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Crystal structure of lanthanum(III) butyrate monohydrate☆

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Abstract

Single crystals of lanthanum butyrate monohydrate were obtained by reaction between lanthanum hydroxide and an aqueous butyric acid solution. The crystal structure (triclinic $P\bar{1}$, $Z=2$, $a=9.940(2)$ Å, $b=12.182(2)$ Å, $c=14.652(2)$ Å, $\alpha=85.98(3)°$, $\beta=75.62(3)°$, $\gamma=78.17(2)°$) consists of layers parallel to (001). The alkyl chains are in an *all-trans* conformation parallel to (110). The layers are constructed by lanthanum chains, which are connected to one another by bridging bidentate carboxylates.

Keywords: X-ray diffraction; Crystal structure and symmetry; Lanthanides; Rare earths; Metal soaps

1. Introduction

The structural chemistry of metal carboxylates is quite fascinating, because carboxylate groups can coordinate in different ways to the central metal ion [1]. In the past, many studies on the crystal structure of rare-earth carboxylates have been reported. The structure of the hydrated rare-earth acetates $Ln(CH_3COO)_3 \cdot xH_2O$ ($x=1$, 1.5, 3, 4) is well-known [2]. In all these crystals, the acetate groups are bridging two rare-earth ions, either forming dimers ($x=3$, 4), chains ($x=1$) or a mixture of both ($x=1.5$). Besides these structural features, coordinating water molecules are incorporated in the crystal structure. The coordination numbers of the rare-earth ions are 9 or 10.

Hardly any crystal structure of the higher homologues of the lanthanide alkanoates is available. Nabar and Barve determined the structural parameters of lanthanide(III) butyrate dihydrate, $Ln(CH_3CH_2CH_2COO)_3 \cdot 2H_2O$ (Ln= Nd, Tb, Er, Tm, Yb and Y) by X-ray powder diffraction and found that they have a monoclinic symmetry with space group $P2_1/m$ ($Z=4$) [3]. To our knowledge, the only crystal structure which has been described is that of praseodymium(III) propionate trihydrate, $Pr(CH_3CH_2COO)_3 \cdot 3H_2O$ [4]. The crystal structure consists of chains parallel to [100]. Two crystallographically different praseodymium ions are coordinated by four bidentate bridging propionate groups. Additionally, Pr1 is coordinated by three water molecules and Pr2 by two bidentate propionate groups. It can be expected that by increasing the length of the alkyl chain of the lanthanide alkanoates, other structural types can be obtained. Indeed, the longer the alkyl chain, the more the structural characteristics are determined by these chains. X-ray powder diffraction of the lanthanide alkanoates with long alkyl chains (also called *lanthanide soaps*) shows that these compounds have a lamellar bilayer structure [5–10].

In this paper, we report on the single-crystal X-ray structure of lanthanum(III) butyrate monohydrate, $La(CH_3CH_2CH_2COO)_3 \cdot H_2O$.

2. Experimental

La(III) butyrate was prepared by reaction between La(III) hydroxide and butyric acid. Pure $La(OH)_3$ was obtained through hydrothermal synthesis. Lanthanum nitrate hexahydrate, $La(NO_3)_3 \cdot 6H_2O$, (1.00 g, 2.28 mmol) and NaOH (3.00 g, 25 mmol) were dissolved in water (15 ml), and the resulting solution was heated in a teflon bomb for 4 days at 220°C. Afterward, the solution was left to slowly cool down to room temperature, at a cooling rate of 4°C/h. Crystalline $La(OH)_3$ was obtained and its purity was checked by X-ray powder diffraction. The pure hydroxide was dissolved in diluted butyric acid (butyric acid:water 1:1). Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solution in air.

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The transparent crystals were lath-like and colourless. The purity was checked on a CE Instruments EA-110 elemental analyser. Calculated: C: 34.46%, H: 5.54%. Experimental: C: 34.84%, H: 5.59%.

