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A polynuclear coordination glutarate of lanthanum(III) with an uncommon cage feature

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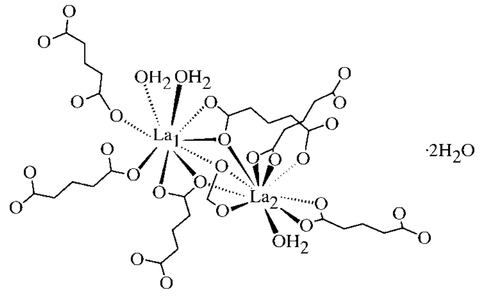
The title compound, triaquatris(glutarato)dilanthanum(III) dihydrate, $\{[La_2(C_5H_6O_4)_3(H_2O)_3]\cdot 2H_2O\}_n$, is the first reported glutarate coordination polymer of lanthanum(III) without a protonated ligand. The noteworthy features in the structure are, firstly, the unusual binuclear lanthanum cage formed by three bridging bonds through O atoms involved in different coordination modes and, secondly, the very rare 'malonate' mode exhibited by a dicarboxylate ligand with an alkyl chain of five C atoms. To our knowledge, this η^7 chelation for the glutarate ligand has not been reported and was thought to be forbidden for steric reasons. The *gauche–gauche* conformation of the corresponding ligand favours cage formation, but *trans* geometries created along the ligating O atoms prevent cluster packing. The two independent La atoms are nine- and tenfold coordinated, leading to distorted one-face-sharing $LaO_7(H_2O)_2$ and $LaO_9(H_2O)$ polyhedra, respectively. In the three-dimensional framework, these asymmetric subunits are linked in a zigzag manner *via* one-edge-sharing $LaO_9(H_2O)$ polyhedra and are connected by the carbon backbone chains of the ligands. The structure is very compact and, unlike many other reported dicarboxylate lanthanides, connectivity between the two metal atoms and the three ligands yields a crystal packing with cavities accommodating two guest water molecules but without an open framework.

Comment

Relatively recently, interest in rare-earth complexes obtained with aliphatic dicarboxylic acids, $HOOC(CH_2)_nCOOH$, has increased owing to the variety of their structural types and the potential uses of these compounds as luminescent sensors, precursors for superconductor oxides or microporous materials. Particular emphasis has been placed on the design, crystal architecture and properties of the resulting coordination polymers, as illustrated by the generation of organic–inorganic hybrids exhibiting open frameworks and mainly obtained with heavier lanthanides [Pr^{3+} (Serpaggi & Férey, 1999; Hernandez-Molina *et al.*, 2000), Eu^{3+}, Nd^{3+}, Ho^{3+} (Wang *et al.*, 2000; Hernandez-Molina *et al.*, 2002), Ce^{3+} (Sun *et al.*, 2002) and La^{3+} (Dimos *et al.*, 2002)]. A typical framework is thought to depend on the chain length of the ligand, the parity of the number of C atoms in the ligand and the size of the metal atom. In this context, we recently investigated the use of the largest lanthanide cation (La^{3+}) for connecting malonate ($n = 1$) or glutarate ($n = 3$) anions (Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000; Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegroune, 2000). The latter contains both glutarate and hydrogen glutarate ligands. In the course of this study, we found that by varying the pH and molar ratio of the starting materials it is possible to obtain the first glutarate lanthanum compound without a protonated ligand or disordered water molecule, *viz.* $[La_2(C_5H_6O_4)_3(H_2O)_3]\cdot 2H_2O$, (I), the structure of which is reported here.



