Revisiting a natural wine salt: calcium (2R,3R)-tartrate tetrahydrate

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The crystal structure of the salt calcium (2R,3R)-tartrate tetrahydrate {systematic name: poly[[diaqua[μ_4-(2R,3R)-2,3-dihydroxybutanedioato]calcium(II)] dihydrate]}, {[Ca(C$_4$H$_8$O$_8$)(H$_2$O)$_2$]·2H$_2$O}$_n$, is reported. The absolute configuration of the crystal was established unambiguously using anomalous dispersion effects in the diffraction patterns. High-quality data also allowed the location and free refinement of all the H atoms, and therefore to a careful analysis of the hydrogen-bond interactions.

1. Introduction

The opening of a bottle of wine is a process that can elicit a variety of expectations, either in terms of the wine's taste, colour, smell, sensations or even in the occasional discovery of brilliant crystals, typically found on the surface of the cork in contact with the wine. The so-called *Weinsteine* or *wine diamonds* (Derewenda, 2008) are regarded by winemakers as a sign of quality, as their presence indicates that wine has been handled with natural methods and proper timing. It is known that such *diamonds* are actually crystalline tartrate salts.

Tartaric acid (Astbury, 1923), also known as 2,3-dihydroxybutanedioic acid, is a naturally occurring substance that is typically found on grapes and other plants. Although two enantiomers (2R,3R/2S,3S) and a meso form (2S,3R/2R,3S) are possible, only the 2R,3R enantiomer, namely L-(+)-tartaric acid, is biologically produced by vining plants. Deprotonation to its tartrate form (Fig. 1) during the fermentation and aging steps of wine production in the presence of alkali earth metal cations, usually K$^+$ and Ca^{2+}, may result in the slow crystallization of 2R,3R salts. This process can extend over a prolonged period, frequently becoming noticeable after commercial release.

Pioneering studies on the unit-cell parameters of the title compound, Ca[(2R,3R)-C$_4$H$_4$O$_6$]·4H$_2$O (**1**), were reported by Evans (1935), yielding a $P2_12_12_1$ space group crystal structure, with unit-cell parameters a = 9.20 (2), b = 10.54 (2) and c = 9.62 (2) Å. Several studies since then have confirmed the crystal structure of this salt, corroborating the space group and unit-cell dimensions (Ambady, 1968; Hawthorne *et al.*, 1982; Boese & Heinemann, 1993; Kaduk, 2007). In all the studies, aqueous solutions of tartaric acid were employed, from which crystals were grown. Although tartaric acid and its derivatives, especially its sodium ammonium salt, have long been central to the analysis of stereochemistry and chirality (Gal, 2008), since the pioneering works of Pasteur and Biott (see Flack, 2009, and references therein), it is important to note that in none of these structural reports about Ca(C$_4$H$_4$O$_6$)·4H$_2$O was
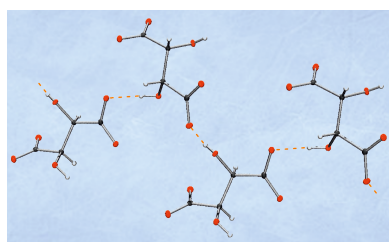
it possible to identify which of the enantiomers was being measured through anomalous dispersion effects.

Interestingly, triclinic polymorphs of racemic **1** (*i.e.* with both enantiomers in the unit cell) have also been reported (Le Bail *et al.*, 2009; Appelhans *et al.*, 2009; Fukami *et al.*, 2016). Furthermore, not only polymorphs, but also hydrates and solvates of Ca and tartrate have been reported. In this context, calcium tartrate has been found to also crystallize as its anhydrous (Appelhans *et al.*, 2009; Aljafree *et al.*, 2024), trihydrate (de Vries & Kroon, 1984) and hexahydrate forms (Ventruti *et al.*, 2015), and has been observed to cocrystallize with other species (Wartchow, 1996). The absolute configuration of these hydrates and solvates has been established experimentally, except in the case of the trihydrate form, which was found to contain the *meso*-tartaric form. Obviously, different hydration is related to dissimilar connectivity and crystal packing.