Intensities of a small crystal of lanthanum butyrate monohydrate (0.15×0.04×0.75 mm) were measured with an image plate diffractometer (IPDS, Stoe) at 293 K. Data acquisition: Mo-Kα (graphite monochromator, λ=0.7107 Å), θ_{max}=26.00°, φ=0–250°, $\Delta\varphi$=2°, 125 images, 13 367 measured reflections, 6178 unique (R_{int}=0.1938). Data processing: program systems SHELXS-97 and SHELXL-97 [11,12], scattering factors according to the International Tables, Volume C [13]. Reliability factors: R_1/wR_2 (6178 reflections with $I_0 > 2\sigma(I)$): 0.0736/0.1687, R_1/wR_2 (all data): 0.1997/0.2098. Goodness-of-fit on F^2: 0.745. Figures of crystal structures were drawn using the graphical software Diamond Version 2.1.

3. Crystal structure of lanthanum(III) butyrate monohydrate

Lanthanum butyrate monohydrate, $La(C_3H_7COO)_3 \cdot H_2O$, crystallises in the triclinic space group *P1* (no. 2). In the crystal structure, two crystallographically different lanthanum ions are present, both having coordination number 9. The coordination polyhedra can be described as monocapped square antiprisms (Fig. 1). La1 is surrounded by two water molecules and by five carboxylate groups.

