

Isolation and Characterization of a Polymeric Lanthanum Citrate

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The first lanthanide citrate coordination polymer with the formula $[\text{La}(\text{Hcit})(\text{H}_2\text{O})]_n$ ($\text{Hcit}^{3-} = \text{C}(\text{OH})(\text{COO}^-)(\text{CH}_2\text{COO}^-)_2$) was prepared from La_2O_3 and citric acid at $\text{pH} = 2.2\text{--}2.5$ under hydrothermal conditions at $120\text{ }^\circ\text{C}$. The compound was characterized by elemental analysis, IR, TG-DTA, and X-ray crystallography. It is thermally stable up to $158\text{ }^\circ\text{C}$ and insoluble in common solvents. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 16.765(3)\text{ \AA}$, $b = 8.822(2)\text{ \AA}$, $c = 14.048(3)\text{ \AA}$, $\beta = 120.64(3)^\circ$, and $Z = 8$. The structure consists of chains of $\text{La}(\text{III})$ cations bridged by $\text{O}\text{--}\text{C}\text{--}\text{O}$ groups with pendant Hcit anions forming a pillar structure. The Hcit ligand is involved in six $\text{La}\text{--}\text{O}$ bonds to five different La centers in a very compact 3D structure.

Introduction

The characterization of hybrid inorganic–organic materials based on transition metal carboxylates is an area of continuous interest because of their relevance in a wide range of applications in material science including superconductors, magnetic materials, catalysis, and luminescent probes.^{1–6} A particularly attractive goal has been the construction of rare-earth carboxylates, due to the wide variety of structural types that may result from the high and variable coordination numbers available to the 4f-block elements and their unique f–f electronic transitions.^{1,7–16} A significant number of 3D

rare-earth-coordination polymers have been reported with di- and tricarboxylates.^{17–23}

Rare-earth citrates are extensively used as precursors in the Pechini method for the isolation of extremely pure multicomponent oxides after calcination.²⁴ A rational design strategy of these high-tech materials requires the use of versatile chemical routes, mostly being sol–gel processing for multioxides. These processes require metallic precursors with suitable properties which should thus be structurally well characterized, among other requirements.²⁵ It is expected

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that the combination of the coordination versatility of the citrate ligand with seven potentially O-donor atoms (citric acid = $\text{H}_4\text{Cit} = \text{C}(\text{OH})(\text{COOH})(\text{CH}_2\text{COOH})_2$) and the high coordination numbers available to rare-earth cations should stabilize different sorts of coordination polymers and oligomers depending on a wide range of synthetic variables. The nature of the interactions of rare-earth cations with the physiological citric acid molecule acquires special significance because of the relevance of rare-earth compounds in biomedical applications.^{26,27} However, despite the importance of binary rare-earth citrates, their key structural features remain unknown. Structural data reported for the related bis-(citrate)–neodymium(III) (hexaammine)cobalt(III) octahydrate²⁸ and citrate(*O, O'*)–(*N, N', N''*)-tris(α -methylbenzylaminocarbonylmethyl)-1,4,7,10-tetraazacyclododecane-*N, N', N'', N''', O, O', O''*)europium(III)²⁹ throw some light on the coordination modes that the ligand may adopt in binary citrates. In both compounds the citrate is triply deprotonated and binds to the neodymium and europium metal ions in a bidentate fashion, through one terminal carboxylate and the central alcoholic OH group. Herein, we report the synthetic, spectroscopic, and first single-crystal X-ray diffraction study of a Ln(III) binary citrate compound, namely the polymeric 1:1:1 $[\text{La}(\text{Hcit})(\text{H}_2\text{O})]_n$ ($\text{Hcit}^{3-} = \text{C}(\text{OH})(\text{COO}^-)(\text{CH}_2\text{COO}^-)_2$).

