

Characterization and structural study of lanthanum citrate trihydrate [La(C₆H₅O₇)(H₂O)₂] · H₂O

G. Vanhoyland^{a,*}, J. Pagnaer^a, J. D'Haen^b, S. Mullens^c, J. Mullens^a

^aLaboratory of Inorganic and Physical Chemistry, IMO, Limburgs Universitair Centrum, B-3590 Diepenbeek, Belgium

^bIMEC VZW, division IMOMECE, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

^cVITO NV, Boeretang 200, B-2400 Mol, Belgium

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Abstract

[La(C₆H₅O₇)(H₂O)₂] · H₂O was synthesized as precursor material for an aqueous solution–gel route to La-containing multimetal oxides. The compound was characterized by means of FTIR, TGA and pycnometry. The crystallographic structure was solved from powder diffraction data. The symmetry is monoclinic [$a = 17.097(3) \text{ \AA}$, $b = 9.765(2) \text{ \AA}$, $c = 6.3166(8) \text{ \AA}$ and $\beta = 90.42(1)^\circ$, $Z_{\text{exp}} = 3.96$] with space group $P2_1/n$ (14). Direct methods were applied and the model was subsequently least-squares refined ($R_B = 5.1\%$ and $R_{\text{wp}} = 12.0\%$). La³⁺ is nine-fold coordinated, the LaO₉ forming a mono-capped square antiprism. The basic unit is a binuclear entity of two LaO₉ polyhedra having one edge in common. These units are connected along the c -axis through citrate molecules. The carboxylate groups of the citrate are coordinated to La³⁺ in monodentate, bidentate and bridging way. Also the alkoxide group, which carries the proton, is coordinated to La³⁺. Two water molecules complete the coordination sphere, while the third one can be found inbetween the La³⁺-citrate network.

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1. Introduction

Over the years, a lot of research has been spent into complexing ligands as for example tartrate, acetate and citrate for their use in chemical synthesis routes, as well as to understand their behavior in biological systems [1]. Citric acid (CitH₃), being a polybasic acid, can take various deprotonated appearances (CitH₂⁻, CitH²⁻, Cit³⁻) in solution, all depending on pH. These carboxylates are known to form stable coordination complexes with various metal ions, often because of chelate formation. These stable metal precursor solutions can be used for the preparation of homogeneous multimetal gels through evaporation of the solvent. This results in a quick increase in viscosity, which decreases

the diffusion of complexes and thus prevents phase segregation. This type of solution–gel route, especially using water as solvent, has been used successfully in the synthesis of several functional multimetallic oxides as for example (La_{1-x}Sr_x)CoO₃ [2], (Bi,La)₄Ti₃O₁₂ [3], etc. In the framework of this research, lanthanum citrate trihydrate is an intermediate in the preparation of a suitable lanthanum precursor. Although extensive literature exists concerning various lanthanum-carboxylate compounds [4–6], the knowledge about lanthanum–citrate compounds in particular is rather limited. Babeshkina et al. [7] pointed out that the water content of lanthanum citrate is heavily depending on the synthesis route. Devi et al. [8] studied the thermal decomposition of a lanthanum citrate hydrate containing 4 water molecules. Milanova et al. [9] published an NMR study of mixed lanthanum-titanium citrate complexes. The aim of this study is to fully characterize

*Corresponding author. Fax: +320 11 26 88 99.

E-mail address: geert.vanhoyland@luc.ac.be (G. Vanhoyland).

the title compound and discuss the results in relation to its crystal structure. For this purpose, the compound was characterized by means of thermal analysis techniques as well as FTIR, while the crystal structure was elucidated using powder diffractometry. At the same time, this study also illustrates the significant advances made in the field of powder diffractometry, which has become a mature technique for detailed structural research.

2. Experimental

For the synthesis of the title compound, the following materials and reagents were used: citric acid (Aldrich 99%) and lanthanum oxide (Alfa Aesar, 99.99%). A suspension of 4.100 g La_2O_3 in 30 mL water was prepared, to which 4.836 g of citric acid was added. Stirring this mixture at 120 °C for 4 h and ageing at 60 °C for 24 h resulted in a white powder. After washing thoroughly with water, this powder was dried at 100 °C in an air-flushed furnace.