Here, we report the crystal structure of the calcium (2*R*,3*R*)-tartrate tetrahydrate salt (**1**), obtained from a crystal which was found and picked up from the cork of a *Crianza* red wine bottle from D.O. Campo de Borja (2016). This tetrahydrated salt crystallizes in the orthorhombic space group $P2_12_12_1$, with the unit-cell dimensions [$a = 9.1587$ (4), $b = 9.5551$ (4) and $c = 10.5041$ (5) Å], which are close to those reported by Evans (1935). High-quality experimental diffraction data allowed us to establish unambiguously the absolute structure and therefore the absolute configuration of the salt, and to analyze intermolecular interactions in the crystal packing.

2. Experimental

2.1. Single-crystal selection

Single crystals were found in the cork of a wine bottle, removed and selected under a microscope.

2.2. Single-crystal X-ray diffraction

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were located in difference Fourier maps and freely refined. High-quality and complete diffraction data, with 99.2% of the reflections measured until a maximal resolution of $(\sin \theta/\lambda)_{max} = 0.667$ Å^{-1} (with almost all the Friedel pairs: number of Friedel pairs measured out to the maximal resolution divided by the number of theoretically possible is 0.981, very close to unity), a mean redundancy higher than 20 and a good agreement factor ($R_{int} = 0.030$) of this Ca-containing crystal allowed us to establish the absolute structure in the solid state and therefore the absolute configuration of the molecule. For that purpose, the Flack parameter (Flack & Bernardinelli, 1999, 2000) has been refined. The obtained values are 0.028 (19) by classical fit to all intensities and 0.023 (3) using 937 quotients (Parsons *et al.*, 2013). The obtained values of the parameter and its standard uncertainty (s.u.) value provide evidence for a strong inversion-distinguishing power and a correct estimation of the absolute structure for this structural model.

Table 1
Experimental details.

Crystal data	
Chemical formula	[Ca(C₄H₄O₆)(H₂O)₂]·2H₂O
M_r	260.22
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	9.1587 (4), 9.5551 (4), 10.5041 (5)
V (Å³)	919.24 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.73
Crystal size (mm)	0.15 × 0.13 × 0.09
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.889, 0.937
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47365, 2275, 2268
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.014, 0.035, 1.09
No. of reflections	2275
No. of parameters	184
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.25
Absolute structure	Flack x determined using 937 quotients [(I^+) − (I^-)]/[(I^+) + (I^-)] (Parsons *et al.*, 2013)
Absolute structure parameter	0.023 (3)

Computer programs: *SAINT* in *APEX3* (Bruker, 2016), *SHELXS2013* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *XCIF* in *PLATON* (Spek, 2020).

3. Results and discussion

The asymmetric unit of Ca[(2*R*,3*R*)-C₄H₄O₆]·4H₂O (**1**) is formed by a Ca^{2+} ion, a tartrate ligand and four water molecules. In the crystal structure, the tartrate ion exhibits typical bonding connections (Ambady, 1968). Salient bond distances and angles are listed in Tables S1 and S2 of the supporting information. The two C—O bonds of each carboxylate group, which, along with the hydroxy substituents, chelate two Ca^{2+}
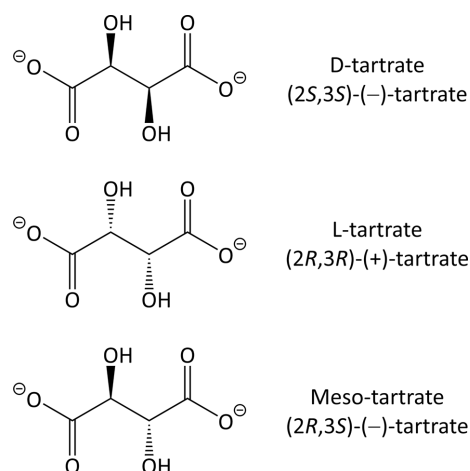