(I)

Fig. 1 shows a view of the coordination around the two crystallographically independent La atoms and reveals some unprecedented and totally unexpected structural features. A novel binuclear cage assembly connects the two La atoms *via* three bridging bonds through O atoms belonging to two ligands. The only previously known glutarate cage compound, involving Ag atoms and two ligands, contains tetranuclear cluster units (Michaelides *et al.*, 1995). In (I), the three independent dicarboxylate ligands, denoted *L*1, *L*2 and *L*3, adopt several different modes of bonding. The least common is shown by *L*1, one of the two ligands involved in the cage structure. Ligand *L*1 exhibits an eight-membered-ring analogue to the so-called 'malonate' mode. This coordination, which gives η^7 chelation in the case of the glutarate ligand ($n = 3$), and is quite common in oxalates ($n = 0$) and malonates ($n = 1$), appearing particularly when the ligand is linked to 3*d* ions. In the higher series ($n > 1$), η^7 chelation was thought to be forbidden for steric reasons (Rodriguez-Martin *et al.*, 2002). The *gauche–gauche* conformation of *L*1, illustrated by the C7—C8—C9—C10 [65.4 (4)°] and C6—C7—C8—C9 [54.6 (4)°] torsion angles, which do not deviate significantly from the ideal *gauche* value (60°), is very similar to that found in the tetranuclear silver glutarate cluster and favours cage formation. However, *trans*-type geometries created along the ligating O atoms (O5/O6 and O7/O8) prevent cluster packing. Despite its conformation and its relatively long alkyl chain, *L*1

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adopts simultaneously the 'malonate' mode and bis-bridging-chelating bonding, behaving overall as tris-chelating, as do the two isostructural malonate compounds obtained with the La (Marrot & Trombe, 1993) or Pr atoms (Hernandez-Molina *et al.*, 2000). The surprising range of bonding offered by *L*1 shows that the glutarate is closely related to malonate or to the simplest dicarboxylate ligand, oxalate, and that it is not affected by the electronic structure of the linked metal ion. Thus, from the point of view of connectivity, within the same ligand, three tridentate O-atom bridges form three different kinds of ring, *viz*. two four-membered rings corresponding to bidentate bonding, one four-membered La/O/La/O ring linking two metal atoms through a μ-oxo bridge, and one eight-membered ring.

Ligand *L*2 adopts a bis-bridging-chelating mode and, unlike *L*1, which involves only one O atom in the cage structure, completes the cage with two O-atom bridges. Ligand *L*3 acts as a bidentate ligand by one function, in which atoms O9 and O10 coordinate to the same La atom, and as a conventional carboxylate bridge by its second function, in which atoms O11 and O12 coordinate to two different La atoms.

The three ligands exhibit different conformations, as indicating by their torsion angles (Table 1). Ligand *L*1 adopts an envelope conformation, while *L*2 and *L*3 are twisted, the conventional bridges of the latter being in a *syn–anti* conformation. In the cage assembly presenting rhombic angles (see Table 1), La2 is ten-coordinated, the coordinating O atoms comprising four atoms from *L*1, three from *L*2, two from *L*3 and one from a water molecule. La1 is nine-coordinated, three O atoms belonging to *L*2, two each belonging to *L*1 and *L*3, and two belonging to the water molecules. The corresponding coordination polyhedra are distorted as a consequence of the bite angles, which are very small [ranging from 47.42 (7) to 49.99 (7)°] and cannot be described easily in terms of regular geometry. On extending the criteria proposed for eight-coordinate complexes (Haigh, 1995) to higher coordinations, we found that the best polyhedral description is a tetracapped trigonal prism around La2 (atoms O10, O7^{iv}, O5 and O9 occupy the equatorial capping positions; all symmetry codes are as in Table 1) and a monocapped dodecahedron around La1 (O5 being in the axial capping position). The dihedral angle [28.8 (1)°] between the triangular faces O7/O*W*3/O8^{iv} and O1/O5/O3^{iii}, and the dihedral angle [82.2 (1)°] between the trapezoidal O11^{ii}/O3^{iii}/O*W*2/O*W*1 and O12^{i}/O1/O5/O6 planes, show that these two geometries are very distorted. The metal–metal distances, ranging from 4.195 (3) Å (La1···La2; connection by face sharing) to 4.525 (3) Å (La2···La2^{iv}; connection by edge sharing) to 4.728 (3) Å [La1···La1^{viii}; connection across the conventional carboxylate bridge; symmetry code: (viii) $1 - x, -y, 1 - z$], are sufficiently large to imply no metal–metal bonding and therefore no cluster packing.

