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Synthesis and X-ray Structure of the Novel Polymeric Lanthanum(III) 2,2′-Oxydiacetate $[La_2(C_4H_4O_5)_3(H_2O)_3\cdot 5H_2O]_n$

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Introduction

The synthesis and structural characterization of new lanthanum(III) carboxylates is an area of current interest for their potential applications in chemical processing of ceramic materials.[1] Lanthanum oxalates have long been used for this purpose.[2] Structural investigations revealed that they are polymeric with the oxalate anions linking equivalent nine-coordinate LaO_9 nuclear cores.[3]

Among related dicarboxylates, the existence of lanthanide oxydiacetates (oxydiacetic acid = $[O(CH_2CO_2H)_2]$) with additional sodium metal ligand units is well documented.[4] The solid state structures of these compounds showed the mononuclear nine-coordinate $(Ln(C_4H_4O_5)_3)^{3-}$ complex anion with Ln = Ce,[4a−c] Nd,[4d] Eu,[4e,f] Gd,[4g] and Yb.[4d] The related $(La(C_4H_4O_5)_3)^{3-}$ species has been reported as nine-coordinate from ^{139}La NMR studies in aqueous solution,[5] but has not been structurally characterized in the solid state.

Retention of the alkali metal in carboxylate, alkoxide, and aryloxide complexes of the lanthanide elements has been extensively reported and can be a pervasive problem in the chemistry of precursor compounds.[6] The preparation of salt free oxydiacetate complexes of composition Ln_2L_3 remains, however, largely unexplored. The crystals formed in the first part of the lanthanide series were reported to be unstable and only the erbium complex $[Er_2(C_4H_4O_5)_3(H_2O)_4\cdot 2H_2O]_n$ could be investigated by single crystal X-ray diffraction methods. The structure is composed of two-dimensional sheets with the oxydiacetate ligands linking eight- and nine-coordinate Er^{3+} ions.[7]

In this note we report the synthesis, characterization and X-ray structure of the novel $[La_2(C_4H_4O_5)_3(H_2O)_3\cdot 5H_2O]_n$ complex containing two non-equivalent nine-coordinate LaO_9 units in a three-dimensional polymeric structure.

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 EA 1108 instrument. Infrared spectra were recorded as KBr disks or as a mull in Nujol with a Nicolet 510P FT-IR spectrophotometer. The Raman spectra of single crystals were obtained from a Jarrel Ash 25-300 spectrophotometer equipped with a Coherent Radiation 52 G argon-ion laser. Thermogravimetric analyses were recorded on a Mettler TG-50 thermal analyzer under an atmosphere of air at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer.

Preparation of $[La_2(C_4H_4O_5)_3(H_2O)_3\cdot 5H_2O]_n$. The compound was prepared by the following two methods. First, oxydiacetic acid (1.20 g, 9.00 mmol) was added in portions of 20 mg to a suspension of La_2O_3 (0.50 g, 1.50 mmol) in water (100 mL). The mixture was heated to boiling with stirring for 10 h and then allowed to cool to room temperature with stirring for 1 h. The pH of the resulting solution was 3.0−3.5. The solution was filtered and the filtrate allowed to stand at room temperature. After 5 d, colorless X-ray quality crystals of the product were collected and dried under vacuum for 2 h. Yield: 0.85 g, 70%. Anal. Calcd (found) for $C_{12}H_{28}La_2O_{23}$: C, 17.60 (17.50), H, 3.40 (3.45). IR (KBr disk, cm^{-1}): 3860 (w), 3408 (s, br), 2916 (w), 1595 (vs, br), 1466 (m), 1441 (vs), 1360 (w), 1311 (s), 1242 (w), 1117 (s), 1051 (s), 966 (w), 939 (w), 733 (w), 600 (m), 565 (s), 347 (w). Raman (single crystal, cm^{-1}): 1585 (vw), 1470 (m), 1440 (s), 1425 (s), 1360 (s), 1310 (s), 1230 (m), 970 (s).

Caution! Perchlorate salts of metal complexes are potentially explosive. They should be handled with great care and in small quantities.[8]

Second, in a procedure analogous to that reported[4b,g] to prepare the double salts $Na_3[Ln(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$ (Ln = Ce, Nd, Gd, and Yb), a water solution (100 mL) of sodium oxydiacetate (15 mmol) was slowly added to a water solution (100 mL) of lanthanum perchlorate (5 mmol) under stirring. The pH of the solution was kept in the range 5−6 by addition of perchloric acid. After being stirred for 12 h at 80 °C, the solution was filtered and after 2 months colorless X-ray quality crystals of the product were collected and vacuum-dried. Yield: 1.20 g, 60%. Both methods provide the same product, which was confirmed by IR, microanalysis, and single crystal X-ray diffraction characterization.

