metal-organic compounds

Polymeric aqua(glutarato)(hydrogen glutarato)lanthanum(III) monohydrate

Belkacem Benmerad,[a] Achoura Guehria-Laidoudi,[a] Fadila Balegroune,[a] Henrik Birkedal[b]* and Gervais Chapuis[b]

[a]Laboratoire de Cristallographie Appliquée, Institut de Chimie, USTHB, BP 32, El-Alia, 16111 Bab-Ezzouar Alger, Algeria, and [b]Institute of Crystallography, University of Lausanne, BSP, Dorigny, CH-1015 Lausanne, Switzerland
Correspondence e-mail: henrik.birkedal@ic.unil.ch

The structure of the title compound, $[La(C_5H_6O_4)(C_5H_7O_4)(H_2O)] \cdot H_2O$, consists of dense layers formed by chains of one-edge-sharing $LaO_9(H_2O)$ polyhedra, linked together by the glutarate ligand. The three-dimensional polymeric structure, built up through connection of these layers by the hydrogen glutarate ligand, exhibits cavities accommodating a guest water molecule. The lanthanum ion is tenfold coordinated by four glutarates, acting as bridging–chelating carboxylate groups, by three hydrogen glutarates, three times monodentate, and by one water molecule. Its coordination polyhedron is highly distorted and intermediate between a bicapped dodecahedron and a tetracapped trigonal prism. Hydrogen bonding links the two water molecules and the framework built up from this polynuclear coordination polymer. A very short hydrogen bond, $D \cdots A = 2.484\,(3)$ Å, links the protonated with the deprotonated acid groups in the hydrogen glutarate.

Comment

Aliphatic dicarboxylic acids, $HOOC(CH_2)_nCOOH$, present interesting complexing properties. This is due to the flexibility of the ligand which may be completely or only partially deprotonated. It has a large variation in coordination behaviour, even with large values of n, showing both poly-monodentate and/or chelating modes. This allows for clusters, cage structures or open frameworks. Combined with metallic cations assuming high coordination numbers, e.g. the rare earths, these ligands often yield infinite frameworks built up of polynuclear coordination polymers. This is due to the low directionality of the mainly electrostatic bonding of these cations. Two structural studies have been published on lanthanide glutarates (Głowiak et al., 1986; Serpaggi & Férey, 1998). Both studies exclude the lanthanum glutarate, which has not been synthesized so far.

We report in this paper the structure of the first lanthanum(III) compound obtained with glutaric acid: $[La(HL)(L)(H_2O)] \cdot H_2O$, (I). It contains hydrogen glutarate (HL)

and glutarate (L) groups. One interesting feature of the structure is the infinite helicoidal chains of one-edge-sharing $LaO_9(H_2O)$ polyhedra running along the [010] direction (Fig. 1). The repeat distance between two nearest-neighbour La^{3+} ions within the chain is 4.429 Å. The La^{3+} ions are slightly displaced, by 0.32 Å, off the helical axis. The structure can be regarded as dense layers parallel to the (100) plane located around $x = \frac{1}{4}$ and $x = \frac{3}{4}$. These are formed by the polyhedral chains described above, linked together by the glutarates running along the [001] direction. The layers are connected through the monodeprotonated glutarates building a three-dimensional polymeric structure. Their packing results in cavities accommodating one guest water molecule (Fig. 2).
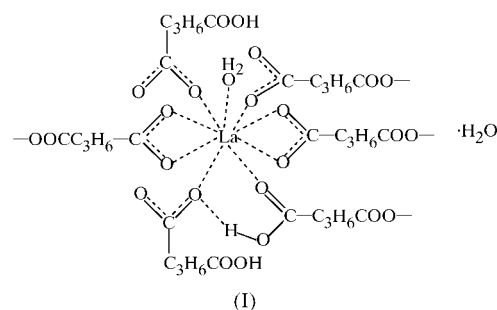

(I)