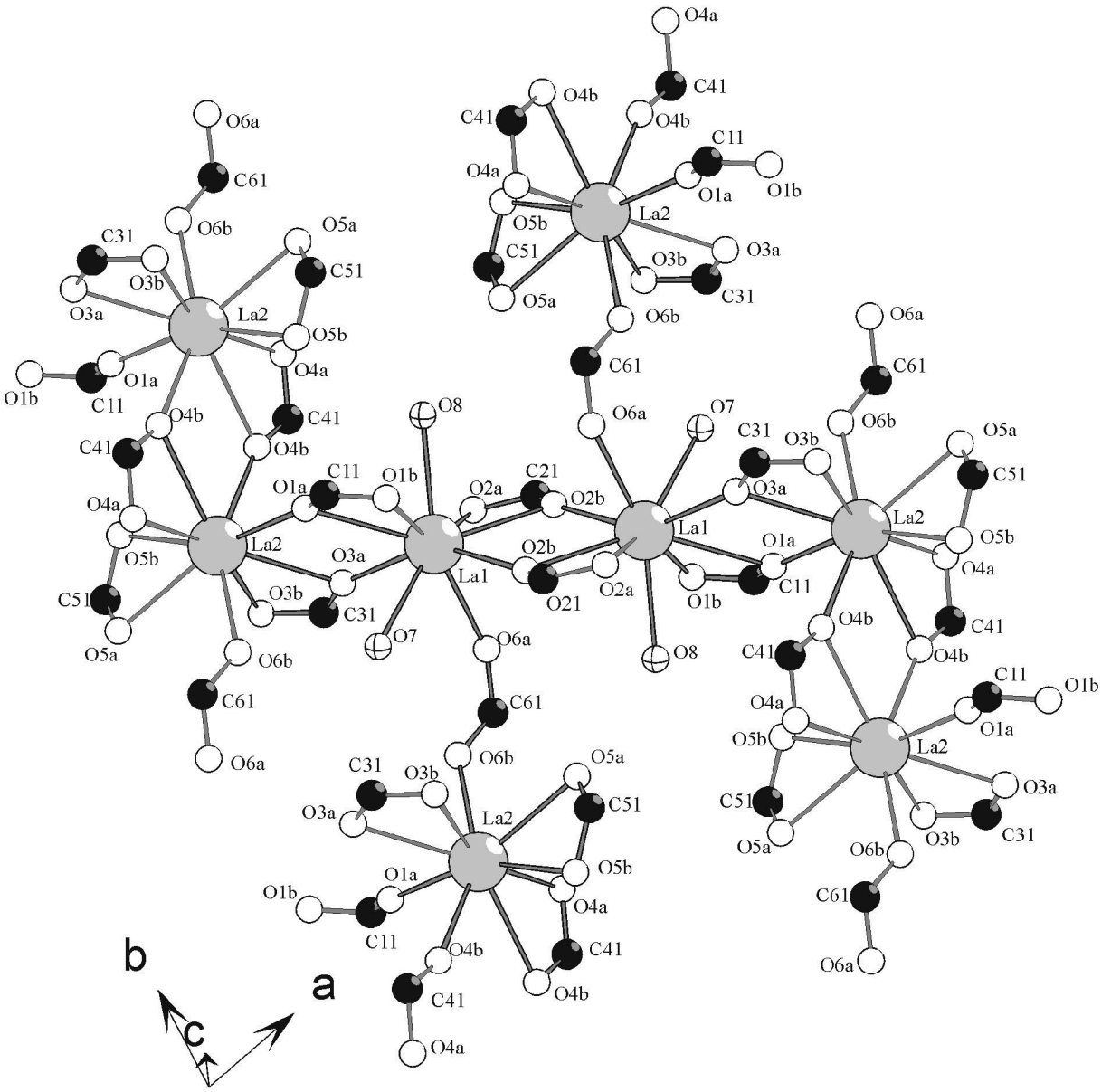

Fig. 1. Drawings of the coordination sphere of La1 and La2 in lanthanum(III) butyrate monohydrate.

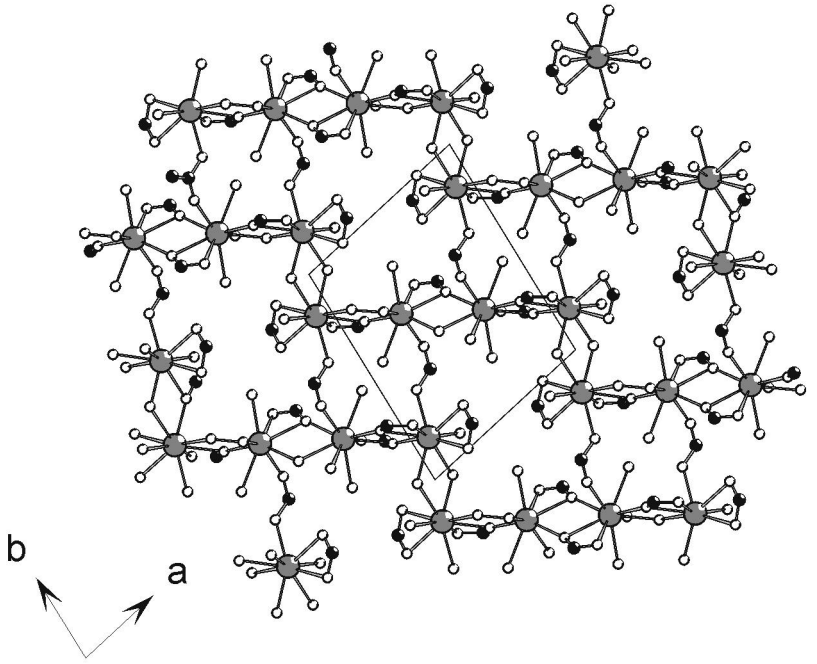

Fig. 2. Zigzag chains of lanthanum(III) ions in lanthanum(III) butyrate monohydrate.

