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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.028
 wR factor = 0.070
 Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

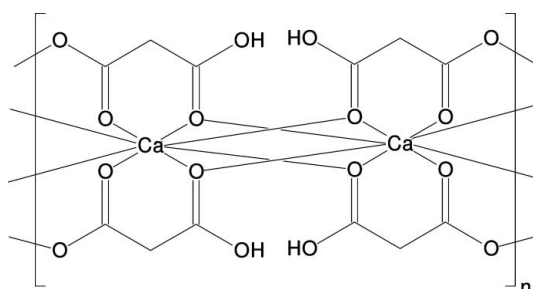
Poly[bis(μ_3 -dihydrogen malonato)calcium(II)]

The title compound, $[\text{Ca}(\text{C}_3\text{H}_3\text{O}_4)_2]_n$, has a polymeric structure, built up from noncentrosymmetric Ca_2O_{12} face-sharing bipolyhedra, linked through the spacers of the ligands and forming a complex three-dimensional framework containing empty channels parallel to the [001] direction. The calcium ion lies on a 2 axis and is coordinated by eight O atoms from six hydrogen malonate ligands in a distorted bicapped dodecahedron. The tridentate ligand displays an η^5 -chelating coordination mode and forms both $\mu_{1,1}$ and $\mu_{1,3}$ bridges. In the extended network, the protonated O atom is involved in a strong hydrogen bond with a deprotonated O atom, forming an infinite array of the ligands. An $M-\text{O}-M$ infinite linkage characteristic of metal-organic frameworks is prevented here by cage assembly around the metal.

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Comment

The binding of alkaline-earth ions to partially or completely deprotonated dicarboxylate ligands often leads to extended structures, depending on the geometric constraints of both the metal ion and the linker. The anions obtained from malonic acid are among the most flexible ligands for building supramolecular frameworks. In the case of calcium, the resulting complex can serve as a model for interactions taking place in supramolecular and biological systems (Li *et al.*, 2002; Zell *et al.*, 1985). Several calcium malonates have been reported (Hodgson & Asplund, 1990; Brusau *et al.*, 1999, 2002). To the best of our knowledge, however, there are few structural reports on hydrogen malonate complexes, especially those involving alkaline-earth metals (Briggman & Oskarsson, 1978), although one barium complex has been reported containing both the malonate ion and malonic acid as ligands (Hodgson & Asplund, 1991). Here we present the crystal structure of the title compound, (I).



(I)

Four $\mu_{1,1}$ oxo-bridges link two crystallographically equivalent Ca^{2+} cations and construct the basic dinuclear unit (Fig. 1).

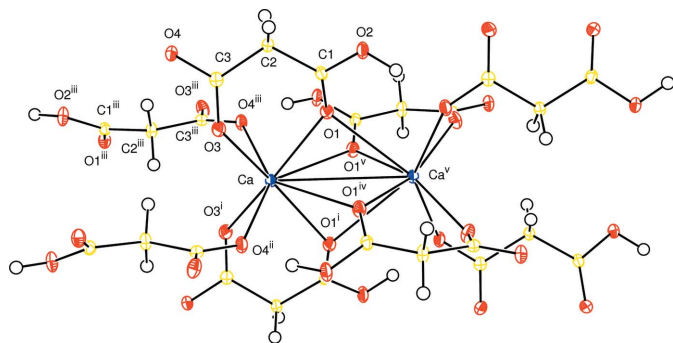


Figure 1
Part of the polymeric structure, with 50% probability displacement ellipsoids. Symmetry codes are as in Tables 1 and 2.

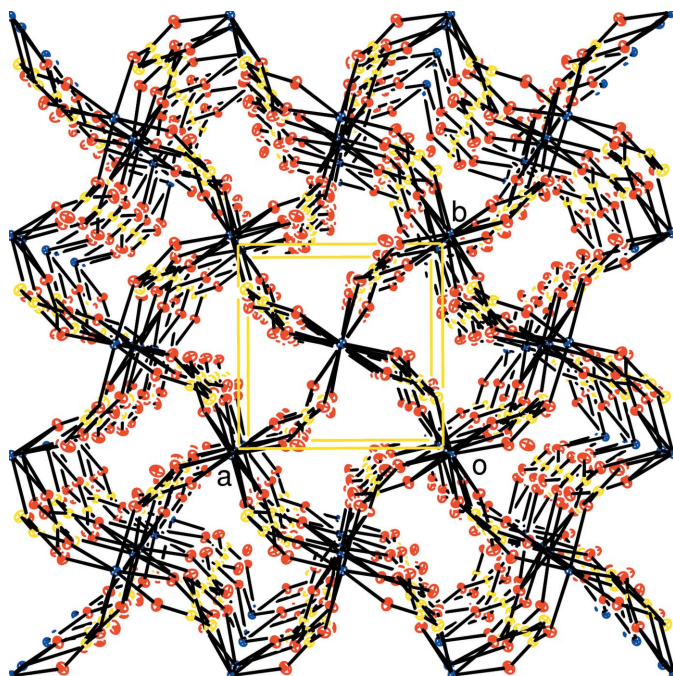


Figure 2
Perspective view of the packing, viewed along the *c* axis. H atoms have been omitted for clarity.

