

Poly[[tetraaquatris(μ_3 -2,2-dimethylmalonato)dilanthanum(III)] monohydrate]

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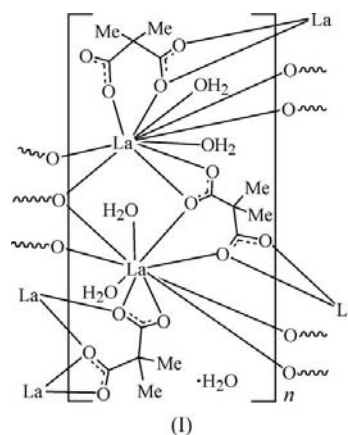
In the title complex, $[[\text{La}_2(\text{C}_5\text{H}_6\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}]_n$, the La atoms are connected by bridging O atoms from carboxylate groups to build, through centres of inversion, two-dimensional layers parallel to the *ac* plane containing decanuclear 20-membered rings. The coordinated water molecules are involved in intralayer hydrogen-bond interactions. Adjacent layers are linked *via* hydrogen bonding to the solvent water molecules. This work represents the first example of a new substituted malonate–lanthanide complex.

Comment

Recently, the design and preparation of novel lanthanide dicarboxylate metal–organic frameworks have received considerable attention because of the interesting properties that they exhibit, such as porosity, luminescence, magnetism and catalytic activity (Shi *et al.*, 2008; Luo *et al.*, 2008; Ghosh & Bharadwaj, 2005; Mahata & Natarajan, 2007; Wang *et al.*, 2007). Of these, malonate has been used as the ligand of choice for the design of such metal–organic frameworks/molecular assemblies because of its manifold coordination modes and the variety of the resulting architectures (Hansson, 1973*a,b*; Canadillas-Delgado *et al.*, 2006). Two complexes with lanthanum have been reported to date, one containing the malonate dianion (Marrot & Trombe, 1993; Benmerad *et al.*, 2000) and the other both the malonate dianion and the hydrogen malonate monoanion as ligands (Marrot & Trombe, 1994). However, in spite of this wealth of possibilities, no complexes of a lanthanide with dimethylmalonate have been reported to date. Using the 2,2-dimethylmalonate dianion as a ligand, we have obtained the novel title ten-coordinate dimethylmalonate–La complex, (I), which is described here.

The asymmetric unit of (I) contains two independent ten-coordinate La atoms, three independent dimethylmalonate dianions, denoted *L1*, *L2* and *L3* (containing O atoms O1–O4, O5–O8 and O9–O12, respectively), four coordinated water

molecules and one solvent water molecule. Selected geometric parameters are given in Table 1. Fig. 1 shows a symmetry-expanded view, which displays the full coordination of the two La atoms and gives details of the symmetry codes used below.



All the symmetry-related La atoms of (I) are related by inversion centres. Thus, the *L1* dianion is coordinated to centrosymmetrically related atoms La1 and La1ⁱ *via* bis-bidentate 1,2-chelating and six-membered ring modes. The *L2* dianion binds to atoms La1, La2 and La2ⁱⁱⁱ, with the two carboxylate groups using two bis-bidentate 1,2-chelating modes and one six-membered ring mode. The *L3* ligand also adopts two bis-bidentate 1,2-chelating modes and one six-membered chelating mode to connect to atoms La2, La1ⁱⁱ and La2ⁱⁱ, but it differs from the *L2* ligand with the bond angle at C12 being smaller than the normal value (Table 1), indicating that there is greater distortion in this six-membered ring. This smaller angle was observed in polymeric tetraaquatrimalonatodilanthanum(III) monohydrate complexes (Benmerad *et al.*, 2000).

The La–O distances in (I) (Table 1) are comparable with the values reported for polymeric tetraaquatrimalonatodilanthanum(III) monohydrate (Benmerad *et al.*, 2000), but with three La–O bonds being considerably longer. These longer distances seem to be rather typical of the chelating carboxyl-