X-ray Crystallography. Crystallographic data are summarized in Table 1. A colorless crystal of good diffracting power was mounted in a glass fiber on a Siemens R3m diffractometer equipped with a graphite-monochromator and Mo Kα (λ = 0.71073 Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections. Intensity data were collected in the range $4.94° \le 2\Theta \le 41.10°$ by the $\omega-2\Theta$ scan technique. Within index ranges ($1 \le h \le 10$, $-10 \le k \le 8$, $-18 \le l \le 18$), 3106 reflections were collected, of which 620 were unique and 607 observed, $F_o^2 > 2\sigma(F_o^2)$. Intensities were corrected for Lorentz and polarization effects, and a semiempirical

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Table 1. Crystallographic Data for **1**

$C_{12}H_{28}La_2O_{23}$	$T = 23$ °C
$a = b = 9.507(1)$Å	$\lambda = 0.71073$ Å
$c = 17.443(4)$Å	$\rho_{calcd} = 1.99$ g cm^{-3}
$V = 1365.3(4)$Å^3	$\mu = 31.8$ cm^{-1}
$Z = 2$	R1^a $[F^2 > 2\sigma(F^2)] = 0.012$
fw = 818.16	wR2^b = 0.032
$P\bar{6}2c$(No. 190)	

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

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **1**

atom	x	y	z	U(eq)^a
La1	0.6667	0.3333	0.2500	0.0177(1)
La2	0.0000	0.0000	0.0000	0.0182(2)
C1	0.3501(3)	0.1850(7)	0.1046(2)	0.0293(7)
C2	0.4009(4)	0.0941(5)	0.0514(2)	0.0460(10)
O1	0.4500(3)	0.2705(3)	0.1549(1)	0.0444(6)
O2	0.2716(3)	0.0000	0.0000	0.0346(9)
O3	0.2146(3)	0.1728(3)	0.0953(1)	0.0401(6)
O1W	0.9888(5)	0.4387(5)	0.2500	0.0583(12)
O2WA	1.1702(15)	0.2907(16)	0.2500	0.080(4)
O2WB	1.0866(35)	0.1947(27)	0.2500	0.094(7)
O3WA	1.3031(39)	0.5069(35)	0.1380(21)	0.083(9)
O3WB	1.2233(66)	0.4646(58)	0.1536(31)	0.096(17)
O3WC	1.3205(63)	0.5326(64)	0.0998(25)	0.087(16)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

absorption correction (ψ scan) was also applied. Two standard reflections, monitored every 98, showed no systematic changes.

The positions of three water molecules (O1w's) bound to La1 were readily found and satisfactorily refined. The remaining five water molecules (O2w's and O3w's) could not be located precisely due to crystallographic disorder. Although other space group assignments of lower symmetry were checked, the structure was best refined in $P\bar{6}2c$ (No. 190). In spite of the observed disorder the final positions of the water molecules did allow to ascertain that they are compressed together in the vicinity of the La−O1w capping bonds and not involved in metal binding. Hydrogen atoms bonded to the carbon atoms were included at calculated positions and refined using a riding model, with C−H = 0.95 Å and a unique common isotropic thermal parameter fixed at 0.08 Å^2. None of the water hydrogen atoms were located. Computer programs used in this study were SHELXL 93 and SHELXLTL/PC software packages,[9,10] and PARST.[11] The final fractional coordinates for the non-hydrogen atoms are given in Table 2 and selected bond distances and angles are listed in Table 3.

Results and Discussion

Addition of oxydiacetic acid to an aqueous suspension of La_2O_3 led to the formation of the $[La_2(C_4H_4O_5)_3(H_2O)_3{\cdot}5H_2O]_n$ (**1**) complex in good yield. Interestingly, the reported procedure[4b,g] for the preparation of the double salts $Na_3[Ln(C_4H_4O_5)_3]{\cdot}2NaClO_4{\cdot}6H_2O$ (Ln = Ce, Nd, Gd, Yb) also resulted in the alkali metal free compound **1**. The complex is a stable colorless crystalline solid and can be stored in a dry atmosphere for extended periods of time. TGA measurements show that the compound is thermally stable up to 50 °C, at which temperature loss of water commences.

