research communications

Crystal structure of a polymeric calcium levulinate dihydrate: *catena*-poly[[diaquacalcium]-bis(μ2-4-oxobutanoato)]

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In the title calcium levulinate complex, $[Ca(C_5H_7O_3)_2(H_2O)_2]_n$, the Ca^{2+} ion lies on a twofold rotation axis and is octacoordinated by two aqua ligands and six O atoms from four symmetry-related carboxylate ligands, giving a distorted square-antiprismatic coordination stereochemistry [Ca—O bond-length range = 2.355 (1)–2.599 (1) Å]. The levulinate ligands act both in a bidentate carboxyl O,O'-chelate mode and in a bridging mode through one carboxyl O atom with an inversion-related Ca^{2+} atom, giving a Ca$\cdots$Ca separation of 4.0326 (7) Å. A coordination polymeric chain structure is generated, extending along the *c*-axial direction. The coordinating water molecules act as double donors and participate in intra-chain O—H$\cdots$O hydrogen bonds with carboxyl O atoms, and in inter-chain O—H$\cdots$O hydrogen bonds with carbonyl O atoms, thus forming an overall three-dimensional structure.

1. Chemical context

Levulinic acid (4-oxopentanoic acid) is a biomass-derived keto acid and is a potential precursor for renewable fuels as well as polymeric materials (Mukherjee *et al.*, 2015). A number of metal salts of levulinic acid have been prepared for a variety of applications and the calcium salt with formula $Ca(C_5H_7O_3)_2\cdot2H_2O$ is the most widely studied levulinate, as it has been used for over 80 years as a calcium supplement (Proskouriakoff, 1933). The revived interest in calcium levulinate is due to a recent discovery that pyrolysis of this readily accessible renewable biomass-based calcium salt can be used to produce biofuels *via* a ketonic decarboxylation process with recycling of calcium as $CaCO_3$ (Schwartz *et al.*, 2010; Case *et al.*, 2012). In addition, we have recently shown that acid-catalyzed hydrothermal degradation of cellulose and neutralization of the filtrate with calcium hydroxide can be used to prepare a mixture of calcium levulinate and calcium formate and the pyrolysis of this mixture at 623 K can be used to produce γ-valerolactone (Amarasekara *et al.*, 2015). Recently, Bryce and co-workers published the solid-state ^{13}C NMR spectrum of calcium levulinate in which they identified only one type of a levulinate anion (Widdifield *et al.*, 2014). However, there are no reports on X-ray crystallographic studies on this well known calcium carboxylate. Our interest in thermal properties and biofuel applications of calcium levulinate has led us to study the structure of this salt and in this communication we report the crystal structure of calcium levulinate dihydrate, $[Ca(C_5H_7O_3)_2(H_2O)_2]_n$.
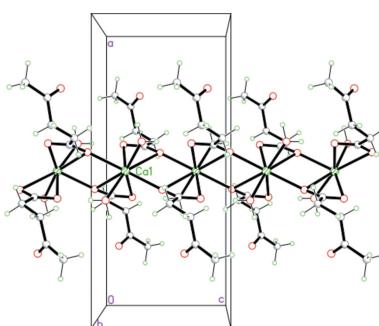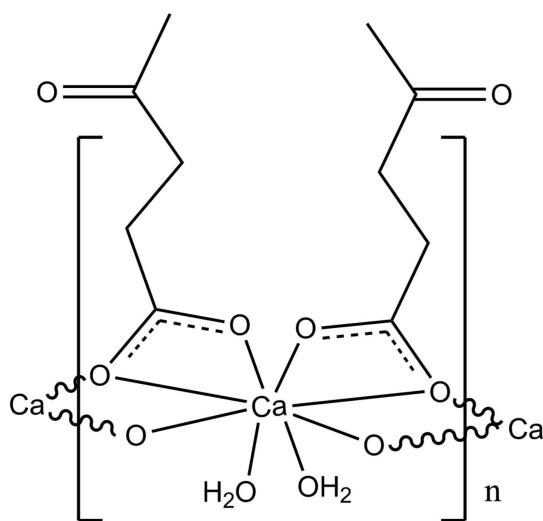
2. Structural commentary

