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Polymeric tetraaquatris(malonato)-dilanthanum(III) monohydrate

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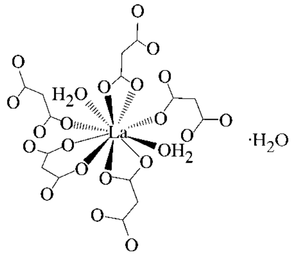
The title compound, $[La_2(C_3H_2O_4)_3(H_2O)_4]\cdot H_2O$, forms a layer-type polymeric structure. The layers, which contain infinite puckered four-membered La—O—La—O rings in a pseudo-ternary symmetry, are formed by the lanthanum and one independent malonate group. They are interconnected by the second independent malonate group, giving a three-dimensional framework in which wide channels accommodate one disordered water molecule of crystallization. The La atom lies on a twofold axis and is ten-coordinated by eight O atoms from carboxylate groups and two water molecules. One malonate group is monodentate and triply bridging chelating, whilst the other is doubly monodentate. The extensive network of hydrogen bonds and bridge bonds observed in this structure enhances the structural stability. Despite some identical subfeatures, this structure is quite different from that observed in $[La_2(C_3H_2O_4)_3(H_2O)_3]\cdot 2H_2O$.

Comment

In the binary complexes of lanthanides with malonic acid, there are three different isostructural series characterized by the number of water molecules and the lanthanoid cation (Hansson, 1973*a*). For the complexes of lanthanum, two structural studies have been published, one containing malonate ions (Marrot & Trombe, 1993) and the other both malonate and hydrogen malonate ions as ligands (Marrot & Trombe, 1994). The complex $[La_2(C_3H_2O_4)_3]\cdot 5H_2O$ was presented as showing two different phases in the monoclinic system and the structure of one of these phases, (I), is the subject of the present publication, only its space group and unit-cell dimensions having been reported previously. Our overall goal is to improve the conditions of the synthesis leading to a pure single phase and to investigate the factors enhancing the stability of solid dicarboxylate lanthanides as a function of the chain length of the carboxylic acid molecule.

The general features of the structure, without the hydrogen bonding, are shown in Fig. 1. There are two crystallographically independent malonate ligands; *L*1, of point symmetry 1, and *L*2, of point symmetry 2. The three-dimensional packing of the ligand complexes is essentially built from a two-dimensional substructure. Indeed, the structure can be described in terms of a layer-type polymeric structure built up from lanthanum–malonate *L*1 layers parallel to (100), including puckered four-membered La—O—La—O rings running in a zigzag manner along the *b* axis. Each La atom is surrounded by three such rings in a pseudo-ternary symmetry. These layers are connected together through *L*2 malonates to form the three-dimensional network. The resulting packing shows wide channels parallel to the *b* axis surrounded by the carbon backbone chain of the *L*2 malonates and by the O atoms of the coordinating water molecules. Of the two and a half nominal water molecules in each asymmetric unit, two are coordinated to the La atom as intra-layer water and the rest located in a disordered fashion in the channels and not coordinated to lanthanum.



(I)

A view of the ten-coordination around the La atom is shown in Fig. 2. The ten coordinating O atoms are made up of seven from four *L*1 malonates, one from one *L*2 malonate and two from two water molecules. One of the *L*1 malonates is monodentate through the O2*A* atom and the other three are chelating, one involving a six-membered chelate ring (called the 'malonate' mode). Moreover, each O atom in *L*1 coordinates to two La atoms leading to bridging interactions, except for O4*A* which only coordinates to one La atom. As a result, there are two kinds of four-membered rings: one is the La—O—C—O chelate ring formed by the bidentate coordi-

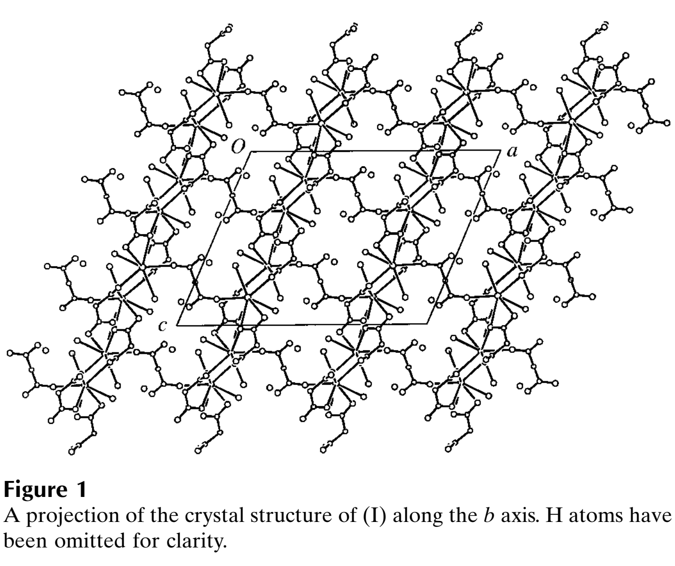


Figure 1
A projection of the crystal structure of (I) along the *b* axis. H atoms have been omitted for clarity.