The distances and angles in the three ligands and the La—O bond lengths in the two polyhedra are similar to those found in the six lanthanum dicarboxylates whose structures are already known (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), with a relatively high dispersion of the La—O bond lengths [2.537 (3)–2.724 (2) Å for atom La1 and 2.502 (2)–2.749 (2) Å for atom La2] and with one longer bond corresponding to one μ-oxo bridge [La2—O7^{iv} = 2.829 (2) Å]. This long distance and the relatively long C—O distances in the ligands are, as expected, associated with the tridentate O atoms [C1—O1 = 1.272 (4) Å, C5—O3 =

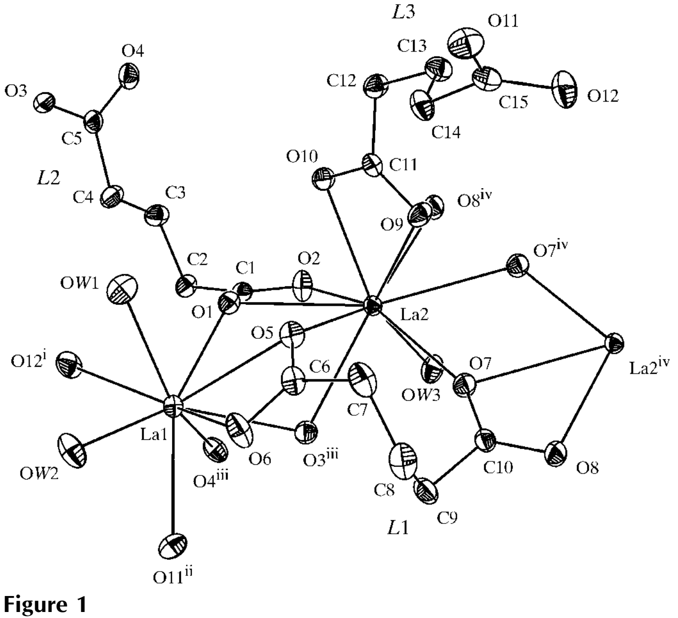

Figure 1
The coordination around the two La atoms, the cage feature, the η^7 chelation and the La/O/La ring in (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as in Table 1.

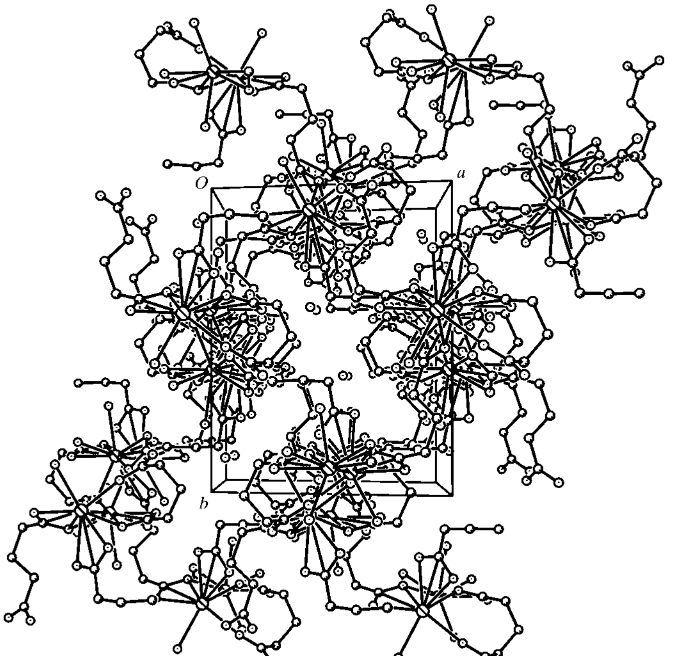

Figure 2
The packing of (I), viewed along the *c* axis. All H atoms have been omitted for clarity.