An infrared spectrum (4000–400 cm^{-1}) was recorded with a Bruker IFS66 spectrometer by mixing 1 wt% of the powder with KBr. TGA measurements (TA-Instruments, model 951-2000) were carried out at a heating rate of 10 °C/min in air. The density of the powder was measured using nitrogen adsorption (Nova 3000, Quantochrome, USA). The powder was outgassed in vacuum at room temperature prior to the measurement. X-ray diffraction patterns were collected on a Siemens D5000 diffractometer equipped with a Ge(111) monochromator (monochromatic $\text{CuK}\alpha_1$ radiation; slit configuration: focal slit 0.1 mm, divergence slit 1.0 mm, antiscatter slit 1.0 mm, 2° soller slit, detector slit 0.2 mm). The angular range was from 8° up to 100° 2θ , with a 50 s counting time at each step of 0.02° 2θ . It turned out that the sample preparation was a critical issue. A high-quality diffraction pattern for structure solution was prepared using a backloading technique and sieving through 325 mesh. With conventional sample preparation techniques, a strong ($hk0$) preferred orientation was observed which prevented successful structure solution. At the origin of this behavior is the pronounced needle-shape of the crystallites as can be seen in Fig. 1. This SEM image was made on a Philips SEM-FEG XL30.

3. Results and discussion

3.1. Characterization

From the observed weight loss (between 57.1% and 57.8% for repeated measurements) in the TGA experiment (Fig. 2), one can calculate the molecular weight of

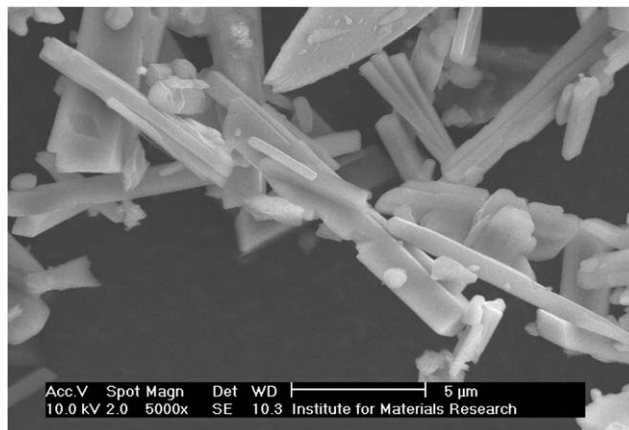


Fig. 1. SEM image.

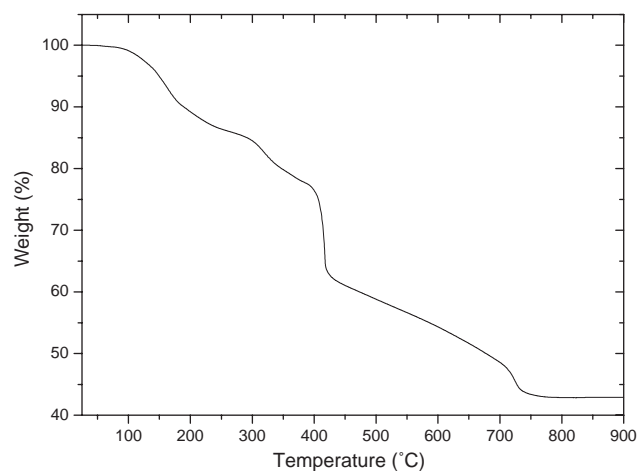


Fig. 2. TGA curve.

the initial compound to be about 380 g/mol. To balance the 3+ charge of the lanthanum ion, the citrate has to be threefold deprotonated. This also means that, within the experimental error, 3 water molecules should be present in the crystal structure in order to arrive at the calculated molecular weight. The first decomposition step up to about 300 °C corresponds to the release of these 3 water molecules (weight loss: theoretical = 14.0%, experimental = 14.5%). In the last decomposition step, $\text{La}_2(\text{CO}_3)_3$ is decomposed into La_2O_3 . Because this last step extends over a large temperature range (400–700 °C), decomposition of the carbonate goes through a series of oxycarbonates, as was also found, e.g. for lanthanum oxalate [10]. Also in Ref. [8] the existence of $\text{La}_2\text{O}_2\text{CO}_3$ was suggested on the basis of IR results.