Within this, as in related compounds (Karipides *et al.*, 1977; Riou-Cavellec *et al.*, 2000), the distance between the two Ca^{2+} ions is very short [3.626 (9) Å] compared with the internuclear distance in calcium metal (Einspahr & Bugg, 1974). Worth mentioning here is that this short distance is associated with weak binding around the Ca^{2+} ion (Table 1). Indeed, the range of Ca—O bond lengths is great [2.3210 (12)–2.8541 (12) Å] and the bonds are much longer than expected for calcium carboxylates (Einspahr & Bugg, 1981), especially the Ca—O bond involving the triply bridging O atom. The Ca^{2+} ion lies on a $\bar{4}$ axis and is coordinated by eight O atoms from six hydrogen malonate ligands, in a distorted bicapped dodecahedral geometry. The crystallographically unique ligand is tridentate, involving all its unprotonated O atoms in the coordination to the metal, and displays a η^5 coordination mode, with chelation and both $\mu_{1,1}$ and $\mu_{1,3}$ bridges. The conventional carboxylate bridge is in an *anti-anti* conformation, while the other end of

the ligand deviates significantly from ideal *syn-anti* behaviour.

The overall network is rather similar to that of barium glutarate (Aliouane *et al.*, 2007). However, the lack of a mirror plane in the space group of this structure affects some features, particularly the basic unit, which is a Ca_2O_{12} bipolyhedron, and the orientation of the binding sites, leading to a complex three-dimensional packing. The protonated O atom is involved in a strong hydrogen bond with a deprotonated one, forming an infinite array of the ligands (Table 2). Despite these differences, there is a similar pseudo-eight-sided grid network exhibiting empty channels (Fig. 2). This study confirms that an *M—O—M* infinite linkage characteristic of metal-organic frameworks is prevented here by cage assembly around the metal.

Experimental

A mixture of malonic acid (0.312 g, 3 mmol) and calcium hydroxide (0.0714 g, 1 mmol) in 15 ml of deionised water was introduced into a 23 ml Teflon-lined stainless steel vessel. The vessel was sealed, heated to 420 K for three days and cooled to room temperature. Crystals were separated by filtration.

Crystal data

[$\text{Ca}(\text{C}_3\text{H}_3\text{O}_4)_2$]
 $M_r = 246.19$
Tetragonal, $P\bar{4}_21c$
 $a = 7.8705$ (1) Å
 $c = 13.4367$ (7) Å
 $V = 832.33$ (5) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.78$ mm⁻¹
 $T = 100$ (2) K
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: part of the refinement model (ΔF) (*DIFABS*; Walker & Stuart, 1983)
 $T_{\min} = 0.804$, $T_{\max} = 0.830$

16443 measured reflections
1215 independent reflections
1183 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.070$
 $S = 1.11$
1215 reflections
72 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³
Absolute structure: Flack (1983), 504 Friedel pairs
Flack parameter: -0.02 (6)

Table 1
Selected geometric parameters (Å, °).

Ca—O3	2.3210 (12)	Ca—O1 ⁱⁱ	2.8541 (12)
Ca—O1	2.3591 (12)	Ca—Ca ⁱⁱⁱ	3.6268 (8)
Ca—O4 ⁱ	2.4137 (12)		
O1 ^{iv} —Ca—O1	103.68 (6)	O1 ⁱⁱ —Ca—O1 ⁱⁱⁱ	81.07 (5)
O1—Ca—O1 ⁱⁱⁱ	61.99 (2)		
Ca ⁱⁱⁱ —O1—C1—C2	-176.83 (10)	C1—C2—C3—O3	3.1 (2)
O1—C1—C2—C3	31.6 (2)	C1—C2—C3—O4	-178.56 (14)
O2—C1—C2—C3	-151.72 (14)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O4^v$	0.957 (18)	1.63 (2)	2.5800 (17)	168.42 (16)

Symmetry code: (v) $-y + \frac{3}{2}, -x + \frac{3}{2}, z - \frac{1}{2}$.

All H atoms were located in a difference Fourier map. Methylene H atoms were treated as riding, with $C-H = 0.99$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom of the carboxylic end of the ligand was refined with a restrained O-H distance of 0.84 (1) Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-MSN* (Otwinowski & Minor, 1997); data reduction: *DENZO-MSN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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