The calcium levulinate structure contains one Ca^{2+} cation, two levulinate anions and two water molecules per formula unit, with the Ca^{2+} cation situated on a twofold rotation axis (Fig. 1). The cation is octacoordinated and exhibits a distorted square antiprismatic stereochemistry with Ca—O bond lengths in the range of 2.355 (1)–2.599 (1) Å (Table 1). The levulinate carboxyl O atoms (O1 and O2) coordinate to Ca^{2+} cations in two coordination modes, a bidentate O,O'-chelate mode and a bridging mode through O1^i with an inversion-related Ca^{2+} centre, giving a Ca1···Ca1^i or Ca1···Ca1^v separation of 4.0326 (7) Å [for symmetry code (i) see Table 1; symmetry code (v): $-x + 1, -y, -z$]. Furthermore, due to this type of coordination environment, the two levulinate anions are almost perpendicular to each other, with an O2—Ca1—O2^{iii}

Table 1
Selected bond lengths (Å).

Ca1—O1^i	2.3546 (10)	Ca1—O2^{iii}	2.4820 (10)
Ca1—O1^{ii}	2.3546 (10)	Ca1—O2	2.4820 (11)
Ca1—O4^{iii}	2.4367 (10)	Ca1—O1	2.5989 (10)
Ca1—O4	2.4367 (10)	Ca1—O1^{iii}	2.5990 (10)

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O4—H4A···O3^{iv}	0.90	2.02	2.8568 (15)	155
O4—H4B···O2^v	0.90	1.87	2.7519 (14)	168

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

angle = 75.78 (5)° [for code (iii), see Table 1]. The extended one-dimensional coordination polymeric chain generated lies parallel to the c axis (Fig. 2) and within each chain, the coordinating water molecules form intra-chain O4—H4B···O2$^v_{carboxyl}$ hydrogen-bonds (Table 2).

3. Supramolecular features

In the crystal, the polymer chains are linked *via* inter-chain hydrogen bonds between the second H atom of the coordinating water molecule and the carbonyl O atom of an adjacent chain (O4—H4A···O3^{iv}), giving an overall three-dimensional structure (Fig. 3) [for symmetry code (iv), see Table 2]. To achieve this hydrogen-bonding interaction, the levulinate molecule is twisted [torsion angle C1—C2—C3—C4 = 73.2 (2)°].


Figure 1
A portion of the crystal structure of the title complex, displaying the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code (v): $-x + 1, -y, -z$; for other codes, see Table 1.
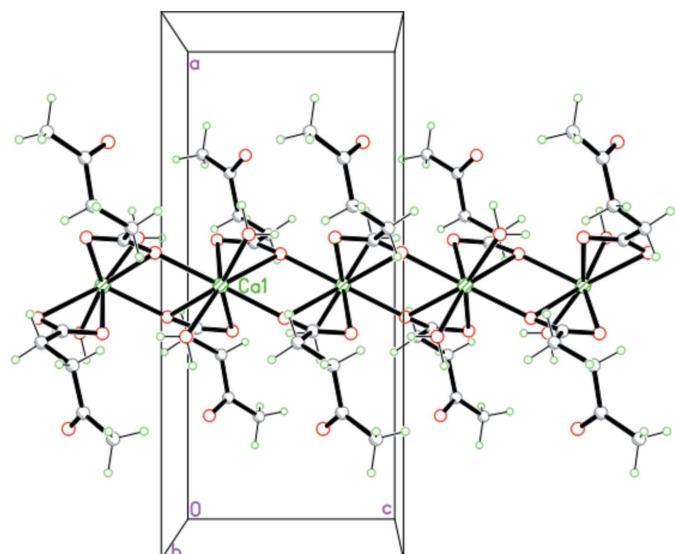
Figure 2
The one-dimensional coordination polymeric chain extending along the c axis.
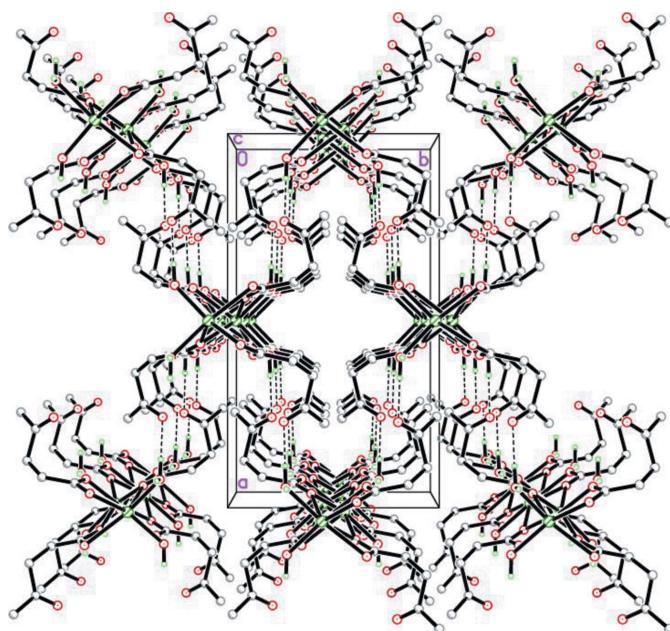
Figure 3
The three-dimensional hydrogen-bonded structure in the unit cell viewed along the *c* axis. Hydrogen-bonding interactions are shown as dashed lines.