Figure 1
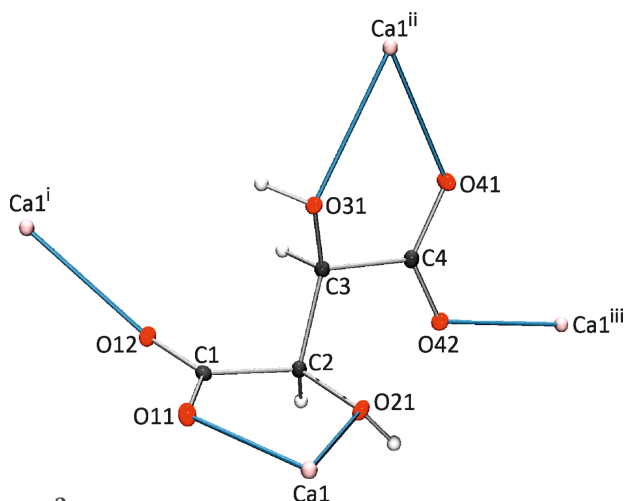The enantiomeric and meso forms of tartrate.

Figure 2
Ca^{2+} cations bonded to a tartrate anion in **1**. [Symmetry codes: (i) $-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}$, $-y + 1$, $z + \frac{1}{2}$; (iii) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$.]

cations, are significantly longer than the other two carboxylate C—O bonds, where the O atoms bind to additional adjacent Ca atoms [C1—O11 = 1.2659 (14) Å and C4—O41 = 1.2681 (14) Å *versus* C1—O12 = 1.2483 (15) Å and C4—O42 = 1.2472 (14) Å]. All the C atoms of the tartrate skeleton exhibit similar C—C separations, and are positioned in an almost coplanar manner, with maximal deviations from the best plane of 0.0020 (6) Å. It is noteworthy that the folding of this di-carboxylate entity is asymmetrical. Specifically, the O21 atom of the alcohol group lies nearly in the plane defined by the C1 atom and the atoms coordinated to its sp^2 hybridization, namely, C1, C2, O11 and O12 [0.069 (2) Å], whereas the alcohol O31 atom is placed significantly out of the analogous plane [atoms C3, C4, O41 and O42, 0.575 (2) Å].

3.1. Ca environment

In the crystal packing, each tartrate anion acts as a tetra-topic ligand, serving as a chelate for two Ca^{2+} cations and as a
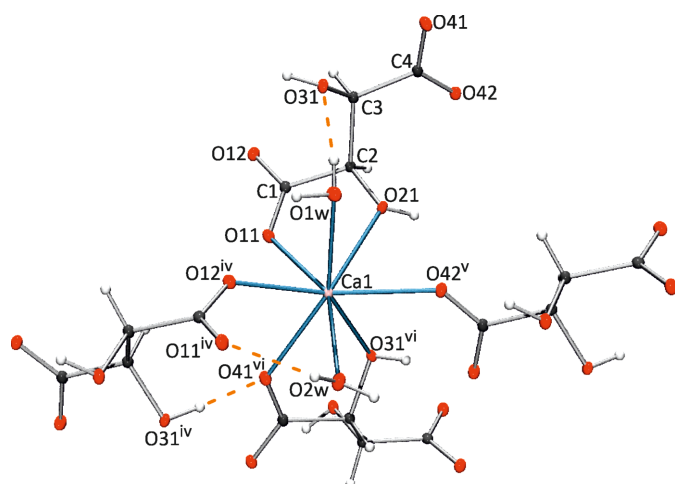
Table 2
Hydrogen-bond geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O31—H31···O41^{vii}	0.84 (3)	1.71 (3)	2.5529 (12)	174 (2)
O21—H21···O4W	0.83 (2)	1.88 (2)	2.7023 (13)	174 (2)
O1W—H2W···O31	0.82 (3)	2.11 (3)	2.9236 (13)	170 (2)
O2W—H3W···O3W	0.82 (2)	1.95 (2)	2.7483 (13)	164 (2)
O2W—H4W···O11^{viii}	0.87 (2)	2.12 (2)	2.8658 (13)	144 (2)
O3W—H5W···O42^{ix}	0.90 (3)	2.26 (3)	3.0318 (13)	144 (2)
O3W—H6W···O11^{x}	0.80 (2)	2.09 (2)	2.8809 (13)	168 (2)
O4W—H7W···O2W^{x}	0.77 (3)	2.16 (3)	2.9199 (14)	170 (2)
O4W—H8W···O1W^{xi}	0.83 (3)	2.31 (3)	3.1263 (15)	171 (2)