Fig. 3 shows the tenfold coordination of La^{3+}. The coordination sphere consists of four glutarates, three hydrogen glutarates and one water molecule. Although the dispersion of the bond lengths of lanthanum to oxygen is high [2.488 (2)–2.774 (2) Å, see Table 1], the average value of these distances is the same as otherwise found for ten-coordinated lanthanum (Marrot & Trombe, 1993, 1994). The glutarate ligand L is a bridging–chelating carboxylate group, in that it is bidentate by its two functions and one of the chelating O atoms bridges an adjacent metal atom. The doubly ligating O atoms (O11 and O13) show one short and one long La—O distance. The long distance is, as expected, associated with the bidentate function. The geometry of the two carboxylate groups of L is almost the same [the differences between the bond lengths are 0.000 (3) (La—O11^{ii}/La—O13$^{i}_{short}$), 0.055 (3) (La—O11/La—O13$^{iii}_{long}$) and 0.017 (3) Å (La—O12/La—O14$^{iii}_{monodentate}$)]. This coordination leads to the infinite chain of pairs along the [010] direction and makes up the dense layers mentioned above.

The hydrogen glutarate ligand, HL, is three times monodentate, coordinating with all its O atoms, except the oxygen which belongs to the hydroxyl function. The dispersion of La—O distances is smaller in this ligand [between 2.590 (2) and 2.699 (2) Å]. The distances within the acid group are somewhat different from what would be expected: they are almost the same in the two ends [C21—O21 1.293 (4) and
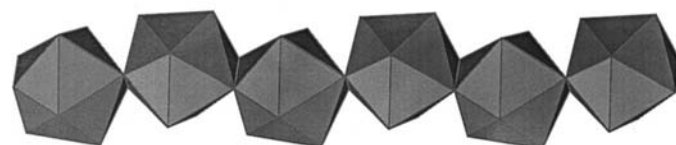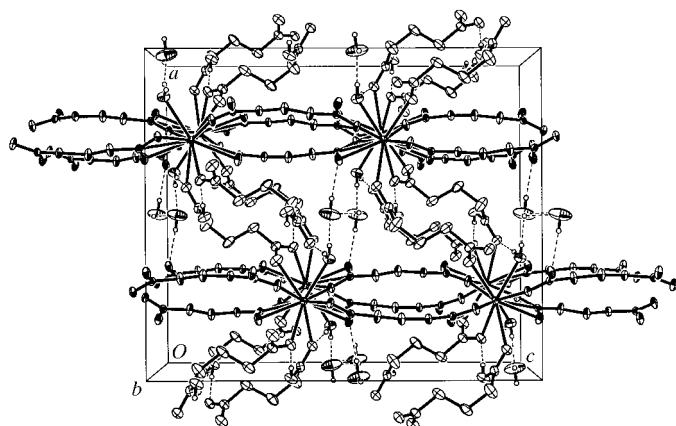

Figure 1
Chains of lanthanum polyhedra running along [010].

metal-organic compounds

Figure 2
Perspective view of the packing seen along the *b* axis. Only H atoms bound to O atoms have been included. Hydrogen bonds are indicated by dashed lines. Note the water-containing cavity in the centre. Full displacement ellipsoids are used for the fully deprotonated ligand *L*, while open ellipsoids are used for H*L*. Ellipsoids are drawn at the 50% probability level.

C25—O24 1.292 (4) Å, and C21—O22 1.240 (4) and C25—O23 1.242 (4) Å], despite the fact that one is deprotonated and the other is protonated. This is different from the expected values if we refer to the usual distances of 1.214 Å for C=O and 1.308 Å for C—OH (Allen *et al.*, 1995). However, this bonding situation resembles that of salts of dicarboxylic acids (Speakman, 1972). In addition, the C—C distances adjacent to the acid groups fit exactly with expected values: C21—C22 is 1.520 (5) Å, which is expected for the C—C distance in C—

COO⁻ (Allen *et al.*, 1995); C24—C25 is 1.504 (5), while the expected C—C distance in C—COOH is 1.502 Å.

The conformation of the two independent ligands *L* and H*L* is completely different, as indicated by the dihedral angles in each ligand (Table 1). *L* adopts an extended conformation, while H*L* is twisted (Fig. 3). All the CCOO groups are planar. In *L*, C13, C14 and C15 are the only coplanar C atoms. This plane forms angles of 30.25 (20) and 17.45 (17)° with the C12—C11—O11—O12 and C14—C15—O13—O14 planes, respectively. In H*L*, atoms C21, C22, C23 and C24 form a plane that has an angle of 71.5 (2)° with the C22—C21—O21—O22 plane and 73.3° with the C24—C25—O23—O24 plane. The angle between the two acid planes is 30.40 (11)° in *L*, while in H*L* it is 40.49 (19)°.