Four of these carboxylate groups are bridging tridentate and one is *Z*,*E*-type bridging bidentate. La2 is coordinated by four bridging tridentate carboxylates, one *Z*,*E*-type bridging bidentate carboxylate group and one chelating-type bidentate. The coordination polyhedra are connected via common edges to zigzag chains (Fig. 2). These common edges consist of two oxygen atoms, each belonging to a bridging tridentate carboxylate group. In the bridging tridentate carboxylate groups, one of the oxygen atoms is bound to two lanthanum atoms, whereas the

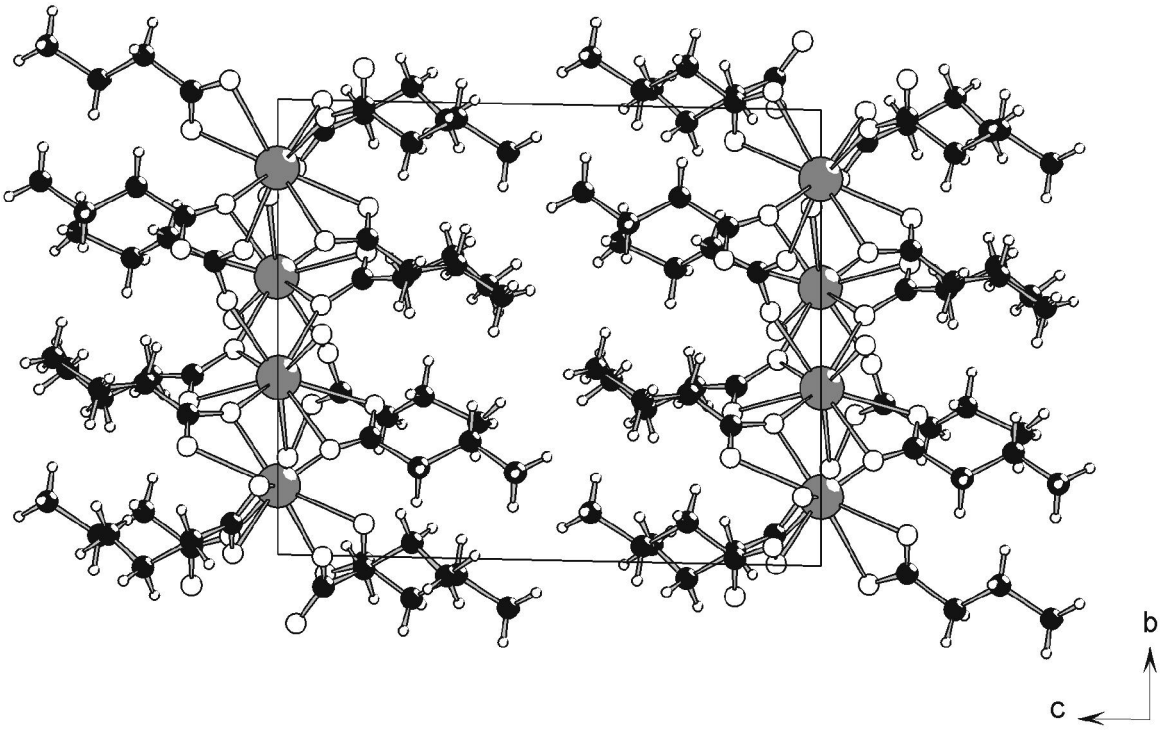

Fig. 3. Crystal structure of lanthanum(III) butyrate monohydrate viewed down the *a* axis.

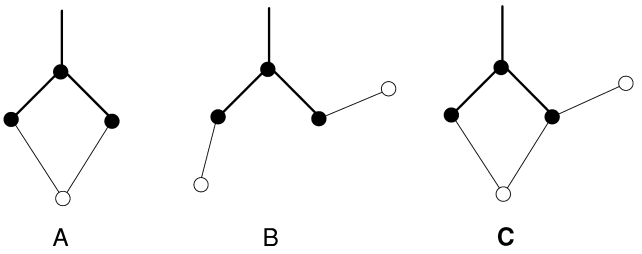

Fig. 4. Schematic representation of coordination modes of carboxylate groups in lanthanum(III) butyrate monohydrate (according to Ouchi et al. [14]). (A) Chelating-type bidentate; (B) *Z,E*-type bridging bidentate; (C) bridging tridentate. Open circles represent lanthanum ions, the black circles represent the carboxylate group COO^-.

second oxygen atom is bound directly to only one lanthanum atom. Such a bridging tridentate coordination of carboxylate groups is discussed by Ouchi et al. [14]. The chains are connected to one another by *Z,E*-type bridging bidentate carboxylate groups. The alkyl chains of the butyrate groups are in an all-*trans* conformation (Fig. 3). The different types of carboxylate coordination are schematically represented in Fig. 4.