The diffraction pattern was indexed using Treor97 [11] and Dicol91 [12]. The resulting monoclinic unit cell (Table 1) was subsequently least-squares refined on the basis of 30 diffraction peaks using Pirum [13]. From the systematic absences, the space group $P21/n$ was derived.

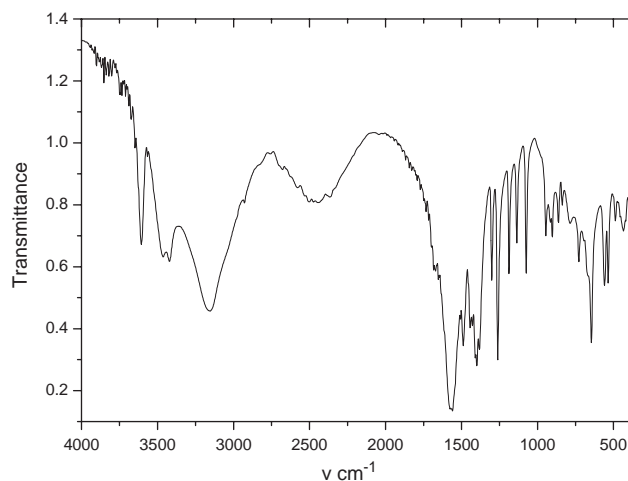


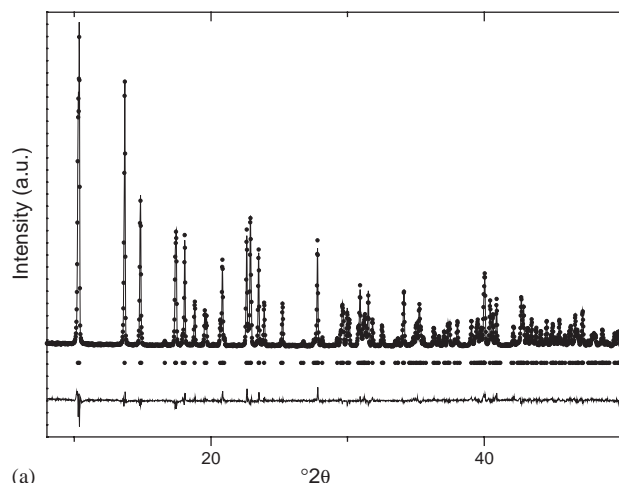
Fig. 3. FTIR spectrum.

Table 1
Experimental information

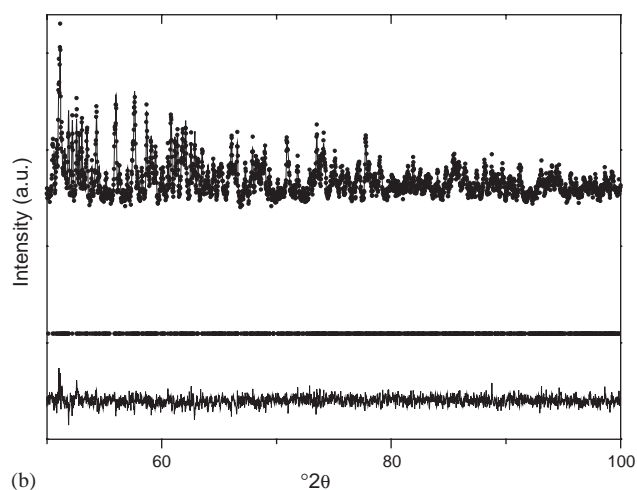
λ	CuK α_1
Chemical formula	[La(C ₆ H ₅ O ₇)(H ₂ O) ₂] · H ₂ O
Formula weight	382.0524 g/mol
Color	White
Space group	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i>	17.097(3) Å
<i>b</i>	9.765(2) Å
<i>c</i>	6.3166(8) Å
β	90.42(1)°
<i>V</i>	1054.5(3) Å ³
<i>M</i> ₂₀	47
<i>F</i> ₃₀	78 (0.0072; 54)
<i>D</i> _{exp}	2.38 g/cm ³
<i>Z</i>	4
<i>R</i> _{wp} ^a	0.120
<i>R</i> _F	0.039
<i>R</i> _B	0.051
Largest difference peak and hole (e Å ⁻³)	+0.42/−0.45

^aBackground corrected.