The coordination polyhedron is very distorted and may be described as intermediate between a bicapped dodecahedron and a tetracapped trigonal prism (Kepert, 1965; Marrot & Trombe, 1993).

Hydrogen-bonding geometries are given in Table 2. The protonated acid group of H*L* donates the H atom to a very short hydrogen bond to the carboxylate end of H*L* (see Fig. 3). This strong hydrogen bond probably stabilizes the coordination geometry. Similar hydrogen bonds are found in acid salts of dicarboxylic acids in which hydrogen dicarboxylate ions are linked by short hydrogen bonds into infinite chains (Speakman, 1972).

Another framework-stabilizing hydrogen bond is present between the coordinating water molecule and the deprotonated acid group of H*L*. The non-coordinating water molecule is kept in place by hydrogen bonding with the coordinating
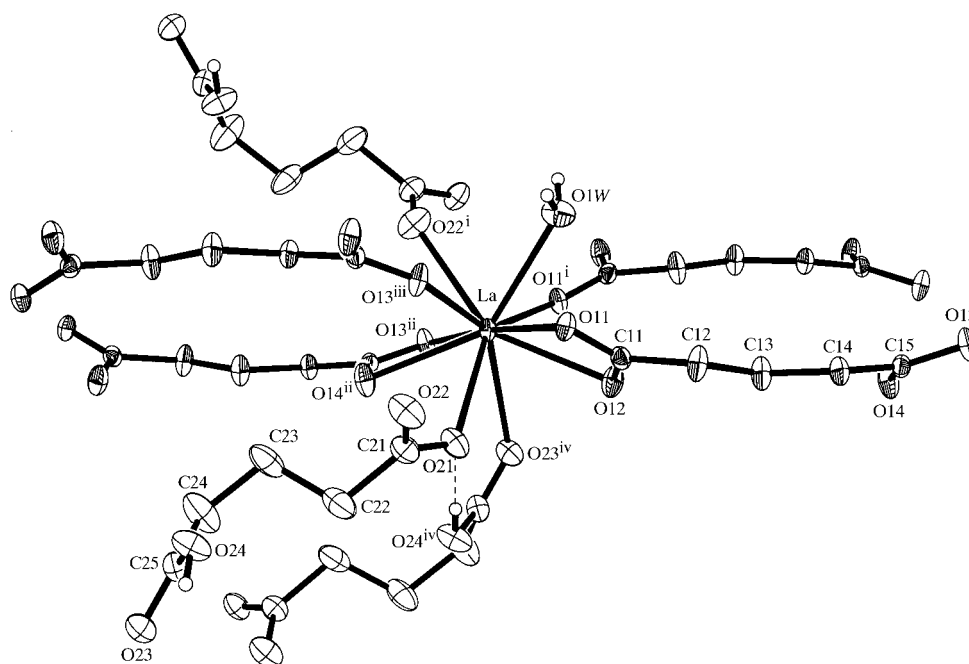
Figure 3
Coordination around the lanthanum ion, including the numbering scheme and anisotropic displacement ellipsoids. Note the strong O24—H24···O21ⁱᵛ hydrogen bond. Only the unique chains have been labelled completely. The symmetry operations are as in Table 1. The view is along the *b* axis. Full displacement ellipsoids are used for the fully deprotonated ligand *L*, while open ellipsoids are used for H*L*. Ellipsoids are drawn at the 50% probability level.

framework (Fig. 2). It is disordered (see *Experimental*), but the disorder could not be resolved with the present data. Due to the disorder, there is a very short hydrogen–hydrogen contact, $H2W1\cdots H2W1^{iii} = 1.90$ Å [symmetry code: (iii) $-x$, $2 - y$, $1 - z$], and the $O2W\cdots O2W$ hydrogen bond has a distorted geometry. It can reasonably be assumed that the non-coordinating water plays a templating role during crystallization.

The framework created by the packing is that of parallelepipeds formed by the La^{3+} ions. The shortest dimensions of the La parallelepipeds are along the b axis (the helical axis). In the ac plane, the dimensions are 9.96×9.78 Å^2, with a major angle of $124.6°$.