Symmetry codes: (vii) $x - \frac{1}{2}$, $-y + \frac{3}{2}$, $-z + 1$; (viii) $-x$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (ix) x, $y - 1$, z; (x) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$; (xi) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$.

terminal ligand for two additional Ca^{2+} cations (Fig. 2), whereas the Ca^{2+} cations (Ca1) are coordinated to four sym-metry-related tartrate anions and two water molecules in a distorted pseudo-octahedral coordination environment (Fig. 3).

Among the eight coordination sites of Ca, two are occupied by monodentate O atoms from carboxylate groups [O12—Ca1—O42 = 137.72 (3)°], with another two sites hosting water molecules [O1W—Ca1—O2W = 97.34 (3)°]. The coordination sphere of Ca1 is completed by two chelating tartrate ligands bonded by different edges, namely, O11—C1—C2—O21 and O31—C3—C4—O41. In both chelates, separation from the deprotonated O atoms to the Ca^{2+} cation [Ca1—O11 = 2.3733 (8) Å and Ca1—O41 = 2.4137 (9) Å] are significantly shorter compared to those of the alcohol groups [Ca1—O21 = 2.4544 (9) Å and Ca1—O31 = 2.5102 (9) Å]. These Ca—O distances range from 2.3733 (8) (Ca1—O11) to 2.5102 (9) Å (Ca—O31), which are consistent with the expected values (Ambady, 1968). It is noteworthy that this coordination of the Ca^{2+} ion in **1** notably differs from that of the triclinic poly-morph, where the eight-coordinated Ca^{2+} ion is bound to two bis-chelated tartrate ligands and four water molecules.

3.2. Hydrogen bonding

The two additional water molecules fulfilling the unit cell of **1**, and which are not coordinated to Ca, are involved in hy-drogen-bonding interactions. The crystal lattice is mainly stabilized by electrostatics and hydrogen bonding. The tartrate

Figure 3
Coordination sphere of the Ca^{2+} cation in **1**. [Symmetry codes: (iv) $-x$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (v) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}$, $-y + 1$, $z - \frac{1}{2}$.]
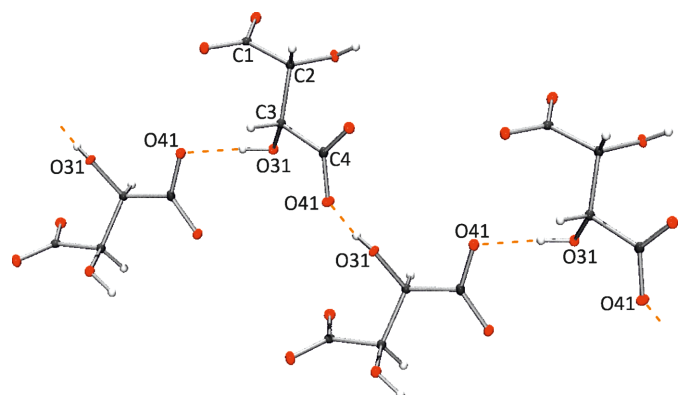

Figure 4
Hydrogen bonding involving tartrate anions in **1**. Calcium cations and water molecules have been omitted for clarity.

anions are connected *via* short hydrogen bonds [O31—H31···O41 = 2.5529 (12) Å] in a zigzag fashion along the *a* axis (Fig. 4). Finally, water molecules participate in eight additional hydrogen bonds involving tartrate anions and other water molecules (Table 2).

