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The first suberate lanthanum(III) complex without uncoordinated water

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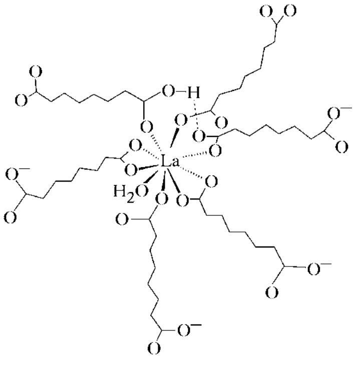
catena-Poly[[aqualanthanum(III)]-μ-(8-carboxyoctanoato)-μ-octanedioato], $[La(C_8H_{12}O_4)(C_8H_{13}O_4)(H_2O)]_n$, is, to our knowledge, the first reported rare-earth complex containing a flexible long-chain ligand that crystallizes without water of crystallization. The layered polymeric structure is built from infinite chains of one-edge-sharing $LaO_8(H_2O)$ polyhedra, connected through the carbon backbone chains of the ligands. The two chemically different ligands act in the same coordination modes, exhibiting chelating bonds and μ-1,1-bridging monodentate linkage, and adopting the same extended conformation. In the relatively limited hydrogen-bonding network, a very strong hydrogen bond between the deprotonated and protonated ligand ends stabilizes the framework.

Comment

In the past decade, a particular emphasis on the design, crystal packing and properties of organic–inorganic compounds has arisen as a result of the wide variety of structural types that lead, when the framework is open, to microporous materials. Polynuclear complexes are constructed of flexible dicarboxylate ligands, completely or partially deprotonated, linked to metal centres (such as lanthanides) with high coordination numbers. Such complexes can be used successfully as drying agents in catalysis or in the environmental domain. Other applications have also been reported (Piguet & Bünzli, 1999; Parker *et al.*, 2002). Most of the resulting neutral lanthanide polymers are hydrated, owing to the fact that their layered structures can accommodate interlayer guest water molecules. These uncoordinated molecules are thought to play a crucial role in the crystalline stability (Antivec-Fidancev *et al.*, 2002). We report here the crystal structure of the title compound [aqua(hydrogensuberato)(suberato)lanthanum(III); Benmerad *et al.*, 2002], (I), which has high stability and good crystallinity, despite the presence of long alkyl chains and the lack of uncoordinated water molecules.



(I)

The title $[La(C_8H_{12}O_4)(C_8H_{13}O_4)(H_2O)]$ complex has a chemical formula similar to those of the isostructural lanthanum(III) glutarate (Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000) and pimelate complexes (Dimos *et al.*, 2002). Like these two compounds, (I) contains both protonated (H*L*) and deprotonated (*L*) ligands. Nevertheless, the crystal structure of the complex is completely different from the glutarate and pimelate analogues, from the point of view of connectivity, interlayer interactions, framework characteristics and packing arrangement. Despite its long-alkyl-chain ligand (eight C atoms) and its open framework, complex (I) remains stable up to 550 K, which is a very high temperature compared with the thermal stability of suberic acid (293–421 K) or of the only known suberate complex $Co(C_8H_{12}O_4)\cdot 1.5H_2O$, which decomposes at 333 K (Allan & Dalrymple, 1993).

Fig. 1 shows the general features of the structure, without the hydrogen bonding. The layered polymeric structure is built from infinite chains of one-edge-sharing $LaO_8(H_2O)$ polyhedra, running along the [100] direction, connected by the carbon backbone of the ligands. The resulting crosslinked single chains form stable layers, despite the lack of additional

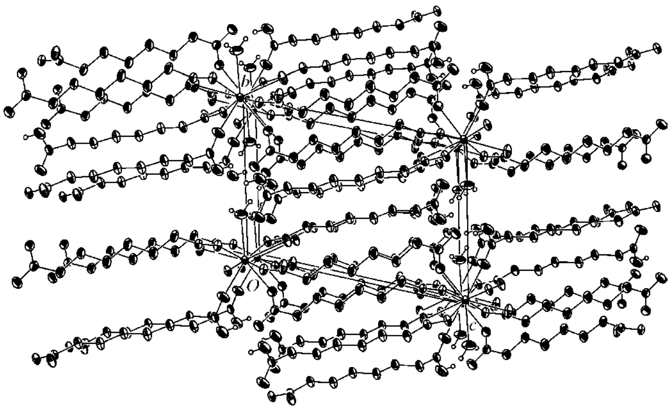


Figure 1
The packing of (I), viewed along the *a* axis. All H atoms have been omitted for clarity.