4. Database survey

The Cu^{2+} levulinate structures represent examples of a very small number of metal levulinates in the crystallographic literature (Zubkowski *et al.*, 1997). Only one of these involves the levulinate ligand alone: a polymeric structure formed through carboxyl O-linked tetracarboxylate-bridged dimers, in which the copper atoms have nearly square-pyramidal coordination geometry. In the same report are the structures of three additional Cu^{2+} complexes with levulinate as well as other ligands: pyridine, 2,2′-bipyridine and triphenyl-phosphine. The crystal structures of two polymorphic forms of the analogous calcium acetate monohydrate salt are also known (Klop *et al.*, 1984; Van der Sluis *et al.*, 1987).

5. Synthesis and crystallization

Levulinic acid (1.160 g, 10.0 mmol) was added to a suspension of calcium hydroxide (0.370 g, 5.00 mmol) in 200 mL of deionized water in a beaker. The mixture was boiled with magnetic stirring on a hot plate to form a clear solution, then transferred to an evaporating dish and allowed to crystallize at room temperature. The product was collected under suction filtration, dried at 363 K for 24 h to give 1.455 g of calcium levulinate dihydrate as white needle-shaped crystals in 95% yield. Found: C, 39.02; H, 6.23; calculated for $[Ca(C_5H_7O_3)_2(H_2O)_2]$: C, 39.21; H, 5.92%. ^1H NMR (DMSO-$d6$) δ 2.05 (3H, *s*), 2.19 (2H, *t*, *J* = 6.8 Hz), 2.54 (2H, *t*, *J* = 6.8 Hz). ^{13}C NMR (DMSO-$d6$) δ 30.2, 31.5, 37.9, 179.6, 208.9. The single crystals for X-ray crystallographic analysis were grown by allowing a saturated solution of calcium levulinate dihydrate in 20% methanol in water to stand at room temperature for five days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were placed in calculated positions and allowed to ride on their carrier atoms: C—H = 0.93–0.97 Å with $U_{iso}(H)$ = $1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms. The water H atoms were found using a Fourier map and were also allowed to ride in the refinement, O—H = 0.90 Å and with $U_{iso}(H)$ = $1.5U_{eq}(O)$.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ca(C_5H_7O_3)_2(H_2O)_2]$
M_r	306.32
Crystal system, space group	Orthorhombic, *Pbcn*
Temperature (K)	100
a, *b*, *c* (Å)	17.644 (3), 9.9627 (19), 7.8160 (15)
V (Å^3)	1373.9 (5)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	0.49
Crystal size (mm)	0.94 × 0.11 × 0.08
Data collection	
Diffractometer	Bruker SMART APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.656, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11806, 1664, 1571
R_{int}	0.020
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.083, 1.16
No. of reflections	1664
No. of parameters	88
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.54

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

Crystal structure of a polymeric calcium levulinate dihydrate: *catena*-poly[[di-aquacalcium]-bis(μ_2-4-oxobutanoato)]