Experimental Section

All commercially available reagents and chemicals were of analytical or reagent-grade purity and used as received. Water was purified by a Millipore milli-Q-system yielding 18 M Ω cm water. Elemental analyses (C, H) were performed by INQUIMAE (Instituto de Química Física de los Materiales, Medio Ambiente y Energía) on a Carlo Erba 1108 instrument. Infrared spectra were recorded as KBr disks and as mulls in Nujol with a Nicolet 510P FT-IR spectrophotometer. Thermogravimetric analyses were recorded on a Shimadzu DTG 50 thermal analyzer, under an air flow of 40 L/min at a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (XRD) data were collected using monochromated Cu K α radiation on a Phillips X'Pert diffractometer.

Preparation of $[\text{La}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})]_n$. The complex was hydrothermally synthesized from a reaction mixture of La_2O_3 (0.60 g, 2 mmol) and citric acid monohydrate (0.50 g, 2 mmol) in water (50 mL) at a pH of about 2.2–2.5, in a stainless steel reactor heated at 120 °C during 5 days. A pure crystalline material was separated from the hot mixture, washed with cold water, and dried under vacuum. The yield was 85%. Phase purity was established by X-ray powder diffraction on a Philips X'Pert diffractometer. The X-ray pattern shows that the positions of the most intense lines remain unchanged relative to the simulated pattern on the basis of the single-crystal data of the complex. Anal. Found (calcd for $\text{C}_6\text{H}_7\text{O}_8\text{-La}$): C, 19.88 (19.80); H, 2.49 (2.47). IR (KBr disk, ν/cm^{-1}): 3450 (s, vbr), 1618 (s), 1569 (vs, $\nu(\text{CO}_2^-)_{\text{asym}}$), 1489 (m), 1432 (m), 1402 and 1400 (s, $\nu(\text{CO}_2^-)_{\text{sym}}$), 1300 (m), 1261 (s), 1187 (m), 1136 (m), 1073 (m), 945 (m, br), 902 (m), 861 (m), 728 (m), 645 (s), 558 (m), 534 (m), 487 (w), 435 (w). The compound is insoluble in

Table 1. Crystal Data and Structure Refinement 1

empirical formula	$\text{C}_6\text{H}_7\text{LaO}_8$
mol wt	346.03
density (g cm^{-3})	2.571
cryst system	monoclinic
space group	<i>C2/c</i>
<i>a</i> (Å)	16.765(3)
<i>b</i> (Å)	8.8220(18)
<i>c</i> (Å)	14.048(3)
β (deg)	120.64(3)
<i>V</i> (Å ³)	1787.6(6)
<i>Z</i>	8
temp (K)	293(2)
radiatn λ_{Mo} (Å)	0.710 73
abs coeff (mm^{-1})	4.804
final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R1(<i>F</i>) = 0.0182, ^a wR2(<i>F</i> ²) = 0.0430 ^b
final R indices (all data)	R1(<i>F</i>) = 0.0297, ^a wR2(<i>F</i> ²) = 0.0459 ^b

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

most common polar and nonpolar solvents. The ¹³C NMR (500 MHz, D₂O) spectrum of a sample washed several times with distilled water shows no traces of citric acid after an acquisition time of 4 h at 25 °C.

X-ray Crystallography. A needle-shaped crystal with well-developed external faces and a neat optical extinction was chosen for data collection. The specimen was mounted on a glass fiber, and a unique room-temperature diffraction data set was collected on a RIGAKU AFC6 four-circle diffractometer up to 56°, using graphite-monochromatized Mo K α radiation ($\lambda = 0.7107$ Å) and the $\omega/2\theta$ scan mode. The usual *LP* and absorption corrections (ψ scans) were applied. The crystal system is monoclinic, space group *C2/c*. Unit cell values were obtained from a high-angle subset of 25 reflections with 25° < 2 θ < 40°. Full crystallographic details given in Table 1.