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hydrogen bonds involving guest water molecules. Adjacent metal centres are doubly bridged by pairs of ligands to form repeated four-membered La/O/La/O rings, within which the distances between two neighbouring La^{3+} ions are almost equal [4.287 (1) (connection across atom O6) and 4.328 (1) Å (connection across atom O3)]. Fig. 2 shows the coordination around the La atom, which involves eight O atoms belonging to carboxylate ligands, equally distributed between three non-independent H*L* and *L* ligands, and one O atom from the aqua ligand. Unlike other known lanthanum dicarboxylates (Marrot & Trombe, 1993, 1994; Kiritsis *et al.*, 1998; Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000; Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegroune, 2000; Dimos *et al.*, 2002) and despite the fact that this long-alkyl-chain ligand is more sterically demanding, the dispersion of the La—O bond lengths is small [2.4772 (12)–2.6807 (13) Å; Table 1].

The two ligands are involved in the same coordination modes. These ligands are bridging–chelating by one function, exhibiting μ-1,1-bridging *via* atom O6 for the H*L* ligand and atom O3 for the *L* ligand, and monodentate chelation by the second function, involving atom O7 for H*L* and atom O1 for *L*. As a consequence, all O atoms of the ligands are bonded to the metal cation, except for atom O8, which is bonded to an H atom (the ligand being protonated), and atom O2 of the deprotonated ligand, which shares the same H atom (H8) with O8 in a hydrogen bond. The H*L* and *L* ligands clearly have different chemical characteristics, despite their identical coordination modes. The *L* ligand exhibits two functions typical of carboxylate groups, whereas in the H*L* ligand, the two different end functional groups seem to have the same character, related to the carboxylate geometry. A similar bonding situation is found in complexes containing protonated ligands (Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000; Dimos *et al.*, 2002). As indicated by the torsion angles (Table 1), the conformations of the *L* and H*L* ligands are almost identical; they adopt an extended conformation. However, the two end functional groups involved in the bridging–chelating mode deviate significantly from the ideal *anti–anti* value (180°) for the H*L* ligand [O6—C9—C10—C11 = −168.2 (2)° and O5—C9—C10—C11 = 13.0 (3)°] and from the *syn–anti* values (60 and 180°) for the *L* ligand [O4—C8—C7—C6 = 50.7 (3)° and O3—C8—C7—C6 = −131.0 (3)°].

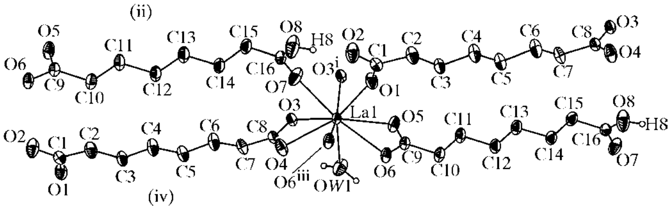

Figure 2
The coordination around the La atom, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

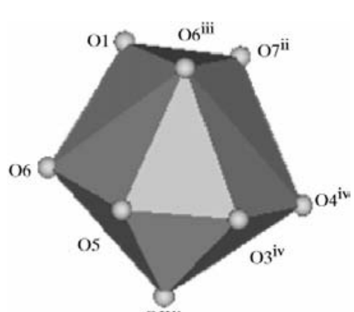

Figure 3
A polyhedral representation of the coordination around the La atom. (The symmetry codes are as in Fig. 2.)

The La atom is nine-coordinate (Fig. 3), forming a mono-capped dodecahedron, the cap being atom O7^{ii} (symmetry codes are given in Fig. 2). This configuration is confirmed by the dihedral angle between the O*W*1/O3^{iv}/O6^{iii}/O1 and O5/O3^{i}/O4^{iv}/O6 planes [65.0 (3)°], which is close to the value for an idealized D_2 geometry (*ca* 60°; Drew, 1977). As shown in Table 2, the hydrogen-bonding network is relatively limited. However, as mentioned above, there is a very strong hydrogen bond between the H*L* and *L* ligands; the protonated acid group donates atom H8 *via* a very short hydrogen bond to atom O2.

In the absence of any uncoordinated water molecules lying between the layers and playing a templating role during crystallization, it can reasonably be assumed that this strong bond stabilizes the open framework. Complex (I) is note-worthy for several characteristics. The lack of any uncoordinated water molecule is very rare in this kind of material.

While 20 hydrated rare-earth complexes obtained with aliphatic HOOC—(CH$_2$)$_n$—COOH acids have been structurally characterized, only two have been reported that contain no water of crystallization, and these contain ligands having either a short alkyl spacer unit (n = 1; Hansson, 1973; Hernandez-Molina *et al.*, 2002) or no alkyl spacer (n = 0; Trollet *et al.*, 1997). In the higher series ($n > 1$), only one family has been reported (Thomas & Trombe, 2001).