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Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

catena-**Poly[[diaquacalcium]-bis(μ_2-4-oxobutanoato)]**

Crystal data

[Ca(C$_5$H$_7$O$_3$)$_2$(H$_2$O)$_2$]	$F(000) = 648$
$M_r = 306.32$	$D_x = 1.481$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 8589 reflections
$a = 17.644$ (3) Å	$\theta = 2.3$–30.5°
$b = 9.9627$ (19) Å	$\mu = 0.49$ mm^{-1}
$c = 7.8160$ (15) Å	$T = 100$ K
$V = 1373.9$ (5) Å^3	Needle, colourless
$Z = 4$	$0.94 \times 0.11 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	11806 measured reflections
Radiation source: fine-focus sealed tube	1664 independent reflections
Graphite monochromator	1571 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$\theta_{max} = 28.0°$, $\theta_{min} = 2.3°$
	$h = -23 \rightarrow 23$
	$k = -13 \rightarrow 13$
$T_{min} = 0.656$, $T_{max} = 0.963$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.030$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.083$	
$S = 1.16$	Hydrogen site location: inferred from neighbouring sites
1664 reflections	
88 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.0525P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.5000	0.04993 (4)	0.2500	0.00808 (12)
O4	0.40994 (5)	0.20740 (10)	0.12520 (12)	0.0141 (2)
H4A	0.3629	0.1929	0.1655	0.021*
H4B	0.4086	0.1988	0.0107	0.021*
O2	0.58523 (5)	−0.14668 (10)	0.21809 (12)	0.0123 (2)
C4	0.71782 (8)	−0.37537 (14)	0.25360 (16)	0.0120 (3)
O1	0.55856 (5)	−0.10067 (9)	0.48715 (12)	0.0115 (2)
C1	0.58068 (7)	−0.18090 (13)	0.37294 (16)	0.0094 (2)
C2	0.59849 (8)	−0.32410 (14)	0.42594 (18)	0.0149 (3)
H2A	0.5507	−0.3682	0.4616	0.018*
H2B	0.6324	−0.3215	0.5269	0.018*
C3	0.63568 (8)	−0.40979 (13)	0.28835 (19)	0.0140 (3)
H3A	0.6326	−0.5052	0.3232	0.017*
H3B	0.6066	−0.3997	0.1807	0.017*
O3	0.74945 (6)	−0.28329 (10)	0.32774 (13)	0.0166 (2)
C5	0.75831 (8)	−0.46004 (14)	0.12409 (18)	0.0155 (3)
H5A	0.8107	−0.4287	0.1123	0.023*
H5B	0.7325	−0.4530	0.0135	0.023*
H5C	0.7583	−0.5539	0.1618	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.00891 (19)	0.00906 (19)	0.00626 (18)	0.000	0.00041 (11)	0.000
O4	0.0144 (5)	0.0187 (5)	0.0092 (4)	0.0031 (4)	0.0010 (3)	0.0003 (4)
O2	0.0133 (4)	0.0152 (5)	0.0084 (4)	0.0034 (4)	0.0011 (3)	0.0007 (4)
C4	0.0140 (6)	0.0107 (6)	0.0113 (6)	0.0030 (5)	−0.0017 (4)	0.0023 (5)
O1	0.0111 (4)	0.0140 (5)	0.0093 (4)	0.0021 (3)	0.0009 (3)	−0.0016 (4)
C1	0.0058 (5)	0.0125 (6)	0.0099 (6)	0.0001 (4)	−0.0001 (4)	0.0001 (5)
C2	0.0168 (6)	0.0136 (6)	0.0142 (6)	0.0041 (5)	0.0044 (5)	0.0032 (5)
C3	0.0136 (6)	0.0114 (6)	0.0172 (6)	0.0020 (5)	0.0007 (5)	−0.0009 (5)
O3	0.0163 (5)	0.0148 (5)	0.0187 (5)	0.0005 (4)	−0.0029 (4)	−0.0037 (4)

C5	0.0154 (6)	0.0153 (6)	0.0160 (6)	0.0011 (5)	0.0024 (5)	−0.0026 (5)

Geometric parameters (Å, º)

