Twinned poly[[diaquacalcium(II)]-μ_4-benzene-1,3-dioxyacetato]

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The water-coordinated Ca atom in the layer structure of the title compound, $[Ca(C_{10}H_8O_6)(H_2O)_2]_n$, is connected to a carboxyl O atom of one $-O-CH_2-CO_2$ arm of the dicarboxylate dianion; it is also linked to an O atom of a carboxylate group of this arm of an adjacent dianion, as well as to the O atoms of the other arm of two different dianions. The six-coordinate octahedral geometry is distorted, owing to a weak interaction with the ether O atom of one of the arms; the dianion functions in a μ_4-bridging mode.

Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.009 Å
R factor = 0.061
wR factor = 0.203
Data-to-parameter ratio = 12.4

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

Comment

This report continues our studies of the metal derivatives of benzene-1,3-dioxyacetic acid; among the studies are two of main group complexes (Gao *et al.*, 2004; Liu *et al.*, 2004). The deprotonated dicarboxylate behaves in a μ_4-bridging mode in the title calcium derivative, (I) (see scheme), to link the $(H_2O)_2Ca$ units into a layer structure; the four carboxylate O atoms of the two $-O-CH_2-CO_2$ arms each bind to a different Ca atom (Fig. 1). However, the six-coordinate environment is distorted towards a pentagonal bipyramid, owing to an interaction involving the ether O atom of one of the arms (Fig. 2). The water molecules further consolidate the layer structure by hydrogen-bonding interactions within the layers (Table 2).

(I)
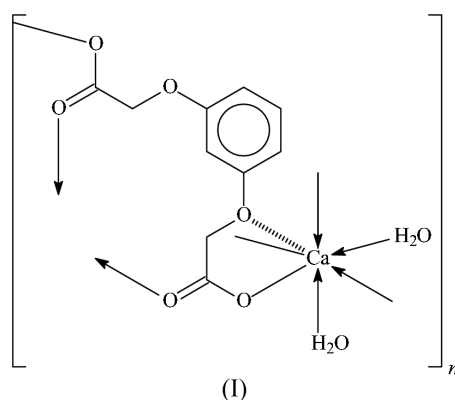
Experimental

Calcium nitrate hexahydrate (0.82 g, 3 mmol) and an excess of triethylamine (1 ml) were added to a hot aqueous solution of benzene-1,3-dioxydiacetic acid (0.68 g, 3 mmol). The solution was vigorously stirred and then set aside for several days to allow the colourless prismatic crystals to form. Elemental analysis calculated for $C_{10}H_{12}CaO_8$: C 40.00, H 4.03%; found C 40.04, H 4.06%.

metal-organic papers

$[Ca(C_{10}H_8O_6)(H_2O)_2]$
$M_r = 300.28$
Monoclinic, $P2_1/c$
$a = 15.795$ (3) Å
$b = 7.917$ (2) Å
$c = 9.829$ (2) Å
$\beta = 90.65$ (3)°
$V = 1229.0$ (4) Å³
$Z = 4$

$D_x = 1.623$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 9802
   reflections
$\theta = 3.3–27.5°$
$\mu = 0.54$ mm⁻¹
$T = 295$ (2) K
Prism, colourless
$0.39 \times 0.26 \times 0.15$ mm

Data collection

Rigaku R-AXIS RAPID
   diffractometer
ω scans
Absorption correction: multi-scan
   (*ABSCOR*; Higashi, 1995)
   $T_{min} = 0.638$, $T_{max} = 0.923$
9687 measured reflections

2153 independent reflections
1933 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 25.0°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.203$
$S = 1.11$
2153 reflections
173 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1067P)^2 + 4.6656P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å⁻³
$\Delta\rho_{min} = -0.96$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Ca1—O1	2.340 (5)	Ca1—O5[iii]	2.344 (5)
Ca1—O2[i]	2.347 (5)	Ca1—O1w	2.443 (5)
Ca1—O3	2.631 (5)	Ca1—O2w	2.409 (6)
Ca1—O6[ii]	2.365 (5)		
O1—Ca1—O2[i]	91.2 (2)	O3—Ca1—O5[iii]	109.0 (2)
O1—Ca1—O3	63.6 (2)	O3—Ca1—O6[ii]	74.4 (2)
O1—Ca1—O5[iii]	172.6 (2)	O3—Ca1—O1w	136.3 (2)
O1—Ca1—O6[ii]	90.1 (2)	O3—Ca1—O2w	137.1 (2)
O1—Ca1—O1w	86.4 (2)	O5[iii]—Ca1—O6[ii]	87.8 (2)
O1—Ca1—O2w	94.5 (2)	O5[iii]—Ca1—O1w	99.9 (2)
O2[i]—Ca1—O3	71.3 (2)	O5[iii]—Ca1—O2w	91.2 (2)
O2[i]—Ca1—O5[iii]	85.9 (2)	O6[ii]—Ca1—O1w	74.7 (2)
O2[i]—Ca1—O6[ii]	140.9 (2)	O6[ii]—Ca1—O2w	145.8 (2)
O2[i]—Ca1—O1w	144.4 (2)	O1w—Ca1—O2w	71.8 (2)
O2[i]—Ca1—O2w	73.0 (2)		