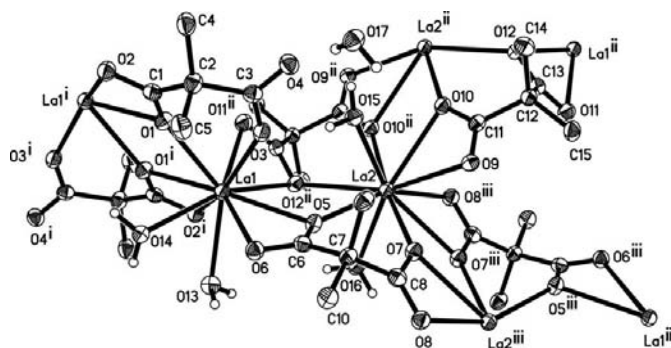
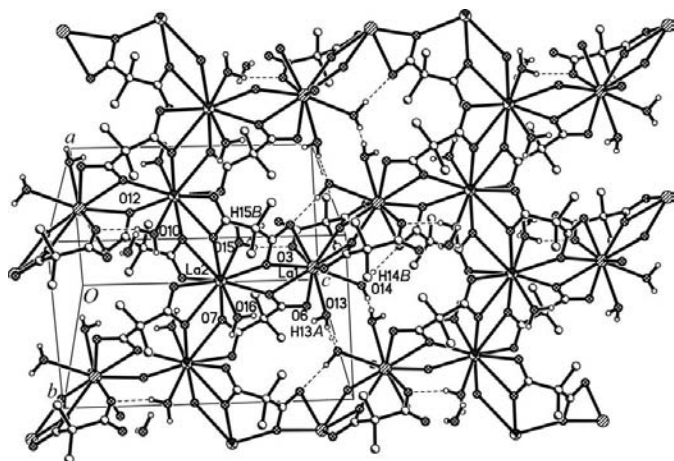


Figure 1

A view of part of the structure of (I), showing the atom-numbering scheme and the coordination for atoms La1 and La2. Displacement ellipsoids are drawn at the 30% probability level. The H atoms of the methyl groups have been omitted for clarity and the remaining H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 2, -y + 2, -z + 2$; (ii) $-x + 2, -y + 2, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$.]

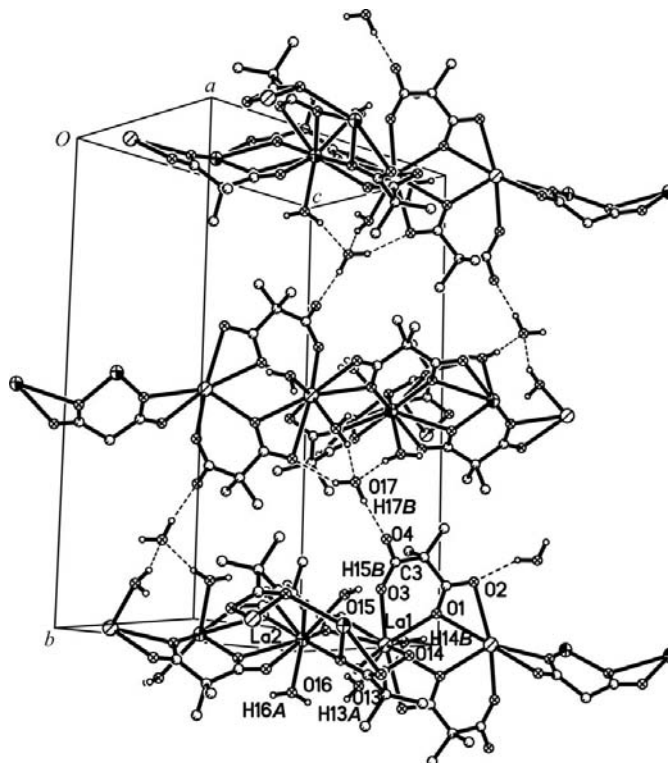

Figure 2

A partial packing diagram for (I), showing the two-dimensional polymeric layer and hydrogen-bonding interactions (as dashed lines) in the direction of the *ac* plane, viewed down the *b* axis. The H atoms of the methyl groups have been omitted for clarity.

ate group (Hansson, 1973*a,b*). The La geometries do not approximate to an idealized polyhedron, a bicapped square antiprism or a bicapped dodecahedron. This is not surprising in view of the steric requirements of the dimethylmalonate ligands in the structure and the large distortions imposed by the bite angles, which are considerably small (Table 1) (see Benmerad *et al.*, 2000). Through the centres of inversion, each group of six La2 atoms and four La1 atoms builds up a decanuclear 20-membered ring. These decanuclear rings are further joined into a two-dimensional layer structure parallel to the *ac* plane (Fig. 2).

Within these layers, strong intra- and intermolecular hydrogen-bond interactions (entries 6 and 7 in Table 2; Brown, 1976) are responsible for the formation of two six-membered hydrogen-bonded *S*(6) and *R*(6) ring graph sets (Bernstein *et al.*, 1995). The two coordinated water molecules, O13 and O14, are involved in a hydrogen bond (entry 9 in Table 2) which crosslinks two La1 atoms together within the decanuclear 20-membered ring *via* an $R_2^2(8)$ motif (Fig. 2), thus enhancing the stability of the decanuclear 20-membered ring. These two-dimensional dianionic (dimethylmalonato)lanthanum metal-organic layers occur near $y = 0$ and $y = \frac{1}{2}$ by way of the crystallographic twofold screw axis. The solvent water molecule (O17), acting as both proton donor and acceptor, provides strong interlayer binding along the *b* axis through further hydrogen bonds (entries 1–3 and 10 in Table 2; Fig. 3).