Ca1—O1ⁱ	2.3546 (10)	C4—C3	1.5138 (19)
Ca1—O1ⁱⁱ	2.3546 (10)	O1—C1	1.2602 (16)
Ca1—O4ⁱⁱⁱ	2.4367 (10)	O1—Ca1ⁱ	2.3546 (10)
Ca1—O4	2.4367 (10)	C1—C2	1.5185 (18)
Ca1—O2ⁱⁱⁱ	2.4820 (10)	C2—C3	1.5218 (19)
Ca1—O2	2.4820 (11)	C2—H2A	0.9900
Ca1—O1	2.5989 (10)	C2—H2B	0.9900
Ca1—O1ⁱⁱⁱ	2.5990 (10)	C3—H3A	0.9900
O4—H4A	0.8999	C3—H3B	0.9900
O4—H4B	0.8994	C5—H5A	0.9800
O2—C1	1.2599 (16)	C5—H5B	0.9800
C4—O3	1.2203 (17)	C5—H5C	0.9800
C4—C5	1.4988 (18)		
O1ⁱ—Ca1—O1ⁱⁱ	155.21 (5)	O2—Ca1—Ca1^{iv}	73.02 (2)
O1ⁱ—Ca1—O4ⁱⁱⁱ	78.38 (3)	O1—Ca1—Ca1^{iv}	123.28 (3)
O1ⁱⁱ—Ca1—O4ⁱⁱⁱ	85.69 (3)	O1ⁱⁱⁱ—Ca1—Ca1^{iv}	33.53 (2)
O1ⁱ—Ca1—O4	85.69 (3)	C1—Ca1—Ca1^{iv}	97.28 (3)
O1ⁱⁱ—Ca1—O4	78.39 (3)	C1ⁱⁱⁱ—Ca1—Ca1^{iv}	58.53 (3)
O4ⁱⁱⁱ—Ca1—O4	99.84 (5)	O1ⁱ—Ca1—Ca1ⁱ	37.57 (2)
O1ⁱ—Ca1—O2ⁱⁱⁱ	79.39 (3)	O1ⁱⁱ—Ca1—Ca1ⁱ	153.97 (2)
O1ⁱⁱ—Ca1—O2ⁱⁱⁱ	121.53 (3)	O4ⁱⁱⁱ—Ca1—Ca1ⁱ	76.76 (2)
O4ⁱⁱⁱ—Ca1—O2ⁱⁱⁱ	149.65 (3)	O4—Ca1—Ca1ⁱ	123.15 (2)
O4—Ca1—O2ⁱⁱⁱ	98.81 (4)	O2ⁱⁱⁱ—Ca1—Ca1ⁱ	73.02 (2)
O1ⁱ—Ca1—O2	121.53 (3)	O2—Ca1—Ca1ⁱ	84.41 (2)
O1ⁱⁱ—Ca1—O2	79.39 (3)	O1—Ca1—Ca1ⁱ	33.53 (2)
O4ⁱⁱⁱ—Ca1—O2	98.81 (4)	O1ⁱⁱⁱ—Ca1—Ca1ⁱ	123.28 (3)
O4—Ca1—O2	149.65 (3)	C1—Ca1—Ca1ⁱ	58.53 (3)
O2ⁱⁱⁱ—Ca1—O2	75.78 (5)	C1ⁱⁱⁱ—Ca1—Ca1ⁱ	97.28 (3)
O1ⁱ—Ca1—O1	71.10 (4)	Ca1—O4—H4A	111.0
O1ⁱⁱ—Ca1—O1	124.87 (4)	Ca1—O4—H4B	110.8
O4ⁱⁱⁱ—Ca1—O1	80.03 (3)	H4A—O4—H4B	108.0
O4—Ca1—O1	156.41 (3)	C1—O2—Ca1	94.50 (8)
O2ⁱⁱⁱ—Ca1—O1	73.36 (3)	O3—C4—C5	121.72 (13)
O2—Ca1—O1	51.33 (3)	O3—C4—C3	121.53 (12)
O1ⁱ—Ca1—O1ⁱⁱⁱ	124.87 (4)	C5—C4—C3	116.75 (12)
O1ⁱⁱ—Ca1—O1ⁱⁱⁱ	71.10 (4)	C1—O1—Ca1ⁱ	152.89 (9)
O4ⁱⁱⁱ—Ca1—O1ⁱⁱⁱ	156.41 (3)	C1—O1—Ca1	89.09 (8)
O4—Ca1—O1ⁱⁱⁱ	80.03 (3)	Ca1ⁱ—O1—Ca1	108.90 (4)
O2ⁱⁱⁱ—Ca1—O1ⁱⁱⁱ	51.33 (3)	O2—C1—O1	121.91 (12)
O2—Ca1—O1ⁱⁱⁱ	73.36 (3)	O2—C1—C2	120.21 (12)
O1—Ca1—O1ⁱⁱⁱ	109.48 (5)	O1—C1—C2	117.82 (11)
O1ⁱ—Ca1—C1	95.60 (4)	O2—C1—Ca1	59.55 (7)
O1ⁱⁱ—Ca1—C1	104.27 (4)	O1—C1—Ca1	64.87 (7)