The temperature factors of the ending methyl groups are relatively large, which is due to a strong disorder of the ends of the alkyl chains. The large *R*-values of the structure can be explained by the fact that it is very difficult to obtain very good crystals of layered structures for structure analysis. Crystallographic information and data collection parameters for lanthanum(III) butyrate monohydrate are summarised in Table 1 and in Section 2. The atomic coordinates are listed in Table 2, selected bond lengths and angles are included in Table 3.

The layer-like structure of $La(C_3H_7COO)_3 \cdot H_2O$ contrasts to the infinite chains of $Pr(CH_3CH_2COO)_3 \cdot H_2O$ [4]. The alkyl chains of the propionate groups are not long enough to force themselves to a parallel alignment in layers. The butyrate compounds are thus the first members in the series of lanthanide(III) alkanoates with the typical bilayer structure of metal soaps [5–10].

Table 1
Summary of crystallographic data for lanthanum(III) butyrate monohydrate

Empirical formula	$C_{24}H_{42}La_2O_{14}$
F_w	832.40
Space group (no.)	$P\bar{1}$ (2)
Unit cell dimensions (Å, deg)	$a = 9.940(2)$
	$b = 12.182(2)$
	$c = 14.652(4)$
	$\alpha = 85.98(3)$
	$\beta = 75.62(3)$
	$\gamma = 78.17(2)$
V (Å^3)	1681.7(7)
Z	2
D (g cm^{-1})	1.643
T (K)	293(2)
λ (Å)	0.7107 (Mo-Kα graphite monochromator)
θ limits (deg)	2.48–26.00
μ (mm^{-1})	2.391
No. of parameters	356
$F(000)$	824
Reflections collected/unique	13 367/6178 [$R_{int} = 0.1938$]
Goodness-of-fit on F^2	0.745
Final R indices [$I_0 > 2\sigma(I_0)$]	$R_1 = 0.0736$, $wR_2 = 0.1687$
R indices (all data)	$R_1 = 0.1997$, $wR_2 = 0.2098$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å^2)