The experimentally measured density of 2.38 g/cm³ in combination with the unit cell volume yielded *Z* ~ 4, which is an additional indication for the correctness of the proposed solution. The diffraction peak intensities were extracted by means of a Le Bail fit with the program EXPO [14]. The same software was used to apply Direct Methods. One phase set showed a markedly higher figure-of-merit (CFOM = 0.847) compared to all others (CFOM < 0.334). Although some changes were necessary in order to meet the chemical requirements, essentially all non-hydrogen atoms could be assigned. The as-obtained model was subsequently optimized by means of a Rietveld refinement using Fullprof [15]. In order to avoid trapping in local minima, some restraints on the bond distances of the citrate molecule (C–C 1.54 Å, C–O_{carboxylate} 1.27 Å and C–O_{alkoxide} 1.42 Å) were added. Moreover, the isotropic



(a)



(b)

Fig. 4. (a) Rietveld plot (low angle region). (b) Rietveld plot (high angle region, zoomed).

thermal parameters were constrained to be the same for chemically equivalent atomic species (thus: *B*_{C,citrate}, *B*_{O,citrate} and *B*_{O,water}). Because all atoms are in a general position, 55 intensity dependent parameters were refined. Additionally, some profile parameters were refined as well: zero, 3 background parameters, 3 Cagliotti parameters, unit cell parameters, profile parameter for the pseudo-Voigt and 4 asymmetry parameters. These asymmetry parameters were refined separately because of strong correlation. Even then, the asymmetry of the first diffraction peak is not entirely accounted for. Nevertheless, as can be seen in Table 1 and Figs. 4(a) and (b), the refinement converged satisfactorily. The atomic coordinates of the refined model can be found in Table 2 and some derived geometrical data in Table 3.

3.2. Structural

The La³⁺ ion is coordinated by nine oxygen atoms (Fig. 5) in a way that the LaO₉ polyhedron can be

Table 2
Atomic coordinates and isotropic temperature factor

Atom	x	y	z	B_{iso}
La	0.43263(8)	0.1821(2)	0.3845(2)	0.69(4)
C1	0.6033(9)	0.124(2)	0.256(3)	1.6(3)
C2	0.6877(9)	0.068(2)	0.187(3)	1.6(3)
C3	0.3272(9)	0.057(2)	0.960(3)	1.6(3)
C4	0.239(1)	0.084(2)	0.003(3)	1.6(3)
C5	0.2338(8)	0.206(2)	0.174(3)	1.6(3)
C6	0.382(1)	0.176(2)	0.884(3)	1.6(3)
O1	0.5618(7)	0.034(1)	0.368(2)	1.1(1)
O2	0.5720(7)	0.237(1)	0.224(2)	1.1(1)
O3	0.2961(6)	0.250(1)	0.267(2)	1.1(1)
O4	0.6697(6)	0.230(1)	0.694(2)	1.1(1)
O5	0.4331(7)	0.210(1)	0.999(2)	1.1(1)
O6	0.3549(7)	0.213(1)	0.707(2)	1.1(1)
O7	0.6359(7)	0.003(1)	0.852(2)	1.1(1)
Ow1	0.0194(6)	0.212(1)	0.177(2)	0.8(2)
Ow2	0.9324(7)	0.054(1)	0.795(2)	0.8(2)
Ow3	0.1301(6)	0.011(1)	0.574(2)	0.8(2)

Table 3
bond lengths (Å)