4. Summary

The title calcium (2*R*,3*R*)-tartrate tetrahydrate salt (**1**) crystallized in the orthorhombic space group $P2_12_12_1$, as anticipated by Evans (1935). In this work, anomalous dispersion effects in the crystal diffraction patterns led to the determination of the absolute configuration of the L-(+)-tartrate salt **1**. The absolute configuration has been resolved on the basis of anomalous dispersion effects in the crystal diffraction patterns and matches the enantiomer expected from a natural winemaking process. The good crystal quality allowed for precise determination of the geometrical arrangement, particularly enabling the localization of H atoms, and therefore the observation and accurate characterization of the hydrogen-bonding network.

Acknowledgements

Funding information

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Computing details

Poly[[diaqua[μ_4-(2*R*,3*R*)-2,3-dihydroxybutanedioato]calcium(II)] dihydrate]

Crystal data

[Ca(C$_4$H$_4$O$_6$)(H$_2$O)$_2$]·2H$_2$O	$D_x = 1.880$ Mg m^{-3}
$M_r = 260.22$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9609 reflections
$a = 9.1587$ (4) Å	$\theta = 4.8$–28.3°
$b = 9.5551$ (4) Å	$\mu = 0.73$ mm^{-1}
$c = 10.5041$ (5) Å	$T = 100$ K
$V = 919.24$ (7) Å^3	Prism, colorless
$Z = 4$	$0.15 \times 0.13 \times 0.09$ mm
$F(000) = 544$	

Data collection

Bruker D8 VENTURE diffractometer	2275 independent reflections
Radiation source: Mo microsource	2268 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.9°$
$T_{min} = 0.889$, $T_{max} = 0.937$	$h = -12 \rightarrow 12$
47365 measured reflections	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.014$	$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2 + 0.187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.035$	
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2275 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
184 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
0 restraints	Absolute structure: Flack x determined using 937 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.023 (3)