The initial model was obtained through direct methods and the completion of the rest of the structure achieved by difference Fourier strategies. The structure was refined by least squares on *F*², with anisotropic displacement parameters for non-H atoms. Hydrogen atoms unambiguously defined by the stereochemistry were placed at their calculated positions and allowed to ride onto their host carbons both in coordinates as well as in thermal parameters (*C*–H, 0.97 Å). Those attached to oxygen and needed for the H-bonding description were located in a late Fourier map and refined with similarity restraints (O–H, 0.82(2) Å; H \cdots H, 1.36(3) Å). The reliability factors converged to R1(*F*) = 0.018 and wR2(*F*²) = 0.043.

All calculations to solve and refine the structures and to obtain derived results were carried out with the computer programs SHELXS 97, SHELXL 97, and SHELXTL/PC.³⁰ Full use of the CCDC package was also made for searching in the CSD Database.³¹ Atomic coordinates and full distances and angles are given in the Supporting Information.

Results and Discussion

The hydrothermal reaction of La_2O_3 and citric acid monohydrate and water at pH = 2.2–2.5 led to the formation of the homonuclear polymer $[\text{La}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})]_n$ (**1**) in good

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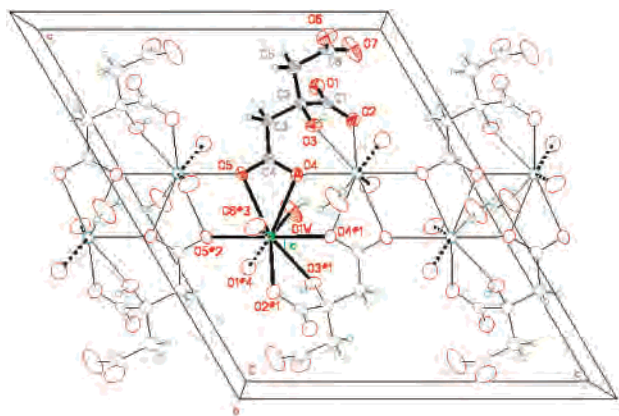


Figure 1. Diagram of **1** projected down *b*, showing the way in which the 2D structure builds up: in full 50% thermal ellipsoids, the asymmetric unit; in open ellipsoids, symmetry-related atoms; in broken bonds, atoms above and below the plane.

Table 2. Selected Bond Lengths (Å) for **1**^a

La–O(6)#1	2.422(3)	O(1)–C(1)	1.249(4)
La–O(1W)	2.455(3)	O(2)–C(1)	1.262(4)
La–O(2)#2	2.515(2)	O(3)–C(2)	1.436(4)
La–O(5)#3	2.524(2)	O(4)–C(4)	1.259(4)
La–O(1)#4	2.538(2)	O(5)–C(4)	1.264(4)
La–O(4)#2	2.560(2)	O(6)–C(6)	1.259(4)
La–O(3)#2	2.607(2)	O(7)–C(6)	1.250(4)
La–O(4)	2.690(2)		
La–O(5)	2.728(2)		

^a Symmetry transformations used to generate equivalent atoms: #1, $x - 1/2, -y + 7/2, z - 1/2$; #2, $-x + 1, -y + 3, -z + 1$; #3, $-x + 1, y, -z + 1/2$; #4, $x - 1/2, -y + 5/2, z - 1/2$.

yield. The product is a stable crystalline material and can be stored in a dry atmosphere for extended periods of time. The compound is insoluble in most common solvents.

Crystal Structure. The structure is polymeric with a repeating unit of formula [La(Hcit)(H₂O)]. Each La(III) cation is surrounded by an O₉ environment provided by one aqua molecule and five symmetry-related Hcit ligands with three deprotonated carboxylates, the reference one at x, y, z and those related to it by symmetry operations (#1, $-x + 1, -y + 3, -z + 1$; #2, $-x + 1, y, -z + 1/2$; #3, $x - 1/2, -y + 7/2, z - 1/2$; #4, $x - 1/2, -y + 5/2, z - 1/2$) (Figure 1). Selected bond distances are summarized in Table 2. The reference ligand provides oxygen donors O4 and O5 from one β -carboxylate bonded in the chelated mode. The Hcit ligand is tridentate and binds through one α -carboxylate (O2), one β -carboxylate (O4), and the α -hydroxyl (O1) oxygen atoms. This is the most common coordination mode found in the literature for transition metal citrates (Ti, Ga, Mn, Co, Ni).³² Other three oxygen donor atoms are provided by the two β -carboxylates O5#2 and O6#3 and the protonated α -hydroxyl group O3#1, respectively. The ninth site is occupied by the water molecule O1W. The La(III) cation lies “sandwiched” between the triangular O1W, O1#4, and O3#1 and the pentagonal O2#1, O4, O5, O4#1, and O5#2 bases, with a dihedral angle of ca. 11° between mean planes. The pentagonal base is capped by O6#3, completing a much distorted geometry of the LaO₉ core. Lanthanum coordination