La–O1	2.64(1)	C1–C2	1.61(2)
La–O1''	2.63(1)	C2–C3	1.55(3)
La–O2	2.65(2)	C3–C4	1.56(2)
La–O3	2.53(1)	C4–C5	1.61(3)
La–O5	2.45(1)	C3–C6	1.57(3)
La–O6	2.46(2)	C1–O1	1.34(2)
La–O7	2.62(1)	C1–O2	1.24(2)
La–Ow1	2.58(2)	C5–O3	1.29(2)
La–Ow2	2.64(1)	C5–O4	1.26(2)
		C6–O5	1.18(2)
		C6–O6	1.26(2)
		C3–O7	1.46(2)

described as a (slightly distorted) mono-capped square antiprism, with O2 in the capping position. Seven of these oxygen atoms belong to three different citrate molecules, while water molecules occupy the two remaining positions in the coordination sphere. Therefore, the correct structural formula should be written as $[\text{La}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. The fact that the water molecules have a different function in the crystal structure (two coordinated to La^{3+} , one inbetween the La^{3+} -citrate network) is reflected in the extended temperature range (up to 280 °C) over which water is released upon heating. Additional evidence comes from the FTIR spectrum (Fig. 3) in which two distinct bands are observed at 3467 and 3421 cm^{-1} besides a broad absorption band about 3155 cm^{-1} . An approximate assignment of IR frequencies based on Refs. [16–18], can be found in Table 4. The former two frequencies are probably due to $\nu(\text{OH})$ of both coordinated water molecules. The small difference in $\text{La}-\text{O}_{\text{water}}$ distance and the formation of hydrogen bridges may be responsible for the splitting of this absorption band

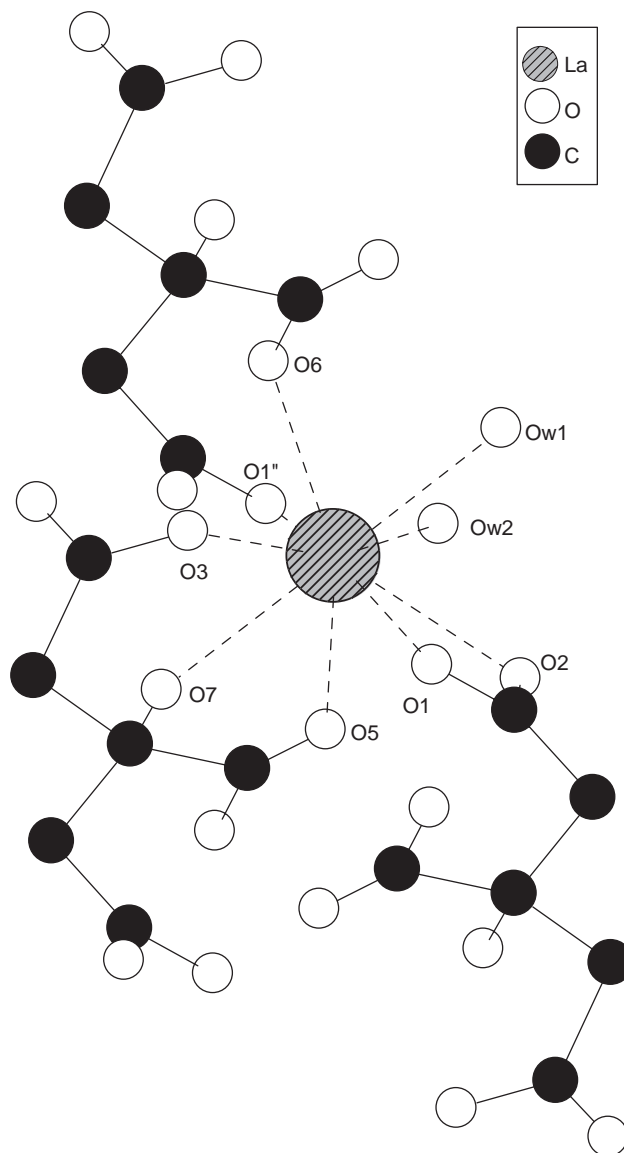


Fig. 5. La^{3+} coordination sphere.

because it indirectly affects the $\nu(\text{OH})$. The broad absorption band can be ascribed to the $\nu(\text{OH})$ of the uncoordinated water and partially overlaps with the ν_{sym} and ν_{as} of the CH_2 groups.