Atom	x	y	z	U_{eq} [a]
La(1)	3037(2)	6112(1)	16(1)	33(1)
La(2)	9128(1)	8492(1)	1(1)	33(1)
O(1A)	10935(12)	7669(10)	961(11)	35(4)
O(1B)	2306(15)	6673(12)	1784(10)	46(4)
O(2A)	4462(14)	6678(13)	−1634(11)	49(4)
O(2B)	5724(16)	5512(12)	−800(11)	45(4)
O(3A)	1160(16)	6908(12)	−875(10)	41(4)
O(3B)	9552(19)	7670(13)	−1667(13)	64(5)
O(4A)	7561(14)	9290(10)	1582(11)	48(4)
O(4B)	10932(15)	9611(12)	−882(10)	42(4)
O(5A)	6654(13)	8501(11)	−341(12)	49(4)
O(5B)	7626(13)	9984(12)	−828(11)	44(4)
O(6A)	3162(18)	4438(12)	−932(13)	63(5)
O(6B)	8396(14)	6686(13)	630(13)	61(5)
O(7)	859(15)	5156(11)	808(11)	43(4)
O(8)	4014(15)	7865(13)	173(14)	73(6)
C(11)	1220(2)	7388(18)	1711(14)	33(5)
C(12)	310(3)	8020(2)	2595(17)	62(7)
C(13)	640(4)	7430(4)	3540(2)	120(15)
C(14)	−330(7)	8090(5)	4370(3)	240(4)
C(21)	5590(2)	6100(2)	−1557(14)	42(6)
C(22)	6940(3)	6130(3)	−2314(19)	81(9)
C(23)	6710(4)	6640(3)	−3220(3)	99(11)
C(24)	6460(9)	6020(6)	−3860(4)	300(5)
C(31)	10720(2)	6965(18)	−1648(15)	35(5)
C(32)	11540(2)	6300(2)	−2432(15)	51(6)
C(33)	10900(3)	6440(3)	−3270(2)	111(15)
C(34)	11800(4)	5780(3)	−4130(2)	122(15)
C(41)	11830(2)	9869(18)	−1581(15)	43(5)
C(42)	12300(3)	9104(17)	−2460(15)	51(7)
C(43)	13220(3)	9650(3)	−3286(18)	93(12)
C(44)	13460(4)	8930(3)	−4230(2)	92(10)
C(51)	6740(2)	9331(17)	−850(19)	46(7)
C(52)	5730(3)	9720(2)	−1581(14)	53(7)
C(53)	6500(3)	10330(2)	−2470(2)	76(8)
C(54)	7730(4)	9620(3)	−3100(3)	115(13)
C(61)	7188(19)	6417(16)	1158(16)	39(5)
C(62)	6500(4)	6930(2)	2010(2)	105(14)
C(63)	5630(6)	6460(4)	2680(2)	180(2)
C(64)	5080(4)	7010(4)	3690(2)	119(14)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U_{ij}}$ tensor [15].

4. Conclusion

A single-crystal X-ray diffraction study of lanthanum butyrate monohydrate shows the presence of two crystallographically different lanthanum ions, both with coordination number 9 and a geometry which can be considered as a distorted monocapped squared antiprism. The alkyl

Table 3
Selected bond lengths (Å) and angles (deg) for lanthanum(III) butyrate monohydrate

Bridging tridentate carboxylates			
La(1)–O(1b)	2.611(14)	O(1b)–C(11)	1.26(2)
La(1)–O(2a)	2.606(15)	O(2a)–C(21)	1.22(2)
La(1)–O(2b)	2.477(16)	O(2b)–C(21)	1.30(3)
La(1)–O(2b)	2.615(15)	O(3a)–C(31)	1.31(2)
La(1)–O(3a)	2.533(16)	O(3b)–C(31)	1.30(3)
La(2)–O(1a)	2.556(13)	O(4a)–C(41)	1.29(2)
La(2)–O(3a)	2.629(15)	O(4b)–C(41)	1.25(2)
La(2)–O(3b)	2.610(18)		
La(2)–O(4a)	2.577(14)		
La(2)–O(4b)	2.520(14)		
La(2)–O(4b)	2.708(14)		
O(1a)–C(11)–O(1b)	122.8(19)		
O(2a)–C(21)–O(2b)	122.3(18)		
O(3a)–C(31)–O(3b)	116.9(19)		
O(4a)–C(41)–O(4b)	122.3(19)		
Chelating bidentate carboxylate			
La(2)–O(5a)	2.626(11)	O(5a)–C(51)	1.22(3)
La(2)–O(5b)	2.547(15)	O(5b)–C(51)	1.31(2)
O(5a)–C(51)–O(5b)	122(2)		
Bridging bidentate carboxylates			
La(1)–O(6a)	2.512(14)	O(6a)–C(61)	1.25(2)
La(2)–O(6b)	2.502(15)	O(6b)–C(61)	1.35(2)
O(6a)–C(61)–O(6b)	117.0(19)		
Coordinated water			
La(1)–O(7)	2.643(13)		
La(1)–O(8)	2.566(13)		

chains of the carboxylate groups are in the all-*trans* conformation, giving rise to a layer-like structure.

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