Special details

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

Refinement. Hydrogen atoms were included in the model in observed positions and freely refined.
Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal was selected and mounted on a MiTeGen MicroMount, protected with Fomblin oil. X-ray diffraction data were collected at 100 K on a D8 VENTURE Bruker diffractometer with Mo Kα radiation from IμS- DIAMOND microfocus source. Images were collected through ω and φ scans with a narrow step strategy. The raw data collection and processing, including absorption corrections, were done using APEX3 software package (Bruker, 2010). Structure was solved with direct methods and refined with Shelxls and Shelxl programs (Sheldrick, 2008, 2015), respectively. All non-hydrogen atoms were anisotropically refined.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.10736 (12)	0.64913 (12)	0.20067 (11)	0.0077 (2)
O11	0.05541 (9)	0.53123 (9)	0.16952 (9)	0.01010 (16)
O12	0.03571 (9)	0.75923 (9)	0.21440 (8)	0.00979 (16)
C2	0.27205 (12)	0.65990 (11)	0.22480 (11)	0.0072 (2)
H2	0.314 (2)	0.7252 (18)	0.1660 (17)	0.013 (4)*
O21	0.33762 (9)	0.52561 (9)	0.21224 (8)	0.00901 (16)
H21	0.414 (2)	0.540 (2)	0.171 (2)	0.024 (5)*
C3	0.29749 (13)	0.72088 (11)	0.35680 (10)	0.0071 (2)
H3	0.256 (2)	0.815 (2)	0.3574 (17)	0.016 (4)*
O31	0.22707 (9)	0.63913 (9)	0.45305 (8)	0.00848 (16)
H31	0.145 (3)	0.677 (2)	0.463 (2)	0.035 (6)*
C4	0.45907 (12)	0.73722 (12)	0.39115 (11)	0.0074 (2)
O41	0.48713 (9)	0.73136 (10)	0.50925 (9)	0.01108 (17)
O42	0.54987 (9)	0.76187 (9)	0.30555 (8)	0.00938 (16)
Ca1	0.18656 (2)	0.31714 (2)	0.17634 (2)	0.00667 (6)
O1W	0.22625 (10)	0.33681 (10)	0.41016 (9)	0.01211 (17)
H1W	0.141 (3)	0.312 (3)	0.435 (2)	0.039 (6)*
H2W	0.234 (3)	0.420 (3)	0.429 (2)	0.033 (6)*
O2W	0.18996 (10)	0.06249 (9)	0.16357 (9)	0.01289 (17)
H3W	0.266 (3)	0.018 (2)	0.153 (2)	0.032 (6)*
H4W	0.139 (3)	0.021 (2)	0.223 (2)	0.029 (5)*
O3W	0.42815 (10)	−0.08403 (10)	0.07665 (9)	0.01504 (18)
H5W	0.500 (3)	−0.113 (3)	0.129 (3)	0.042 (6)*
H6W	0.465 (2)	−0.058 (2)	0.012 (2)	0.022 (5)*
O4W	0.57266 (12)	0.57406 (12)	0.06310 (11)	0.0228 (2)
H7W	0.594 (3)	0.533 (3)	0.003 (3)	0.039 (6)*
H8W	0.621 (3)	0.647 (3)	0.063 (2)	0.034 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0078 (5)	0.0107 (5)	0.0046 (5)	−0.0001 (4)	−0.0001 (3)	0.0010 (4)

O11	0.0083 (4)	0.0089 (3)	0.0131 (4)	−0.0008 (3)	−0.0017 (3)	−0.0009 (3)
O12	0.0089 (4)	0.0098 (3)	0.0107 (4)	0.0019 (3)	0.0001 (3)	−0.0001 (3)
C2	0.0066 (5)	0.0074 (5)	0.0076 (5)	0.0006 (4)	−0.0003 (4)	−0.0005 (4)
O21	0.0069 (4)	0.0081 (4)	0.0121 (4)	0.0009 (3)	0.0016 (3)	−0.0020 (3)
C3	0.0068 (5)	0.0074 (5)	0.0070 (4)	0.0000 (4)	0.0001 (4)	0.0002 (3)
O31	0.0063 (4)	0.0119 (4)	0.0073 (4)	−0.0005 (3)	0.0016 (3)	0.0013 (3)
C4	0.0068 (5)	0.0058 (4)	0.0095 (5)	−0.0004 (4)	−0.0005 (4)	−0.0008 (4)
O41	0.0082 (4)	0.0171 (4)	0.0080 (4)	−0.0028 (3)	−0.0007 (3)	0.0007 (3)
O42	0.0076 (4)	0.0114 (3)	0.0092 (4)	−0.0010 (3)	0.0013 (3)	0.0000 (3)
Ca1	0.00612 (10)	0.00727 (10)	0.00663 (10)	0.00011 (8)	−0.00011 (7)	−0.00023 (8)
O1W	0.0110 (4)	0.0151 (5)	0.0102 (4)	−0.0030 (3)	0.0008 (3)	−0.0006 (3)
O2W	0.0103 (4)	0.0106 (4)	0.0178 (4)	0.0010 (3)	0.0025 (4)	0.0010 (3)
O3W	0.0116 (4)	0.0179 (4)	0.0157 (5)	0.0014 (4)	0.0022 (4)	0.0057 (4)
O4W	0.0236 (5)	0.0228 (5)	0.0220 (5)	−0.0094 (4)	0.0124 (4)	−0.0101 (4)

Geometric parameters (Å, º)