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1w—H1w1···O1[iv]	0.85	2.09	2.942 (7)	173
O1w—H1w2···O5[ii]	0.85	1.99	2.807 (7)	160
O2w—H2w1···O2[i]	0.85	2.26	3.004 (7)	147
O2w—H2w2···O1w[v]	0.85	2.12	2.960 (8)	174

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

The initial refinement converged at an R index of 0.20, although there were no large peaks in the difference Fourier map. An analysis of the observed and calculated structures factors for twinning by *PLATON* (Spek, 2003) showed that about half of the reflections (1210 out of 2153) had I_{obs} larger than I_{calc}. The use of the twin law suggested by *PLATON* lowered the R index to an acceptable level of about 0.08. The reflections beyond $2\theta_{max}$ of 50° were then excluded to lower the index further to 0.061. The final difference Fourier map had
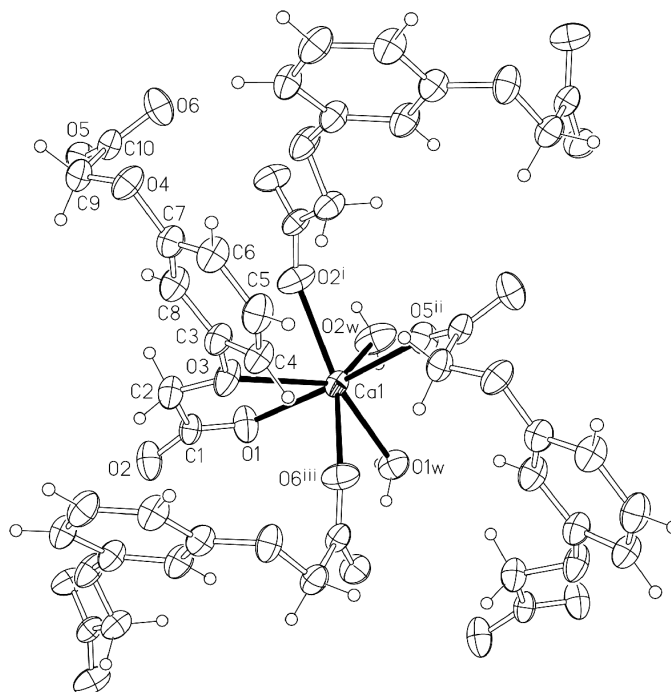

Figure 1
ORTEPII plot (Johnson, 1976) of a fragment of the layer structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. Symmetry codes are as used in Table 1.
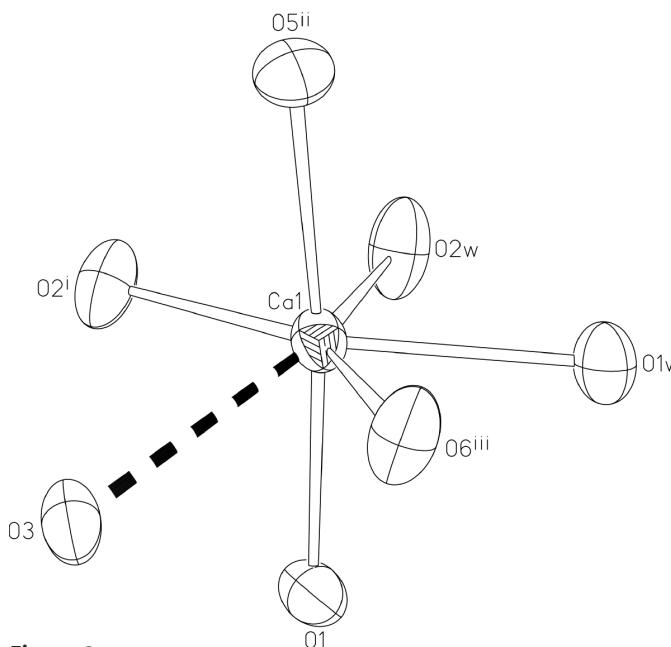

Figure 2
*ORTEP*II plot (Johnson, 1976), illustrating the distortion of the octahedral geometry of the Ca atom.

a large hole at about 1 Å from Ca1. The methylene and benzene H atoms were positioned geometrically [C—H = 0.97 Å for the methylene H atoms and 0.93 Å for the benzene H atoms; $U_{iso}(H) = 1.2U_{eq}(C)$] and were included in the refinement in the riding-model approximation. The water H atoms were placed in positions appropriate for hydrogen bonding, but were not refined; $U_{iso}(H) = 1.2U_{eq}(O)$.

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