The structure of a suberate–nickel(II) complex has been published recently (Zhang & Zheng, 2003). This complex, like (I), is distinguished by its good crystallinity, which is unexpected when the acid has a long aliphatic chain (Bussien Gaillard *et al.*, 1998). These results highlight the need for caution about the specific character of the rare-earth dicarboxylates, the templating role of water molecules during crystallization and the effect of the hydrogen-bond network on enhancing the crystalline stability. One important structural feature influencing the kind of framework seems to be four-membered rings and creates, in some cases, a packing with a grid-like arrangement of the metal ions. In view of the limited number of complexes studied (Kiritsis *et al.*, 1998; Wang *et al.*, 2000; Sun *et al.*, 2002), we cannot yet assess whether this feature depends on the parity of *n*, but we note that an even number of C atoms in the alkyl spacer can introduce higher local symmetry, which in turn may influence the interlayer interactions.

Experimental

Compound (I) was prepared according to a previously reported procedure (Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000; Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegroune, 2000), using a mixture of La_2O_3 and suberic acid in a 1:3 molar ratio and a reflux time of 10 h. Single crystals of the complex were deposited after one week when the cooled reaction mixture was allowed to stand in air at 313 K.

Crystal data

$[La(C_8H_{12}O_4)(C_8H_{13}O_4)(H_2O)]$
$M_r = 502.28$
Triclinic, $P\overline{1}$
$a = 8.582$ (2) Å
$b = 9.079$ (1) Å
$c = 13.092$ (4) Å
$\alpha = 100.59$ (1)°
$\beta = 103.66$ (1)°
$\gamma = 97.83$ (1)°
$V = 957.0$ (4) Å^3
$Z = 2$
$D_x = 1.743$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 38 534 reflections
$\theta = 2.5$–30.5°
$\mu = 2.28$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.4 × 0.3 × 0.3 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: empirical (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.47$, $T_{max} = 0.51$
38 534 measured reflections

5739 independent reflections
5279 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 30.5°$
$h = -11 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.09$
5739 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -1.21$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0549 (15)

Table 1
Selected geometric parameters (Å, °).

La1—O3^{v}	2.4772 (12)	O1—C1	1.235 (3)
La1—O1	2.4799 (15)	O2—C1	1.267 (2)
La1—O7^{vi}	2.4920 (16)	O3—C8	1.278 (2)
La1—O6^{vii}	2.5057 (12)	O4—C8	1.246 (2)
La1—O*W*1	2.5688 (18)	O5—C9	1.239 (2)
La1—O4^{viii}	2.5779 (14)	O6—C9	1.289 (2)
La1—O5	2.5984 (14)	O7—C16	1.221 (3)
La1—O6	2.6331 (13)	O8—C16	1.273 (3)
La1—O3^{viii}	2.6807 (13)	O8—H8	1.04 (3)
O1—La1—O7^{vi}	79.29 (6)	La1^{v}—O3—La1^{ix}	114.02 (5)
O1—La1—O5	74.22 (5)	La1^{vii}—O6—La1	113.03 (5)
O6^{vii}—La1—O6	66.96 (5)	O1—C1—O2	123.85 (19)
O5—La1—O6	49.55 (4)	O4—C8—O3	120.06 (16)
O3^{v}—La1—O3^{viii}	65.98 (5)	O5—C9—O6	120.36 (16)
O4^{viii}—La1—O3^{viii}	49.09 (4)	O7—C16—O8	123.2 (2)
C1—C2—C3—C4	174.54 (19)	C9—C10—C11—C12	174.9 (2)
C2—C3—C4—C5	−176.4 (2)	C10—C11—C12—C13	−178.0 (2)
C3—C4—C5—C6	178.5 (2)	C11—C12—C13—C14	177.9 (2)
C4—C5—C6—C7	−176.8 (2)	C12—C13—C14—C15	−178.8 (2)
C5—C6—C7—C8	−175.64 (19)	C13—C14—C15—C16	179.6 (2)

Symmetry codes: (v) $2 - x, 2 - y, 1 - z$; (vi) $x - 1, y - 1, z - 1$; (vii) $2 - x, 2 - y, -z$; (viii) $x - 1, y, z - 1$; (ix) $1 + x, y, 1 + z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8···O2^{x}	1.04 (3)	1.46 (3)	2.441 (3)	153
O*W*1—H2*W*···O2^{xi}	0.93	1.98	2.782 (3)	144
O*W*1—H1*W*···O8^{viii}	0.92	2.37	2.947 (3)	120
O*W*1—H1*W*···O3^{viii}	0.92	2.41	2.908 (3)	114

Symmetry codes: (viii) $x - 1, y, z - 1$; (x) $1 + x, 1 + y, 1 + z$; (xi) $x, 1 + y, z$.

All H atoms bonded to C atoms were placed in calculated positions, 0.97 Å from their parent atoms, and modelled as riding. Atom H8 on O8 was located from the Fourier syntheses and its position was refined freely, with $U_{iso}(H)$ constrained to $1.2U_{eq}(O8)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1323). Services for accessing these data are described at the back of the journal.

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