1.277 (4) Å, C6—O5 = 1.275 (4) Å and C10—O7 = 1.268 (4) Å]. It seems, moreover, that such distances are typical of the chelating carboxylate groups in rare-earth complexes (Hansson, 1973*a*,*b*,*c*; Benmerad, Guehria-Laïdoudi, Balegroune *et al.*, 2000; Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegroune, 2000; Thomas & Trombe, 2001). The other distances and angles in the free ligands have typical values. The co-existence of a binuclear cage assembly with the coordination scheme exhibited by *L*1 yields corrugated sheets extending along the [001] direction and based on repeated units consisting of three lanthanum polyhedra, *viz*. the La1 polyhedron, sharing one face (O1/O3^{iii}/O5) with the La2 tetracapped trigonal prism, which shares, in turn, one edge (O7/O7^{iv}) with another La2 ligand. As shown in Fig. 2, these dense sheets are connected *via* the carbon backbone chains of *L*2, which link the one-face-sharing polyhedra approximately in the [110] direction, and of *L*3, running along [100], which link the one-edge-sharing polyhedra. The framework is also strengthened by extensive hydrogen bonding (Table 2). A comparison of this structure with other known lanthanide glutarates (Głowiak *et al.*, 1986, 1987; Serpaggi *et al.*, 1998; Serpaggi, Férey & Antic Fidancev, 1999; Serpaggi, Luxbacher *et al.*, 1999; Thomas & Trombe, 2001) reveals the singular behaviour of this lanthanum glutarate. Even though its chemical formula is similar to those of the isostructural La (Marrot & Trombe, 1993) and Pr malonates (Hernandez-Molina *et al.*, 2000), the crystal structure of (I) is completely different and exhibits interesting structural features not predicted by recent calculations made on dicarboxylates of Eu, Nd and Ho (Wang *et al.*, 2000). Unlike most of the recently published α,ω-dicarboxylate lanthanides, the connectivity of the two La atoms in (I) yields a three-dimensional packing without an open framework. From this point of view, this compound is similar to the terbium complex containing both oxalate and glutarate (Thomas & Trombe, 2001) ligands. However, the resulting polymeric structure accommodates two guest water molecules. The unusual structural features of this compound highlight the need for caution in defining a unified set of criteria governing the specific crystal packing of the lanthanide coordination polymers.

Experimental

The title compound was prepared according to the procedure described for the preparation of $[La(C_5H_6O_4)(C_5H_7O_4)(H_2O)]\cdot H_2O$ by Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegroune (2000), using La_2O_3 and glutaric acid in a 1:4 molar ratio. Single crystals suitable for X-ray diffraction were grown at 313 K after being stored for a few days in the mother liquor at the same temperature.

Crystal data

$[La_2(C_5H_6O_4)_3(H_2O)_3]\cdot 2H_2O$
$M_r = 756.18$
Monoclinic, $P2_1/n$
$a = 11.438\ (2)$ Å
$b = 13.869\ (2)$ Å
$c = 15.635\ (5)$ Å
$\beta = 109.75\ (5)^\circ$
$V = 2334.3\ (12)$ Å^3
$Z = 4$

$D_x = 2.152$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8008 reflections
$\theta = 3.1$–32.5°
$\mu = 3.69$ mm^{-1}
$T = 293\ (2)$ K
Needle, colourless
0.4 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: empirical (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.32$, $T_{max} = 0.54$
54 342 measured reflections

8032 independent reflections
5517 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 32.5^\circ$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -21 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.084$
$S = 1.05$
8032 reflections
307 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.1548P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

