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. William. *Science*, **283**, 1148 (1999).
[8] (a) A. Michaelides, S. Skoulika, V. Kiritsis, A. Aubry. *J. Chem. Soc., Chem. Commun.*, 1415 (1995); (b) A. Michaelides, V. Kiritsis, S. Skoulika, A. Aubry. *Angew. Chem. Int. Ed. Engl.*, **32**, 1495 (1993).
[9] (a) E. Lee, Y. Kim, D.-Y. Jung. *Inorg. Chem.*, **41**, 501 (2002); (b) Y. Kim, E. Lee, D.-Y. Jung. *Chem. Mater.*, **13**, 2684 (2001); (c) Y. Kim, D.-Y. Jung. *Bull. Korean Chem. Soc.*, **21**, 656 (2000); (d) Y. Kim, D.-Y. Jung. *Inorg. Chem.*, **39**, 1470 (2000).
[10] (a) C. Livage, C. Egger, M. Nogues, G. Férey. *C. R. Acad. Sci. Paris, Chim./Chem.*, **4**, 221 (2002); (b) C. Livage, C. Egger, G. Férey. *Chem. Mater.*, **13**, 410 (2001); (c) C. Livage, C. Egger, G. Férey. *Chem. Mater.*, **11**, 1546 (1999).
[11] (a) P.M. Forster, A.K. Cheetham. *Angew. Chem. Int. Ed. Engl.*, **41**, 457 (2002); (b) P.M. Forster, P.M. Thomas, A.K. Cheetham. *Chem. Mater.*, **14**, 17 (2002).
[12] (a) Y.-Q. Zheng, Z.-P. Kong. *J. Solid State Chem.*, **166**, 279 (2002); (b) Y.-Q. Zheng, J. Sun. *J. Solid State Chem.*, **172**, 288 (2003).
[13] A. Dimos, D. Tsaousis, A. Michaelides, S. Skoulika, S. Golhen, L. Ouahab, C. Didierjean, A. Aubry. *Chem. Mater.*, **14**, 2616 (2002).
[14] (a) E. Hansson. *Acta Chem. Scand.*, **27**, 2441 (1973); (b) E. Hansson. *Acta Chem. Scand.*, **27**, 2813 (1973); (c) E. Hansson. *Acta Chem. Scand.*, **27**, 2827 (1973).
[15] W. Xue, Q. Wang, L. Yan, R. Yang. *Polyhedron*, **11**, 2051 (1992).
[16] F. Marrot, J.-C. Trombe. *Polyhedron*, **12**, 1931 (1994).
[17] B. Benmerad, A. Guehria-Laidoudi, F. Balegroune, H. Birkedal, G. Chapuis. *Acta Cryst.*, **C56**, 789 (2000).
[18] M. Hernández-Molina, P.A. Lorenzo-Luis, T. Loópez, C. Ruiz-Pérez, F. Lloretd, M. Julve. *Cryst. Eng. Comm.*, **31**, 1 (2000).
[19] B. Benmerad, A. Guehria-Laidoudi, G. Bernardinelli, F. Balegroune. *Acta Cryst.*, **C56**, 321 (2000).

[20] F. Marrot, J.C. Trombe. *C. R. Acad. Sci.*, **317**, 319 (1993).

[21] F. Serpaggi, T. Luxbacher, A.K. Cheetham, G. Férey. *J. Solid State Chem.*, **145**, 580 (1999).

[22] M. Fleck. *Z. Kristallogr.*, **NCS 217**, 569 (2002).

[23] F. Serpaggi, G. Férey. *Micro. Meso. Mater.*, **32**, 311 (1999).

[24] F. Serpaggi, G. Férey. *J. Mater. Chem.*, **8**, 2737 (1998).

[25] T. Glowiak, J. Legendziewicz, C.N. Dao, E. Huskowska. *J. Less-Comm. Met.*, **134**, 153 (1987).

[26] T. Glowiak, C.N. Dao, J. Legendziewicz. *Acta Cryst.*, **C42**, 1494 (1986).

[27] V. Kiritsis, A. Michaelides, S. Skoulika, S. Golhen, L. Ouahab. *Inorg. Chem.*, **37**, 3407 (1998).

[28] Y. Kim, M. Suh, D.-Y. Jung. *Inorg. Chem.*, **43**, 245 (2004).

[29] Z.-G. Sun, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng. *Inorg. Chem. Comm.*, **5**, 629 (2002).

[30] G.M. Sheldrick. *SHELXS-97. Programm zur Lösung von Kristallstrukturen*, University of Göttingen, Germany (1997).

[31] G.M. Sheldrick. *SHELXL-97. Programm zur Verfeinerung von Kristallstrukturen*, University of Göttingen, Germany (1997).

[32] M.T. Casey, M. McCann, M. Devereux, M. Curran, C. Cardin, M. Convery, V. Quillet, C. Hardivy. *J. Chem. Soc., Chem. Commun.*, 2643 (1994).

[33] B.-S. Zhang, Y.-Q. Zheng. *Z. Kristallogr.*, **NCS 218**, 231 (2003).

[34] J. Sun, Y.-Q. Zheng. *Z. Anorg. Allg. Chem.*, **629**, 1001 (2003).

[35] Y.-Q. Zheng, J.-L. Lin, J. Sun. *Z. Anorg. Allg. Chem.*, **627**, 1993 (2001).

[36] Y.-Q. Zheng, J.-L. Lin, J. Sun, A.-Y. Pan. *Z. Kristallogr.*, **NCS 215**, 161 (2000).

[37] Y.-Q. Zheng, A.-Y. Pan, J.-L. Lin. *Z. Kristallogr.*, **NCS 216**, 267 (2001).