Crystal Structure. The structure of **1** reveals that the complex is a three-dimensional polymer built up from two nonequivalent nine-coordinate lanthanum complex ions, each of which is surrounded by an O_9 donor set. The geometry around each lanthanum atom can be viewed as a tricapped trigonal prism (TCTP) formed by the piling up of three triangular layers. The outer layers are symmetry related, resulting in two sets of independent La−O distances; one set of six La−O prismatic bonds and a second set of three La−O capping bonds. A schematic drawing of the two crystallographically independent complex ions in **1** and the labeling of atoms is illustrated in Figure 1 with the packing pattern in Figure 2. Selected bond lengths and angles are listed in Table 3.

Table 3. Selected Bond Lengths (Å) and Angles [deg] for **1**^{a}

La1−O1	2.474(2)	La1−O1W	2.704(4)
La2−O3	2.504(2)	La2−O2	2.582(3)
C1−O3	1.245(4)	C1−O1	1.249(4)
C1−C2	1.504(6)	C2−O2	1.419(4)
O1−La1−O1^a	136.46(5)	O1−La1−O1^b	79.96(9)
O1−La1−O1^e	84.20(13)	O1^c−La1−O1W	66.62(8)
O1−La1−O1W	137.85(6)	O1−La1−O1W^d	69.85(8)
O1W−La1−O1W^d	120.0	O1−La1−O1W^b	66.60(8)
O3−La2−O3^f	151.18(11)	O3−La2−O3^g	80.77(9)
O3−La2−O3^i	121.77(11)	O3−La2−O3^j	85.31(13)
O3−La2−O2^h	137.34(6)	O3−La2−O2	60.88(5)
O3^h−La2−O2	75.59(6)	O2^h−La2−O2	120.0
O3−C1−O1	124.6(5)	O3−C1−C2	118.7(3)
O1−C1−C2	116.7(3)	O2−C2−C1	109.0(2)
C2−O2−C2^i	113.1(3)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $-y + 1, x - y, -z + {}^1/_2$; (b) $-y + 1, x - y, z$; (c) $-x + y + 1, -x + 1, -z + {}^1/_2$; (d) $-x + y + 1, -x + 1, z$; (e) $x, y, -z + {}^1/_2$; (f) $-x, -x + y, -z$; (g) $-y, x - y, z$; (h) $-x + y, -x, z$; (i) $x - y, -y, -z$; (j) $y, x, -z$.

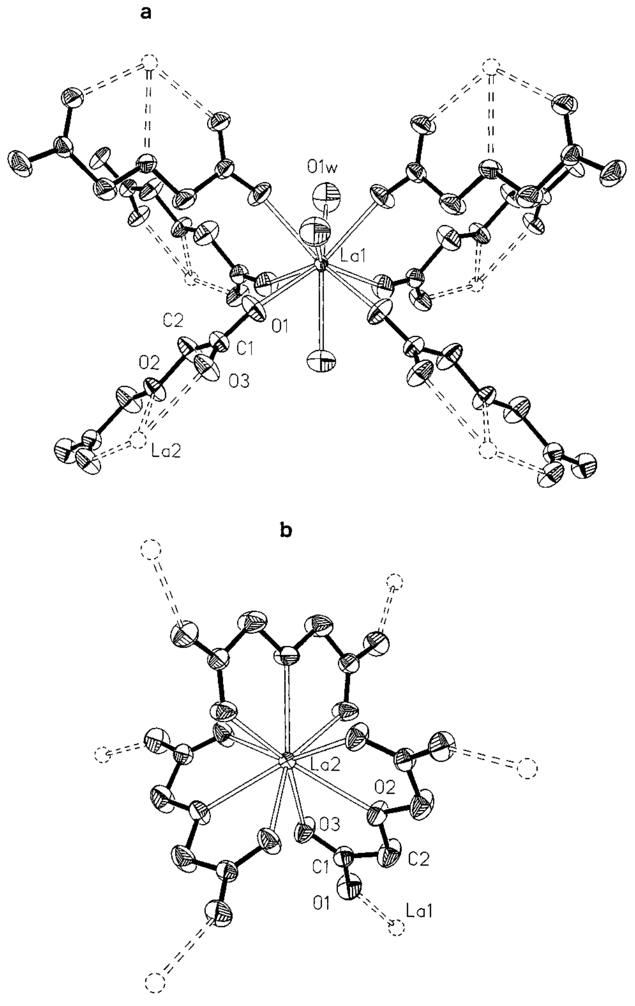

Figure 1. Schematic diagrams showing the structures with atom labels (50% thermal ellipsoids) of the two building units of **1**.