The $\text{La}-\text{O}$ bond distances correspond well to those found in similar compounds such as $\text{La}(\text{H}_2\text{O})_2M(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ with $M = \text{K}$ or NH_4 [5], $[\text{La}(\text{H}_2\text{O})](\text{C}_2\text{O}_4)_2 \cdot (\text{CN}_3\text{H}_6)$ [4] or $[\text{La}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_5\text{H}_7\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [6]. The $\text{La}-\text{O}$ bond lengths for the α -carboxylate group (mean distance: 2.46(1) Å) are on average shorter than those of the β -carboxylate groups (mean distance: 2.62(5) Å). The $\text{La}-\text{O}$ bond distance for the α -hydroxy group is of the same length as for the β -carboxylate groups.

The basic unit in the crystal structure (see Fig. 7) is a binuclear complex of two LaO_9 polyhedra having one

Table 4
Assignment of IR frequencies

Band position (cm ⁻¹)	Approximate assignment
3608(s)	$\nu(\text{OH})_{\text{free}}$, α -hydroxyl
3467(s), 3421(s)	$\nu(\text{OH})_{\text{water}}$, coordinated
3155(vs)	$\nu(\text{OH})_{\text{water}}$
2931(w), 2820(vw)	$\nu(\text{CH}_2)_{\text{as}}$, $\nu(\text{CH}_2)_{\text{sym}}$
2700–2300(m)	Overtone vibrations, intramolecular H-bridges
1676(sh, w), 1620(sh, w), 1570(vs), 1508(m)	$\nu(\text{COO}^-)_{\text{as}}$, $\delta(\text{HOH})_{\text{water}}$
1489(m)	$\delta(\text{COH})_{\alpha}$ -hydroxyl
1444(m), 1429(m)	$\delta(\text{CH}_2)$
1410(s), 1400(s), 1383(m)	$\nu(\text{COO}^-)_{\text{sym}}$
1301(m), 1261(s), 1188(m), 1136(m), 1076(m)	$\rho(\text{CH}_2)$, $\iota(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\nu(\text{C-OH})_{\alpha}$ -hydroxyl, $\nu(\text{C-O})_{\text{carbonyl}}$, $\nu(\text{C-C})$
947(w), 916(vw), 903(w), 862(w), 839(w), 787(vw), 729(w), 696(vw), 669(sh, w), 646(s), 559(m), 536(m), 488(vw), 436(vw)	$\tau(\text{C-O})$, $\tau(\text{C-C})$, $\delta(\text{COO}^-)$, $\gamma(\text{COO}^-)$, $\nu(2\mu_2\text{O})_{1,3,4}$, $\nu(\text{C-C})$, $\nu(\text{M-O})$

(vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak, (sh) shoulder.

edge (O1...O1'') in common. As a result, a dioxo-bridge ($2\mu_2\text{O}$) is formed between both metal centers. This feature is often found in citrates, e.g. $[\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)]_n \cdot n\text{-H}_2\text{O}$ [1] or $\text{K}_2[\text{VO}(\text{O}_2)(\text{C}_6\text{H}_6\text{O}_7)]_2 \cdot 2\text{H}_2\text{O}$ [19], as well as for other complexing carboxyligands such as glutarate [6] or oxalate [20]. The distance between both La^{3+} centers is 4.480(3) Å and the LaO-La angle 116.4(4)°. Although the latter would suggest a monooxo-bridged system according to Ref. [21], such large angular values have also been found for other dioxo-bridged systems in more recent literature [1,6]. Moreover, in the FTIR spectrum ν_1 , ν_3 and ν_4 for a dioxo-bridge are observed between 750 and 600 cm⁻¹. For the title compound, the dioxo-bridge is formed through β -carboxylate groups. All bond distances within the citrate molecule match quite well the expected values with the exception of the C–C bonds towards both β -carboxylate groups. With a length of 1.61(3) Å, they are significantly longer. However, a survey of the citrate compounds mentioned in the references shows that the C–C bonds towards the β -carboxylate groups in general deviate more from the expected value than the central C–C bonds, although the tendency is towards shorter bond lengths. Also the C1–O1 bond is somewhat elongated, thus resembling more single bond character. This could have been an indication for the presence of an acid –COOH group. However, as there is no IR absorption in the region 1800–1700 cm⁻¹, carboxylic acid groups are absent. As a result, it is the alkoxide group that has to carry the proton. The elongated C1–O1 bond may therefore be due the O1 involvement in the dioxo-bridge between two La^{3+} centers, which have quite a large ionic radius (~1.20 pm). The carboxylate groups are coordinated to