C1—O12	1.2483 (15)	O41—Ca1[ii]	2.4137 (9)
C1—O11	1.2659 (14)	O42—Ca1[iii]	2.4784 (9)
C1—C2	1.5330 (15)	Ca1—O12[iv]	2.4016 (9)
O11—Ca1	2.3733 (8)	Ca1—O41[v]	2.4136 (9)
O12—Ca1[i]	2.4015 (9)	Ca1—O2W	2.4371 (9)
C2—O21	1.4229 (13)	Ca1—O42[vi]	2.4784 (9)
C2—C3	1.5220 (15)	Ca1—O1W	2.4900 (9)
C2—H2	0.959 (18)	Ca1—O31[v]	2.5102 (9)
O21—Ca1	2.4544 (9)	Ca1—H1W	2.75 (2)
O21—H21	0.83 (2)	O1W—H1W	0.86 (3)
C3—O31	1.4312 (13)	O1W—H2W	0.82 (3)
C3—C4	1.5313 (16)	O2W—H3W	0.82 (2)
C3—H3	0.974 (19)	O2W—H4W	0.87 (2)
O31—Ca1[ii]	2.5102 (9)	O3W—H5W	0.90 (3)
O31—H31	0.84 (3)	O3W—H6W	0.80 (2)
C4—O42	1.2472 (14)	O4W—H7W	0.77 (3)
C4—O41	1.2681 (14)	O4W—H8W	0.83 (3)
O12—C1—O11	125.61 (10)	O41[v]—Ca1—O21	129.72 (3)
O12—C1—C2	116.20 (10)	O2W—Ca1—O21	144.25 (3)
O11—C1—C2	118.18 (10)	O11—Ca1—O42[vi]	132.76 (3)
C1—O11—Ca1	124.68 (7)	O12[iv]—Ca1—O42[vi]	137.72 (3)
C1—O12—Ca1[i]	134.03 (8)	O41[v]—Ca1—O42[vi]	131.06 (3)
O21—C2—C3	111.42 (9)	O2W—Ca1—O42[vi]	77.23 (3)
O21—C2—C1	109.84 (9)	O21—Ca1—O42[vi]	67.18 (3)
C3—C2—C1	109.08 (9)	O11—Ca1—O1W	92.21 (3)
O21—C2—H2	110.9 (11)	O12[iv]—Ca1—O1W	70.71 (3)
C3—C2—H2	106.0 (10)	O41[v]—Ca1—O1W	145.89 (3)
C1—C2—H2	109.6 (11)	O2W—Ca1—O1W	97.34 (3)
C2—O21—Ca1	120.55 (6)	O21—Ca1—O1W	72.84 (3)
C2—O21—H21	104.9 (14)	O42[vi]—Ca1—O1W	78.36 (3)