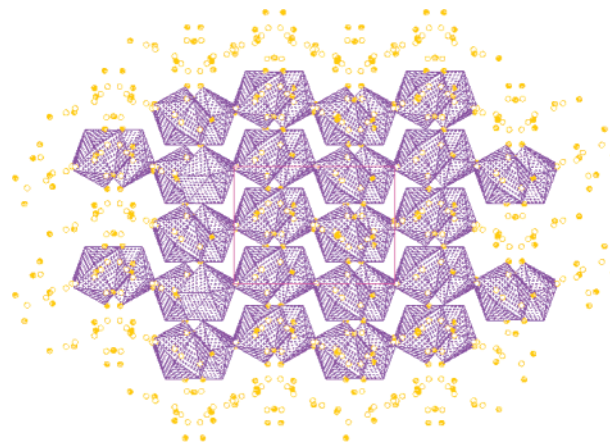


Figure 2. Polyhedral scheme viewed down *a*, showing the undulated chains. Oxygen and carbon atoms are drawn as shaded and open circles, respectively (connections not drawn, for clarity).

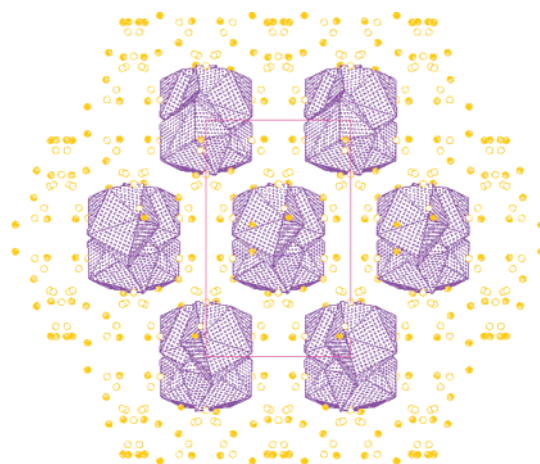


Figure 3. Polyhedral scheme viewed down *c*, showing chains perpendicular to the page plane. Oxygen and carbon atoms are drawn as shaded and open circles, respectively (connections not drawn, for clarity).

Table 3. Geometrical Parameters of Hydrogen Bonding (Å, deg) for **1**^a

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
O(3)–H(3O)···O(2)#5	0.83(5)	1.86(5)	2.688(3)	171(5)
O(1W)–H(1WB)···O(7)#4	0.84(5)	1.85(5)	2.681(4)	172(5)
O(1W)–H(1WA)···O(7)#6	0.80(5)	1.87(5)	2.648(4)	167(6)

^a Symmetry transformations used to generate equivalent atoms: #4, $x - 1/2, -y + 5/2, z - 1/2$; #5, $-x + 3/2, y + 1/2, -z + 3/2$; #6, $-x + 3/2, y - 1/2, -z + 3/2$.