O4ⁱⁱⁱ—Ca1—C1	93.35 (4)	C2—C1—Ca1	161.22 (9)
O4—Ca1—C1	166.72 (4)	C1—C2—C3	115.05 (11)
O2ⁱⁱⁱ—Ca1—C1	68.56 (4)	C1—C2—H2A	108.5
O2—Ca1—C1	25.95 (3)	C3—C2—H2A	108.5
O1—Ca1—C1	26.04 (3)	C1—C2—H2B	108.5
O1ⁱⁱⁱ—Ca1—C1	88.47 (4)	C3—C2—H2B	108.5
O1ⁱ—Ca1—C1ⁱⁱⁱ	104.27 (4)	H2A—C2—H2B	107.5
O1ⁱⁱ—Ca1—C1ⁱⁱⁱ	95.60 (4)	C4—C3—C2	114.37 (11)
O4ⁱⁱⁱ—Ca1—C1ⁱⁱⁱ	166.72 (4)	C4—C3—H3A	108.7
O4—Ca1—C1ⁱⁱⁱ	93.35 (4)	C2—C3—H3A	108.7
O2ⁱⁱⁱ—Ca1—C1ⁱⁱⁱ	25.95 (3)	C4—C3—H3B	108.7
O2—Ca1—C1ⁱⁱⁱ	68.56 (4)	C2—C3—H3B	108.7
O1—Ca1—C1ⁱⁱⁱ	88.47 (4)	H3A—C3—H3B	107.6
O1ⁱⁱⁱ—Ca1—C1ⁱⁱⁱ	26.04 (3)	C4—C5—H5A	109.5
C1—Ca1—C1ⁱⁱⁱ	73.51 (5)	C4—C5—H5B	109.5
O1ⁱ—Ca1—Ca1ⁱᵛ	153.97 (2)	H5A—C5—H5B	109.5
O1ⁱⁱ—Ca1—Ca1ⁱᵛ	37.57 (2)	C4—C5—H5C	109.5
O4ⁱⁱⁱ—Ca1—Ca1ⁱᵛ	123.15 (2)	H5A—C5—H5C	109.5
O4—Ca1—Ca1ⁱᵛ	76.76 (2)	H5B—C5—H5C	109.5
O2ⁱⁱⁱ—Ca1—Ca1ⁱᵛ	84.41 (2)		
O1ⁱ—Ca1—O2—C1	−2.30 (9)	O1ⁱ—Ca1—C1—O2	178.03 (8)
O1ⁱⁱ—Ca1—O2—C1	163.32 (8)	O1ⁱⁱ—Ca1—C1—O2	−16.92 (8)
O4ⁱⁱⁱ—Ca1—O2—C1	79.43 (8)	O4ⁱⁱⁱ—Ca1—C1—O2	−103.32 (8)
O4—Ca1—O2—C1	−153.18 (8)	O4—Ca1—C1—O2	83.05 (17)
O2ⁱⁱⁱ—Ca1—O2—C1	−70.07 (7)	O2ⁱⁱⁱ—Ca1—C1—O2	101.76 (8)
O1—Ca1—O2—C1	9.82 (7)	O1—Ca1—C1—O2	−162.35 (12)
O1ⁱⁱⁱ—Ca1—O2—C1	−123.41 (8)	O1ⁱⁱⁱ—Ca1—C1—O2	53.14 (8)
C1ⁱⁱⁱ—Ca1—O2—C1	−96.30 (8)	C1ⁱⁱⁱ—Ca1—C1—O2	74.78 (8)
Ca1ⁱᵛ—Ca1—O2—C1	−158.49 (8)	Ca1ⁱᵛ—Ca1—C1—O2	20.71 (8)
Ca1ⁱ—Ca1—O2—C1	3.79 (7)	Ca1ⁱ—Ca1—C1—O2	−175.57 (9)
O1ⁱ—Ca1—O1—C1	159.32 (9)	O1ⁱ—Ca1—C1—O1	−19.62 (9)
O1ⁱⁱ—Ca1—O1—C1	−42.09 (8)	O1ⁱⁱ—Ca1—C1—O1	145.43 (7)
O4ⁱⁱⁱ—Ca1—O1—C1	−119.65 (7)	O4ⁱⁱⁱ—Ca1—C1—O1	59.02 (7)
O4—Ca1—O1—C1	148.55 (9)	O4—Ca1—C1—O1	−114.60 (15)
O2ⁱⁱⁱ—Ca1—O1—C1	75.10 (7)	O2ⁱⁱⁱ—Ca1—C1—O1	−95.90 (7)
O2—Ca1—O1—C1	−9.79 (7)	O2—Ca1—C1—O1	162.35 (12)
O1ⁱⁱⁱ—Ca1—O1—C1	37.99 (6)	O1ⁱⁱⁱ—Ca1—C1—O1	−144.52 (6)
C1ⁱⁱⁱ—Ca1—O1—C1	53.67 (9)	C1ⁱⁱⁱ—Ca1—C1—O1	−122.87 (9)
Ca1ⁱᵛ—Ca1—O1—C1	3.63 (8)	Ca1ⁱᵛ—Ca1—C1—O1	−176.95 (7)
Ca1ⁱ—Ca1—O1—C1	159.32 (9)	Ca1ⁱ—Ca1—C1—O1	−13.22 (6)
O1ⁱ—Ca1—O1—Ca1ⁱ	0.0	O1ⁱ—Ca1—C1—C2	83.2 (3)
O1ⁱⁱ—Ca1—O1—Ca1ⁱ	158.59 (4)	O1ⁱⁱ—Ca1—C1—C2	−111.8 (3)
O4ⁱⁱⁱ—Ca1—O1—Ca1ⁱ	81.03 (4)	O4ⁱⁱⁱ—Ca1—C1—C2	161.8 (3)
O4—Ca1—O1—Ca1ⁱ	−10.77 (10)	O4—Ca1—C1—C2	−11.8 (4)
O2ⁱⁱⁱ—Ca1—O1—Ca1ⁱ	−84.22 (4)	O2ⁱⁱⁱ—Ca1—C1—C2	6.9 (3)
O2—Ca1—O1—Ca1ⁱ	−169.10 (6)	O2—Ca1—C1—C2	−94.8 (3)
O1ⁱⁱⁱ—Ca1—O1—Ca1ⁱ	−121.33 (4)	O1—Ca1—C1—C2	102.8 (3)