nation and the other involves the La—O—La—O rings formed by the bridging structure. Across this latter, the closest distance between two La^{3+} ions is 4.5479 (4) Å. Each *L*1 malonate is surrounded by four La atoms, while the *L*2 malonate, which is doubly monodentate, bridges two La atoms. The two metal-bonded O atoms in this ligand are *trans* as a consequence of its twofold symmetry. Despite this feature, and the fact that the malonate ligand is less sterically demanding than other dicarboxylates, the coordination polyhedron is a very distorted bicapped dodecahedron. This is probably due to the large distortions imposed by the bite angles which are considerably smaller [46.90 (5) and 48.41 (6)°] than those found in other malonate compounds (Tapparo *et al.*, 1996; Barbaro *et al.*, 1997) as a consequence of the two coordinating water molecules which are far from a *trans* coordination, the angle between them being 134.07 (7)°. Within the layers described above, each polyhedron shares three common edges (O1*A*—O2*A*, O1*A*^{i}—O2*A*^{i} and O3*A*—O3*A*^{ii}; see Table 1 for symmetry codes) with three adjacent polyhedra.

The distances and angles in the two independent ligands and the La—O bond lengths agree with those found in analogous compounds (Marrot & Trombe, 1993, 1994), with one La—O bond being considerably longer. This kind of distance seems to be rather typical of the chelating carboxylate group (Hansson, 1973*a*,*b*).

All water molecules are involved in an extensive network of hydrogen bonds amongst themselves and with the non-bridging O atoms of the ligands (O2*B* and O4*A*). It appears that, in addition to the oxygen bridge bonds involving the *L*1 malonate, the hydrogen bonds are responsible for the stability of the structure. This explains why all known well defined crystalline dicarboxylate lanthanides are hydrated, except for one complex of neodymium (Hansson, 1973*c*) and one of gadolinium (Trollet *et al.*, 1997).

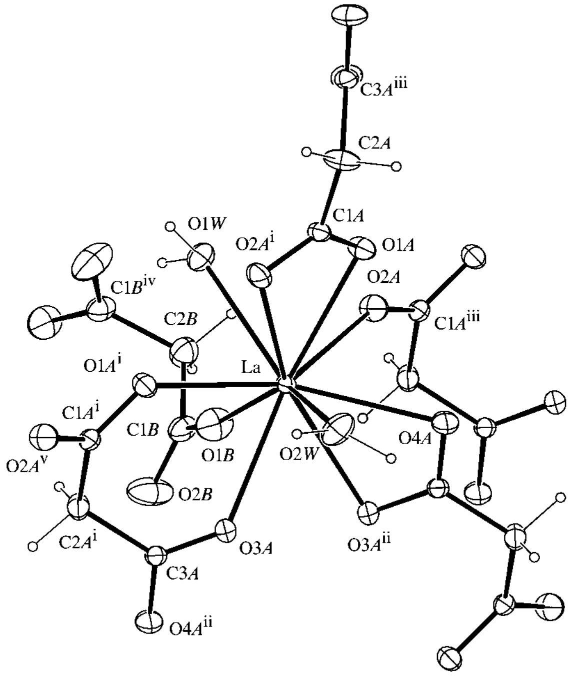


Figure 2
Perspective drawing showing the local coordination environment, the labelling scheme and 50% probability displacement ellipsoids [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $1 - x, y, \frac{1}{2} - z$; (v) $x, y + 1, z$].

A comparison with other recently reported dicarboxylate lanthanides (Wen Mei *et al.*, 1992; Serpaggi & Férey, 1998; Serpaggi *et al.*, 1999) reveals that all these structures contain the same structural subfeature, including four-membered rings. However, the phase $[La_2(C_3H_2O_4)_3(H_2O)_3]\cdot 2H_2O$ reported earlier (Marrot & Trombe, 1993) is quite different as two crystallographically independent La atoms are present. One is coordinated to nine malonate O atoms and one water molecule, whilst the other is bonded to eight malonate O atoms and two water molecules. Moreover the three independent malonate ligands exhibit different coordination modes including a triply monodentate mode.

Experimental

The preparation procedure is comparable to that used by Marrot & Trombe (1993), with carefully controlled pH (4) and temperature (353 K). The single crystals were grown at 313 K after having been stored for one month in mother liquor at the same temperature.