This structure is closely related to the two isostructural compounds $Nd_2(C_5H_6O_4)_3(H_2O)_2 \cdot 2H_2O$ (Głowiak *et al.*, 1986) and $Nd_2(C_5H_6O_4)_3(H_2O)_2 \cdot 4H_2O$ (Serpaggi & Férey, 1998). The heavier lanthanide structures (Nd and heavier) are all isostructural, at least when using the same synthesis path (Serpaggi & Férey, 1998). Nd is ninefold coordinated while here we find tenfold coordination. The Nd structures crystallize in $C2/c$ and show an almost square grid of Nd ions. The Nd structures are related to that of (I) by exchanging a and b. The solvent-containing cavities are truly open in the Nd compound, leading to open solvent channels. In the present structure, they are collapsed into isolated cavities from which no easy solvent-diffusion path is present.

The differences between the heavier lanthanides and the La structure point to the possibility of obtaining new phases by varying the synthesis temperature and pH, and, consequently, the number of water molecules of crystallization. The importance of this factor is underlined by the fact that the glutarates of all the lanthanoids have been obtained previously except the glutarate of lanthanum.

Experimental

The title compound was obtained by applying grown phase under reflux, the preparation process being comparable with that used by Marrot & Trombe (1994). After mixing appropriate amounts of glutaric acid and lanthanum oxide, with carefully controlled pH and temperature, single crystals were obtained from the mother liquor after 10 d.

Crystal data

$[Ln(C_5H_6O_4)(C_5H_7O_4)(H_2O)] \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 436.15$	Cell parameters from 10 492
Orthorhombic, $Pbca$	reflections
$a = 16.4027 (6)$ Å	$\theta = 3.56–27.72°$
$b = 8.76805 (19)$ Å	$\mu = 3.088$ mm^{-1}
$c = 19.5576 (4)$ Å	$T = 293 (2)$ K
$V = 2812.76 (13)$ Å^3	Needle, colourless
$Z = 8$	$0.27 \times 0.07 \times 0.03$ mm
$D_x = 2.060$ Mg m^{-3}	

Data collection

Kuma CCD diffractometer	2764 reflections with $I > 2\sigma(I)$
Oscillation method, φ and ω scans	$R_{int} = 0.040$
Absorption correction: Gaussian	$\theta_{max} = 27.72°$
(*XPREP*; Siemens 1996a)	$h = -20 \rightarrow 18$
$T_{min} = 0.576$, $T_{max} = 0.906$	$k = -11 \rightarrow 11$
25 012 measured reflections	$l = -25 \rightarrow 25$
2992 independent reflections	

Table 1
Selected geometric parameters (Å, °).

La—O11	2.776 (2)	C12—C13	1.522 (4)
La—O12	2.584 (2)	C13—C14	1.524 (4)
La—O11^i	2.488 (2)	C14—C15	1.517 (4)
La—O13^{ii}	2.721 (2)	C15—O13	1.276 (3)
La—O14^{ii}	2.601 (2)	C15—O14	1.255 (3)
La—O13^{iii}	2.488 (2)	C21—O21	1.293 (4)
La—O21	2.692 (2)	C21—O22	1.240 (4)
La—O22^i	2.590 (2)	C21—C22	1.520 (5)
La—O23^{iv}	2.699 (2)	C22—C23	1.531 (5)
La—O1W	2.603 (2)	C23—C24	1.528 (5)
C11—O11	1.275 (3)	C24—C25	1.504 (5)
C11—O12	1.256 (3)	C25—O23	1.242 (4)
C11—C12	1.514 (4)	C25—O24	1.292 (4)
O11—La—O12	48.27 (6)	La^v—O11—La	114.47 (7)
O11—La—O11^i	113.91 (7)	La^{vi}—O13—La^{vii}	116.41 (7)
O11^i—La—O12	78.25 (7)	O12—C11—O11	120.6 (3)
O13^{ii}—La—O14^{ii}	48.76 (6)	O14—C15—O13	120.7 (3)
O13^{ii}—La—O13^{iii}	120.95 (8)	O22—C21—O21	122.8 (3)
O13^{iii}—La—O14^{ii}	83.29 (7)	O23—C25—O24	122.8 (3)
O21—La—O22^i	131.69 (7)		
O11—C11—C12—C13	−158.3 (3)	O21—C21—C22—C23	−107.7 (4)
O12—C11—C12—C13	20.7 (5)	O22—C21—C22—C23	70.5 (4)
C11—C12—C13—C14	174.3 (3)	C21—C22—C23—C24	−179.9 (3)
C12—C13—C14—C15	−169.2 (3)	C22—C23—C24—C25	61.7 (5)
O13—C15—C14—C13	162.2 (3)	O23—C25—C24—C23	−156.1 (4)
O14—C15—C14—C13	−17.1 (5)	O24—C25—C24—C23	23.4 (5)
O11—C11—C15—O13	9.9 (5)	O21—C21—C25—O23	49.8 (5)
O11—C11—C15—O14	−148.3 (4)	O21—C21—C25—O24	169.5 (4)
O12—C11—C15—O13	165.5 (4)	O22—C21—C25—O23	−138.5 (4)
O12—C11—C15—O14	7.4 (3)	O22—C21—C25—O24	−18.8 (3)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 6.3345P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.049$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.188$	$\Delta\rho_{max} = 1.28$ e Å^{-3}
2992 reflections	$\Delta\rho_{min} = -0.71$ e Å^{-3}
204 parameters	Extinction correction: *SHELXL*97
H atoms treated by a mixture of	(Sheldrick, 1997)
independent and constrained	Extinction coefficient: 0.00071 (7)
refinement	