C1—Ca1—O1—Ca1^i	−159.32 (9)	O1^{iii}—Ca1—C1—C2	−41.7 (3)
C1^{iii}—Ca1—O1—Ca1^i	−105.65 (4)	C1^{iii}—Ca1—C1—C2	−20.0 (3)
Ca1^{iv}—Ca1—O1—Ca1^i	−155.69 (2)	Ca1^{iv}—Ca1—C1—C2	−74.1 (3)
Ca1—O2—C1—O1	−18.87 (13)	Ca1^i—Ca1—C1—C2	89.6 (3)
Ca1—O2—C1—C2	158.21 (10)	O2—C1—C2—C3	11.36 (18)
Ca1^i—O1—C1—O2	150.77 (13)	O1—C1—C2—C3	−171.45 (11)
Ca1—O1—C1—O2	17.93 (12)	Ca1—C1—C2—C3	95.1 (3)
Ca1^i—O1—C1—C2	−26.4 (2)	O3—C4—C3—C2	−2.20 (18)
Ca1—O1—C1—C2	−159.21 (10)	C5—C4—C3—C2	177.69 (12)
Ca1^i—O1—C1—Ca1	132.83 (18)	C1—C2—C3—C4	73.21 (15)

Symmetry codes: (i) −x+1, −y, −z+1; (ii) x, −y, z−1/2; (iii) −x+1, y, −z+1/2; (iv) −x+1, −y, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3^v	0.90	2.02	2.8568 (15)	155
O4—H4B···O2^{iv}	0.90	1.87	2.7519 (14)	168

Symmetry codes: (iv) −x+1, −y, −z; (v) x−1/2, y+1/2, −z+1/2.