Ca1—O21—H21	121.7 (15)	O11—Ca1—O31^v	89.30 (3)
O31—C3—C2	111.45 (9)	O12^{iv}—Ca1—O31^v	138.76 (3)
O31—C3—C4	108.95 (9)	O41^v—Ca1—O31^v	63.91 (3)
C2—C3—C4	113.68 (9)	O2W—Ca1—O31^v	96.36 (3)
O31—C3—H3	108.8 (11)	O21—Ca1—O31^v	80.26 (3)
C2—C3—H3	107.4 (11)	O42^{vi}—Ca1—O31^v	78.48 (3)
C4—C3—H3	106.3 (11)	O1W—Ca1—O31^v	149.66 (3)
C3—O31—Ca1^{ii}	115.29 (6)	O11—Ca1—H1W	88.3 (5)
C3—O31—H31	104.6 (16)	O12^{iv}—Ca1—H1W	52.8 (5)
Ca1^{ii}—O31—H31	95.5 (16)	O41^v—Ca1—H1W	128.0 (5)
O42—C4—O41	125.35 (11)	O2W—Ca1—H1W	92.2 (5)
O42—C4—C3	119.59 (10)	O21—Ca1—H1W	87.0 (5)
O41—C4—C3	114.95 (10)	O42^{vi}—Ca1—H1W	93.8 (5)
C4—O41—Ca1^{ii}	125.89 (7)	O1W—Ca1—H1W	17.9 (5)
C4—O42—Ca1^{iii}	129.37 (8)	O31^v—Ca1—H1W	166.9 (5)
O11—Ca1—O12^{iv}	77.52 (3)	Ca1—O1W—H1W	98.7 (16)
O11—Ca1—O41^v	79.05 (3)	Ca1—O1W—H2W	108.8 (16)
O12^{iv}—Ca1—O41^v	75.20 (3)	H1W—O1W—H2W	106 (2)
O11—Ca1—O2W	149.92 (3)	Ca1—O2W—H3W	122.1 (16)
O12^{iv}—Ca1—O2W	78.88 (3)	Ca1—O2W—H4W	114.1 (15)
O41^v—Ca1—O2W	77.10 (3)	H3W—O2W—H4W	109 (2)
O11—Ca1—O21	65.82 (3)	H5W—O3W—H6W	108 (2)
O12^{iv}—Ca1—O21	126.25 (3)	H7W—O4W—H8W	107 (2)
O12—C1—O11—Ca1	−169.66 (9)	O21—C2—C3—C4	58.87 (11)
C2—C1—O11—Ca1	9.98 (14)	C1—C2—C3—C4	−179.70 (9)
O11—C1—O12—Ca1^i	47.52 (17)	C2—C3—O31—Ca1^{ii}	163.52 (7)
C2—C1—O12—Ca1^i	−132.12 (9)	C4—C3—O31—Ca1^{ii}	37.29 (10)
O12—C1—C2—O21	176.93 (10)	O31—C3—C4—O42	156.19 (10)
O11—C1—C2—O21	−2.74 (14)	C2—C3—C4—O42	31.26 (14)
O12—C1—C2—C3	54.54 (13)	O31—C3—C4—O41	−27.48 (13)
O11—C1—C2—C3	−125.12 (10)	C2—C3—C4—O41	−152.41 (10)
C3—C2—O21—Ca1	115.99 (8)	O42—C4—O41—Ca1^{ii}	−179.72 (8)
C1—C2—O21—Ca1	−5.00 (11)	C3—C4—O41—Ca1^{ii}	4.20 (14)
O21—C2—C3—O31	−64.72 (11)	O41—C4—O42—Ca1^{iii}	−2.40 (18)
C1—C2—C3—O31	56.71 (11)	C3—C4—O42—Ca1^{iii}	173.52 (7)

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

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O31—H31⋯O41^{vii}	0.84 (3)	1.71 (3)	2.5529 (12)	174 (2)
O21—H21⋯O4W	0.83 (2)	1.88 (2)	2.7023 (13)	174 (2)
O1W—H2W⋯O31	0.82 (3)	2.11 (3)	2.9236 (13)	170 (2)
O2W—H3W⋯O3W	0.82 (2)	1.95 (2)	2.7483 (13)	164 (2)
O2W—H4W⋯O11^{iv}	0.87 (2)	2.12 (2)	2.8658 (13)	144 (2)
O3W—H5W⋯O42^{viii}	0.90 (3)	2.26 (3)	3.0318 (13)	144 (2)

O3*W*—H6*W*···O11^{ix}	0.80 (2)	2.09 (2)	2.8809 (13)	168 (2)
O4*W*—H7*W*···O2*W*^{ix}	0.77 (3)	2.16 (3)	2.9199 (14)	170 (2)
O4*W*—H8*W*···O1*W*ⁱⁱⁱ	0.83 (3)	2.31 (3)	3.1263 (15)	171 (2)

Symmetry codes: (iii) $-x+1, y+1/2, -z+1/2$; (iv) $-x, y-1/2, -z+1/2$; (vii) $x-1/2, -y+3/2, -z+1$; (viii) $x, y-1, z$; (ix) $x+1/2, -y+1/2, -z$.