polyhedra connect to each other through the sharing of a pair of edges (O4–O4#1, bisected by a center of symmetry, and O5–O5#2, bisected by a 2-fold axis) to define waving stripes parallel to the *c* axis and shown in the lateral view in Figure 2. These stripes constitute the basic structural units and are, in turn, connected with each other into a compact 3D network through bonds involving carboxylate oxygens O1 and O6 (heavy dashed lines pointing upward and downward in Figure 3) as well as strong H-bonds involving the water and the hydroxyl hydrogens as donors and O7 and O2 as acceptors, as summarized in Table 3. The citrate anion Hcit is a rigid short-chain ligand with an almost planar C2–C3–C4–C5–C6 backbone and a mean deviation from the best plane of 0.06 Å. The terminal carboxylate groups are, in turn, rotated from this plane around their C–C bonds,

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O4–C4–O5 by 7.4(1) and O6–C6–O7 by 119.8(1)°, respectively. Six oxygen atoms, O1–O6, are engaged in bonds to La metal centers and O7 in an H-bond. The intrachain La···La distances within the stripes are almost identical to the interchain distances: 4.435(1) and 4.411(1) Å, respectively. The La–O bond distances vary in the range 2.423(3)–2.729(3) Å with a mean value of 2.561(3) Å, in line with reported values for La–O(–C) bond lengths in LaO₉ cores (mean: 0.256(9) Å for 2020 entries in the CSD),³¹ with the two longest such bonds (La–O4, 2.690(2), and La–O5, 2.728(2) Å) falling in the extreme end of the range of reported values (9% and 6%, respectively) and corresponding to the chelating β-carboxylate group.

It is of interest to note that unlike the open networks in lanthanum oxydiacetate²¹ and lanthanum adipate,⁶ the lanthanum citrate framework presents a quite compact structure (density: 2.57 vs 1.99 and 1.89 g cm⁻³, respectively), highlighting the effect of the hydrothermal preparation of the latter, a method which generally leads to relatively more compact crystal structures and reduces metal–aqua coordination inducing a condensed metal–oxygen framework.¹ The connectivity between the lanthanum metal atom and the Hcit ligand yields a crystal packing with small cavities without an open framework. The presence of pendant OH and COO groups provides a set of reactive centers which may be favorable for the onset of polymerization reactions in the Pechini method.

Vibrational Spectra. Upon complex formation the strong IR absorptions of citric acid at 1730, 1393, and 1217 cm⁻¹ indicative of carboxylic acid and tertiary alcohol groups are replaced by a very strong band at ca. 1560 and a strong band at 1460 cm⁻¹. The former corresponds to the asymmetric vibrations of the COO⁻ groups and overlaps with the coordinated water deformation mode at 1640 cm⁻¹. The band at 1460 cm⁻¹ is assigned to the symmetric vibrations of the COO⁻ groups. The Δ value [$\nu(\text{COO}^-)_{\text{asym}} - \nu(\text{COO}^-)_{\text{sym}}$] of 100 cm⁻¹ suggests that the coordination of the carboxylate groups is most probably of the chelating bridging type.

Although the splitting criterion is often satisfactory to probe the carboxylate coordination in monocarboxylic acids,³³ its applicability to polycarboxylates in which more than one type of carboxylate coordination may be present is limited, as shown by the results of the present X-ray study. Thus, structural comparison between the reported structure and those generated in the standard sol–gel process and based on spectroscopic measurements alone are not satisfactory.

Thermal Behavior. The thermal stability and decomposition pattern of the complex were investigated by thermogravimetric analysis. The first weight loss of 5.4% from 158 to 209 °C corresponds to the coordinated water molecule (calculated: 5.2%). The next mass reduction of 54.7% occurs in the range 343–832 °C and shows an exothermic reaction due, undoubtedly, to the combustion of the organic components. The residue consists of hexagonal La₂O₃, as shown by the X-ray diffraction pattern.³⁴

In summary, mild hydrothermal conditions allowed the isolation of the first polymeric lanthanum citrate [La(Hcit)(H₂O)]_n as single crystals. The structure exhibits arrays of La(III) nodes bridged by O–C–O groups with citric connectors and intermolecular H-bonds between arrays. The OH and COO reactive groups of the Hcit ligand reside in a very compact La–O framework. Studies on other rare-earth citrates and their properties are ongoing.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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