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1W—H1W2$\cdots$O23^i	0.82	2.04	2.857 (3)	174
O1W—H1W1$\cdots$O2W^{ii}	0.82	1.94	2.764 (4)	178
O2W—H2W1$\cdots$O2W^{iii}	0.82	2.35	2.960 (8)	132
O2W—H2W2$\cdots$O12	0.82	2.04	2.856 (4)	173
O24—H24$\cdots$O21^{iv}	0.82	1.67	2.484 (3)	176

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

H atoms on C atoms were generated (after having been observed in the difference map) and refined in the riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The acid-group H atom was refined as a rotating riding atom. The water H atoms were picked from the difference map and included with restraints $d(O—H) = 0.820 (5)$ and $d(H\cdots H) = 1.30 (1)$ Å, producing an angle of $\sim 104.5°$. These restraints are so hard that the internal water geometry is given by them and the data determine only the orientation of the water molecules. For all H atoms bound to O atoms, $U_{iso}(H) = 1.5U_{eq}(O)$. Water molecule

metal-organic compounds

2 (O2*W*) shows some anisotropy in the anisotropic displacement parameters, the ratio of the largest and smallest eigenvalues of the anisotropic displacement parameter tensor being 4.6. In addition, the equivalent isotropic displacement parameter of O2*W* is 2.33 (6) times larger than that of O1*W*. This, together with the rather small hydrogen-bond angle between two symmetry-related water molecules (132°), points toward some residual disorder. Attempts to resolve this were not successful. It should be noted that even with a split description of the O atom, only one position for each H atom was visible in the difference map.

Data collection: *KM*4*CCD* (Kuma, 1999); cell refinement: *KM*4*RED* (Kuma, 1999); data reduction: *KM*4*RED* and *XPREP* (Siemens 1996*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens 1996*b*) and *CRYSTALMAKER* (CrystalMaker Software, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1364). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, ch. 9.5, pp. 685–760. Dordrecht: Kluwer Academic Publishers.

CrystalMaker Software (2000). *CRYSTALMAKER* 3.01. CrystalMaker Software, Oxfordshire, England.

Głowiak, T., Dao-Cong-Ngoan & Legendziewicz, J. (1986). *Acta Cryst.* C**42**, 1494–1496.

Kepert, D. L. (1965). *J. Chem. Soc.* p. 4736.

Kuma (1999). *KM*4*CCD* and *KM*4*RED*. Kuma Diffraction Instruments GmbH, PSE–EPFL, CH-1015 Lausanne, Switzerland.

Marrot, F. & Trombe, J. C. (1993). *C. R. Acad. Sci.* **317**, 319–324.

Marrot, F. & Trombe, J. C. (1994). *Polyhedron*, **13**, 1931–1935.

Serpaggi, F. & Férey, G. (1998). *J. Mater. Chem.* **8**, 2737–2741.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1996*a*). *XPREP*. Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996*b*). *XP*. Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Speakman, J. C. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.