Crystal data

$[La_2(C_3H_2O_4)_3(H_2O)_4]\cdot H_2O$
$M_r = 674.0$
Monoclinic, C_2/c
$a = 19.2890$ (10) Å
$b = 7.0740$ (6) Å
$c = 14.575$ (2) Å
$\beta = 113.448$ (9)°
$V = 1824.5$ (4) Å^3
$Z = 4$
$D_x = 2.454$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 14$–25°
$\mu = 4.706$ mm^{-1}
$T = 293$ K
Plate, colourless
0.37 × 0.26 × 0.07 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical (*Xtal LSABS*; Hall *et al.*, 1992)
$T_{min} = 0.244$, $T_{max} = 0.719$
4447 measured reflections
3995 independent reflections
3640 reflections with $F_o > 4\sigma(F_o)$
$R_{int} = 0.018$
$\theta_{max} = 35°$
$h = -30 \rightarrow 28$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 23$
2 standard reflections
frequency: 30 min
intensity decay: 2.3%

Refinement

Refinement on F
$R = 0.022$
$wR = 0.028$
$S = 1.162$
3640 reflections
162 parameters
H atoms: see below
$\omega = 1/[\sigma^2(F_o) + 0.00025(F_o^2)]$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.82$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}
Extinction correction: isotropic type 1 (Zachariasen, 1967)
Extinction coefficient: 30 (2) × 10^2

The uncoordinated water molecule (O3*W*) is disordered and its population parameter has been refined to 0.501 (11). The H atoms of *L*1 and *L*2 were observed and refined with isotropic displacement parameters and the H atoms of the coordinated water molecules were refined with restraints on bond lengths and angles. The H atoms of the uncoordinated disordered water molecule could not be located. C2*B* is located on the special position 4*e*.

Table 1
Selected geometric parameters (Å, °).

La—O1*A*	2.669 (2)	O1*A*—C1*A*	1.268 (3)
La—O2*A*	2.5844 (17)	O2*A*—C1A^{iii}	1.255 (3)
La—O3*A*	2.6281 (17)	O3*A*—C3*A*	1.270 (3)
La—O4*A*	2.6625 (17)	O4*A*—C3A^{ii}	1.248 (4)
La—O1*B*	2.412 (3)	C1*A*—C2*A*	1.507 (5)
La—O1*W*	2.6354 (16)	C2*A*—C3A^{iii}	1.515 (3)
La—O2*W*	2.527 (2)	O1*B*—C1*B*	1.259 (4)
La—O1A^{i}	2.5723 (16)	O2*B*—C1*B*	1.245 (4)
La—O2A^{i}	2.821 (3)	C1*B*—C2*B*	1.525 (4)
La—O3A^{ii}	2.6877 (17)		
O1*A*—La—O2A^{i}	46.90 (5)	O3*A*—C3*A*—C2A^{i}	120.4 (3)
O3*A*—La—O1A^{i}	65.43 (6)	O3*A*—C3*A*—O4A^{ii}	121.20 (18)
O4*A*—La—O3A^{ii}	48.41 (6)	C2A^{i}—C3*A*—O4A^{ii}	118.4 (3)
O1*W*—La—O2*W*	134.07 (7)	O1*B*—C1*B*—O2*B*	123.4 (3)
O1*A*—C1*A*—C2*A*	119.7 (2)	O1*B*—C1*B*—C2*B*	118.4 (3)
O1*A*—C1*A*—O2A^{i}	120.3 (3)	O2*B*—C1*B*—C2*B*	118.2 (2)
C2*A*—C1*A*—O2A^{i}	119.9 (3)	C1*B*—C2*B*—C1B^{iv}	107.6 (3)
C1*A*—C2*A*—C3A^{iii}	114.7 (3)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *LATCON* in *Xtal*3.2 (Hall *et al.*, 1992); data reduction: *DIFFRAC* (Flack *et al.*, 1992) and *Xtal*3.2; program(s) used to solve structure: *MULTAN*87 (Main *et al.*, 1987); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.2; molecular graphics: *Xtal_GX*3 (Hall & du Boulay, 1997); software used to prepare material for publication: *BONDLA CIFIO in Xtal*3.2.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1092). Services for accessing these data are described at the back of the journal.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*W*—H2*W*1···O1W^{i}	1.06 (3)	1.77 (3)	2.779 (3)	158 (3)
O1*W*—H1*W*2···O4A^{i}	1.02 (4)	1.67 (4)	2.688 (3)	172 (3)
O1*W*—H1*W*1···O2B^{ii}	1.00 (3)	1.70 (3)	2.699 (3)	173 (3)
O2*W*—H2*W*2···O2B^{iii}	1.02 (3)	1.84 (4)	2.763 (3)	149 (4)

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

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