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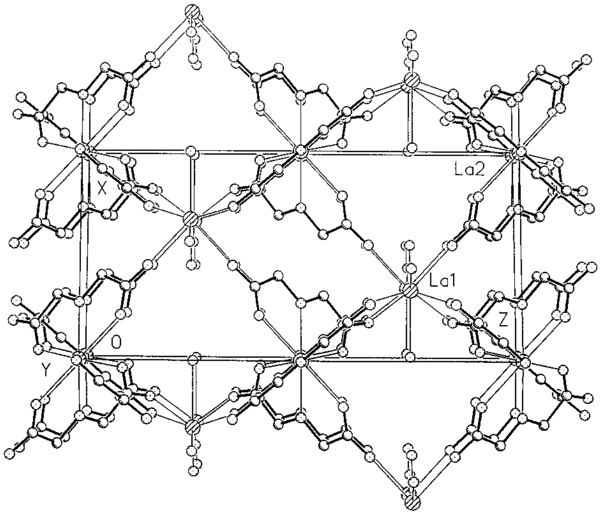

Figure 2. Packing diagram along the *b*-axis of **1**. Hydration water molecules are not included for clarity.

The La1 ion is coordinated by six outer carboxylate oxygen atoms belonging to six different La2 polyhedra and by three oxygen water atoms. The La1 ion lies on a 6-fold rotary inversion axis. The geometry of the LaO_9 polyhedron at La1 is best described as an eclipsed D_{3h} tricapped trigonal prism. The La1−O bond lengths fall into two sets. One set consists of the six prismatic La1−O1 distances to the outer carboxylate oxygens of 2.474(2) Å. The second set includes the three capping La1−O1w bonds to the water oxygens of 2.704(4) Å. These are significantly longer than the former and show the comparative weakness of the less polar La−O(water) bonds.

The La2 ion is nine-coordinate with three tridentate oxydiacetate ligands, coordinating two carboxylate oxygens and the ether oxygen of each ligand. The ligands are completely deprotonated. The two carboxylate oxygens of each ligand are attached to the opposite top and bottom vertices of the prism, while the middle ether oxygen caps the rectangular face. The three oxygens are thus attached diagonally ("*mer* conformation") across a long rectangular face of the trigonal prism. The La2 ion lies on the intersection of a 3-fold and a 2-fold axis and has a staggered D_3 tricapped trigonal prism geometry. The lower symmetry coordination is a result of the rigidity of the chelating ligands which causes the triangular faces of the prism to be rotated relative to one another ($\Theta = 21°$). The six La2−O prismatic distances and the three La2−O capping distances are 2.504(2) and 2.582(3) Å respectively, with the longer distances corresponding to the less polar La−O(ether) bonds. The coordination geometry of $[La(C_4H_4O_5)_3]^{3-}$ in **1** closely parallels those observed in the mononuclear $[Ln(C_4H_4O_5)_3]^{3-}$ complex anions (Ln = Ce, Nd, Eu, Gd, Yb). In the related $[Er_2(C_4H_4O_5)_3(H_2O)_4{\cdot}2H_2O]_n$ the Er−O(carboxylate) distances in the nine-coordinate unit average to 2.35[2] Å, which is 0.15 Å shorter than the corresponding value in **1**, in accordance with the decrease in ionic radius[12] of 0.15 Å between La^{3+} and Er^{3+}. The weak capping Er−O(ether) distances average to 2.49[1] Å which is only 0.08 Å shorter than the corresponding value in **1**.

The La−O(carboxylate) distances in **1**, ranging from 2.474(2) to 2.504(2) Å (average 2.489[15]) Å) may be compared with the average La−O(carboxylate) distance of 2.545[11] Å in the lanthanum oxalate complexes. The donor−acceptor La−O(water) bond lengths in **1** of 2.704(4) Å are, however, significantly longer than the values normally found for this bond[13] (2.556[62] Å). This lengthening may arise from the engagement of the O1w's in hydrogen bonding with crystal water molecules. Short O···O contacts have been encountered between coordinated O1W's and some of the disordered O2W's (2.72(2)−2.90(4) Å) and O3W's (2.72(6)−2.99(3) Å), suggesting that hydrogen-bonding interactions may occur. However, since none of the water hydrogen atoms were located, any precise interpretation along this line is precluded.