La1—O12^{i}	2.522 (3)	La2—O7	2.509 (2)
La1—O11^{ii}	2.537 (3)	La2—O*W*3	2.532 (3)
La1—O*W*2	2.543 (3)	La2—O2	2.578 (3)
La1—O*W*1	2.563 (3)	La2—O10	2.592 (2)
La1—O1	2.564 (3)	La2—O9	2.596 (2)
La1—O6	2.567 (3)	La2—O8^{iv}	2.602 (3)
La1—O4^{iii}	2.617 (3)	La2—O3^{iii}	2.686 (2)
La1—O3^{iii}	2.704 (2)	La2—O1	2.749 (2)
La1—O5	2.724 (3)	La2—O7^{iv}	2.830 (2)
La2—O5	2.503 (3)		
O*W*2—La1—O*W*1	70.92 (9)	La2^{v}—O3—La1^{v}	102.22 (9)
O1—La1—O3^{iii}	65.56 (8)	C6—O5—La2	136.8 (2)
O4^{iii}—La1—O3^{iii}	48.71 (8)	La2—O5—La1	106.71 (9)
O1—La1—O5	63.79 (8)	C10—O7—La2	153.9 (2)
O6—La1—O5	48.94 (9)	O2—C1—O1	120.1 (3)
O3^{iii}—La1—O5	62.40 (7)	C4—C3—C2	112.8 (3)
O5—La2—O7	82.29 (8)	O4—C5—O3	119.8 (3)
O10—La2—O9	50.02 (7)	O6—C6—O5	120.4 (3)
O5—La2—O1	64.17 (8)	C6—C7—C8	111.5 (3)
O2—La2—O1	48.51 (8)	C7—C8—C9	114.8 (3)
O3^{iii}—La2—O1	63.36 (7)	C10—C9—C8	110.8 (3)
O7—La2—O7^{iv}	64.26 (9)	O8—C10—O7	120.7 (3)
O8^{iv}—La2—O7^{iv}	47.42 (7)	O9—C11—O10	120.8 (3)
La1—O1—La2	104.24 (9)	C12—C13—C14	114.0 (3)
O2—C1—C2—C3	−96.6 (4)	La2—O7—C10—O8	−176.9 (3)
O1—C1—C2—C3	82.6 (4)	C8—C9—C10—O8	87.1 (4)
C2—C3—C4—C5	170.7 (3)	C8—C9—C10—O7	−90.0 (4)
C3—C4—C5—O3	82.6 (4)	O9—C11—C12—C13	−4.1 (5)
La2—O5—C6—O6	−122.8 (3)	O10—C11—C12—C13	178.0 (3)
O6—C6—C7—C8	55.3 (5)	La1^{vi}—O11—C15—O12	161.1 (4)
O5—C6—C7—C8	−122.5 (4)	La1^{vii}—O12—C15—C14	169.4 (3)
C6—C7—C8—C9	54.6 (4)	C13—C14—C15—O12	−53.2 (5)
C7—C8—C9—C10	65.4 (4)		

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, -y, -z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H11···O8^{i}	0.83 (7)	1.98 (2)	2.80 (1)	166 (3)
O*W*1—H12···O*W*5^{ii}	0.81 (9)	2.15 (5)	2.94 (1)	162 (3)
O*W*2—H21···O10^{iii}	0.85 (5)	1.98 (5)	2.82 (1)	166 (3)
O*W*2—H22···O4^{iii}	0.83 (1)	1.94 (5)	2.77 (1)	176 (3)
O*W*3—H31···O9^{iv}	0.81 (1)	1.96 (9)	2.76 (1)	168 (3)
O*W*3—H32···O*W*5	0.81 (2)	1.90 (6)	2.71 (1)	173 (3)
OW5—H51···O2^{v}	0.87 (9)	2.03 (7)	2.88 (1)	161 (3)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{3}{2}$; (iv) $1-x, -y, -z$; (v) $-x, -y, -z$.

All H atoms bonded to C atoms were initially located from difference Fourier maps and were then placed in calculated positions (0.97 Å from their parent atoms) and modelled as riding. The two H atoms bonded to water atom O*W*4 were not found in the Fourier maps but are accounted for in the formula.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (CCDC, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1038). Services for accessing these data are described at the back of the journal.

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