A comparison with the two previously reported lanthanum malonate compounds (Marrot & Trombe, 1993; Benmerad *et al.*, 2000) reveals that all these structures contain the same number of water molecules. However, the two crystallographically independent La atoms of the former are nine- and eight-coordinate, respectively, while in the latter there is only one crystallographically independent La atom and two independent malonate dianions. The present work therefore represents a new example of the substituted malonate series of lanthanide complexes.


Figure 3

A partial packing diagram for (I), showing the connection between neighbouring layers generated by the twofold screw axis. Interlayer hydrogen-bond interactions are shown as dashed lines. The H atoms of the methyl groups have been omitted for clarity.

Experimental

La_2O_3 (0.4 g, 1.2 mmol) was dissolved in dilute hydrochloric acid and the solvent evaporated to dryness. The resulting $\text{LaCl}_3 \cdot n\text{H}_2\text{O}$ was dissolved in distilled water (20 ml) at room temperature, and then dimethylmalonic acid (0.3 g, 2.3 mmol) and sodium dimethylmalonate (0.6 g, 3.4 mmol) were added under continuous stirring. After filtration, slow evaporation over a period of two weeks at room temperature provided colourless needle-shaped crystals of (I).

Crystal data

$[\text{La}_2(\text{C}_5\text{H}_6\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$	$V = 2388.2$ (8) \AA^3
$M_r = 758.19$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.3835$ (17) \AA	$\mu = 3.61$ mm^{-1}
$b = 20.229$ (4) \AA	$T = 133$ K
$c = 14.101$ (3) \AA	$0.12 \times 0.08 \times 0.06$ mm
$\beta = 92.989$ (3)°	

Data collection

Rigaku Saturn diffractometer	13664 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MS, 2005)	4177 independent reflections
$T_{\min} = 0.715$, $T_{\max} = 0.802$	3140 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	313 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 0.94$	$\Delta\rho_{\text{max}} = 1.04$ e \AA^{-3}
4177 reflections	$\Delta\rho_{\text{min}} = -0.81$ e \AA^{-3}

Table 1

Selected geometric parameters (Å, °).

La1—O3	2.421 (4)	La2—O7	2.544 (4)
La1—O1	2.490 (4)	La2—O9	2.574 (4)
La1—O13	2.550 (4)	La2—O5	2.590 (3)
La1—O5	2.594 (4)	La2—O10 ⁱⁱ	2.599 (4)
La1—O1 ⁱ	2.604 (4)	La2—O8 ⁱⁱⁱ	2.604 (4)
La1—O11 ⁱⁱ	2.620 (4)	La2—O12 ⁱⁱ	2.617 (4)
La1—O12 ⁱⁱ	2.623 (4)	La2—O7 ⁱⁱⁱ	2.712 (4)
La1—O14	2.625 (4)	La2—O10	2.756 (4)
La1—O6	2.645 (4)	O3—C3	1.260 (6)
La1—O2 ⁱ	2.747 (4)	O4—C3	1.222 (6)
La2—O15	2.466 (4)	O6—C6	1.251 (7)
La2—O16	2.498 (4)	O7—C8	1.273 (6)
O11 ⁱⁱ —La1—O12 ⁱⁱ	49.23 (12)	O9—La2—O10	48.49 (11)
O13—La1—O14	66.83 (12)	C1—C2—C3	114.8 (4)
O5—La1—O6	49.18 (11)	C8—C7—C6	112.8 (4)
O15—La2—O16	140.22 (13)	C13—C12—C11	105.7 (4)
O8 ⁱⁱⁱ —La2—O7 ⁱⁱⁱ	48.59 (11)		

Symmetry codes: (i) $-x+2, -y+2, -z+2$; (ii) $-x+2, -y+2, -z+1$; (iii) $-x+1, -y+2, -z+1$.**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O17—H17B ^{iv} ···O4	0.85	1.84	2.681 (5)	171
O17—H17A···O2 ^{iv}	0.85	2.06	2.810 (6)	146
O16—H16B···O17 ^v	0.85	1.98	2.819 (5)	169
O16—H16A···O9 ⁱⁱⁱ	0.85	1.99	2.773 (5)	153
O15—H15B···O8 ^{vi}	0.85	2.00	2.777 (5)	151
O15—H15A···O3	0.85	1.90	2.709 (5)	160
O14—H14B···O11 ^{vii}	0.85	1.82	2.667 (6)	176
O14—H14A···O6 ^{viii}	0.85	2.01	2.754 (5)	145
O13—H13B···O14 ^{viii}	0.85	1.99	2.828 (5)	168
O13—H13A···O17 ^v	0.85	1.91	2.707 (5)	155

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

The H atoms of the water molecules were found in a difference Fourier map. However, during refinement, they were treated as riding

with O—H = 0.85 Å and their U_{iso} values were set at $1.2U_{\text{eq}}(\text{O})$. The H atoms of the C—H groups were treated as riding, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3119). Services for accessing these data are described at the back of the journal.

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