Because of the 2-fold axis along the La2−O(ether) bonds, half of the oxydiacetate ligand is independent. The two five-membered chelate rings, with a common La−O bond for each ligand, are nearly planar with maximum deviation of 0.016 Å from the medium plane. Looking down the 3-fold axis, the oxydiacetate ligands form a three-bladed propeller configuration about the central metal with angles between them of 96.7°. Other distances and angles within the ligand molecules are consistent with the values reported for related complexes.[4,14]

The crystal structure of **1** is a complex three dimensional network of two nonequivalent lanthanum TCTP polyhedra with the carboxylate groups of the oxydiacetate ligands bridging pairs of La atoms in a bidentate anti−anti mode.[2] Each La1 ion is linked to six different La2 ions and vice versa at a noninteracting distance of 7.01 Å. This is unlike the erbium analog where interaction between eight-coordinate and nine-coordinate erbium polyhedra generates a two-dimensional sheet structure in which each erbium atom in the former is linked to four erbium atoms in the latter and vice versa.[7] The different crystal structures illustrate the diversity that can result in lanthanide compounds due mainly to effects of metal cation size.

Vibrational Spectra. As a result of complex formation, the strong IR absorptions of oxydiacetic acid at 1734, 1420, and 1194 cm^{-1} indicative of carboxylic acid groups are replaced by a very strong and broad band centered at ca. 1595 cm^{-1} and a strong band at 1441 cm^{-1}. The band at 1595 cm^{-1} corresponds to the asymmetric vibrations of the RCO_2^- groups and overlaps with the coordinated and lattice water deformation modes usually assigned at 1640 and at 1625 cm^{-1}, respectively.[15] The band at 1441 may be assigned to the symmetric vibrations of the RCO_2^- groups. The Raman counterparts for **1** are a very weak line at 1585 cm^{-1} and two strong lines at 1440 and 1425 cm^{-1}, respectively. The Δ values [$\Delta = \nu(CO_2^-)asym - \nu(CO_2^-)sym$] of ca. 160 cm^{-1} suggest that the coordination of the carboxylate groups are most probably bridging, as confirmed above in the structure of **1**. In fact, low values of Δ are expected for chelating or bidentate bridging groups whereas Δ values of above 200 cm^{-1} are usually expected for unidentate coordination.[16]

No clear evidence was found in the range 600−500 cm^{-1} of new bands that could be confidently associated with the La−O vibrations of the LaO_9 units. In fact, assignments of these modes are expected to be difficult because of the low energies associated with these vibrations.[17]

Thermolysis. Thermal decomposition of **1** was investigated by thermal gravimetric analysis (TGA), and the final white residue was examined by XRD. No attempt was made to identify the intermediate products formed during this thermolysis. The first step in the thermogram in Figure 3 corresponds

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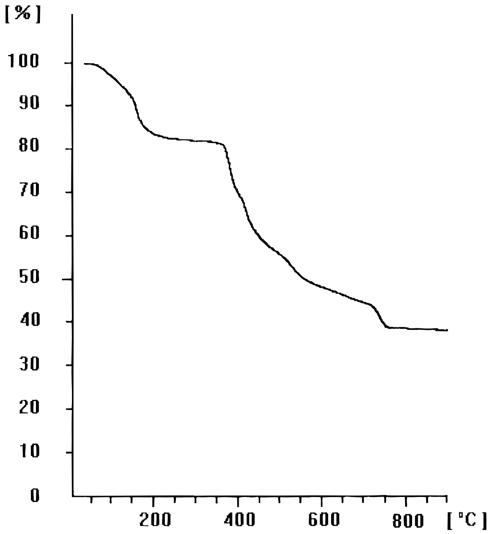

Figure 3. TGA diagram of **1** under an atmosphere of air. Theoretical values for weight changes: 82%, **1** − 8(H_2O); 40%, La_2O_3/**1**.

to the distinct loss of the eight water molecules. The mass of the final product corresponds to the complete combustion of **1** to hexagonal La_2O_3 as shown by the X-ray powder diffraction pattern.[18]

In summary, a simple route to **1**, the first lanthanum(III) oxydiacetate complex in the solid state is reported. The present structure shows that the oxydiacetates serve as tridentate ligands to a La^{3+} ion and at the same time form carboxylate bidentate bridges with six adjacent La^{3+} ions giving rise to a complex three-dimensional structure of LaO_9 cores. Also, complex **1** is a stable inorganic precursor to hexagonal La_2O_3.

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Supporting Information Available: Tables listing crystal data, full bond lengths and angles, anisotropic thermal parameters, and hydrogen positional parameters (7 pages). Ordering information is given on any current masthead page.

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(18) The diffraction pattern was matched with that of La_2O_3: The JCPDS International Center for Diffraction Data, 1992, Powder Diffraction File No. 05−0602.