the metal ion in several ways (Fig. 6): the α -carboxylate forms a bridge between two La^{3+} centers, one of the β -carboxylates is coordinated both in a bidentate as well as a bridging way (in order to form the dioxo-bridge), while the second β -carboxylate is coordinated in a monodentate way. IR-data support these results because ν_{sym} can be found about 1400 cm⁻¹ and ν_{as} about 1570 cm⁻¹, which results in $\Delta(\nu_{\text{as}}-\nu_{\text{sym}})$ between 160 and 200 cm⁻¹. According to Ref. [22] this value is characteristic for bridging carboxylates. Actually, the absorption peak at 1570 cm⁻¹ appears to be a double peak (at 1575 and 1560 cm⁻¹), which is not surprising in view of the difference in La–O bond lengths for the α - and β -carboxylates. Taking a closer look at the IR spectrum, a shoulder at 1675 cm⁻¹ can be found as well. In this case $\Delta(\nu_{\text{as}}-\nu_{\text{sym}})$ is larger than 200 cm⁻¹, which is characteristic for monodentate coordinated carboxylate groups, although in this region also the $\delta(\text{HOH})$ bending vibration has to be taken into account. Finally, the weak band at about 1508 cm⁻¹, resulting in $\Delta(\nu_{\text{as}}-\nu_{\text{sym}})$ much smaller than 150 cm⁻¹, is believed to belong to the bidentate coordinated carboxylate group (Fig. 7).

Although the resolution of the powder dataset was not sufficient to resolve the position of the hydrogen

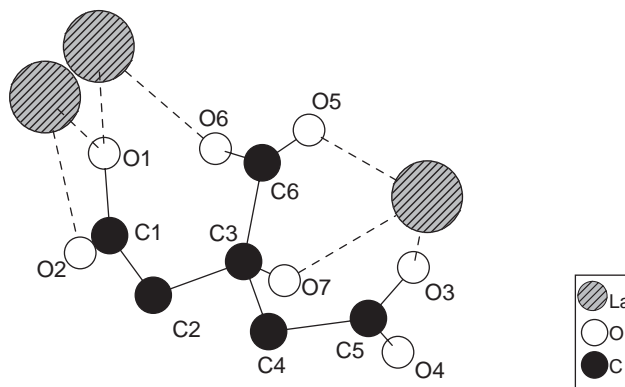


Fig. 6. Citrate coordination.

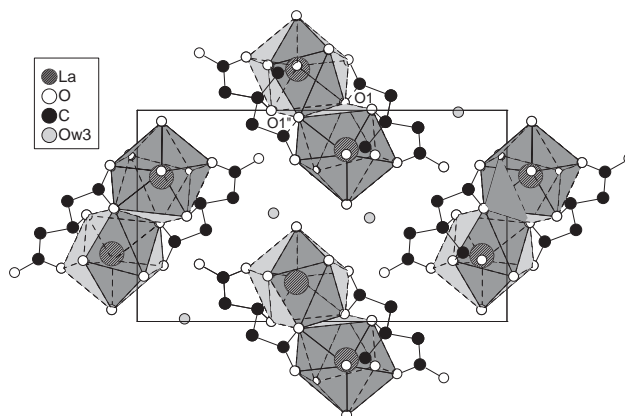


Fig. 7. View along the *c*-axis.

atoms, analysis of the O...O distances suggests that an extensive network of hydrogen bonds exists in the crystal structure. However, the α -hydroxyl group of the citrate molecule does not take part in any H-bridge formation, as evidenced by the sharp absorption band at 3608 cm^{-1} in the FTIR spectrum, which is typical for a free (tertiary) alcohol group. This is in contrast to some other citrates with mainly small metal ions (Na^+ [23], Mg^{2+} [24]) in which the α -hydroxyl forms hydrogen bridges with the terminal β -carboxylate groups.

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Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 249063. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; *E-mail address*: deposit@ccdc.cam.ac.uk)

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