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Poly[[μ -aqua-aqua[μ_4 -ethyl (dichloromethylene)diphosphonato]sesquicalcium(II)] acetone hemisolvate 4.5-hydrate]

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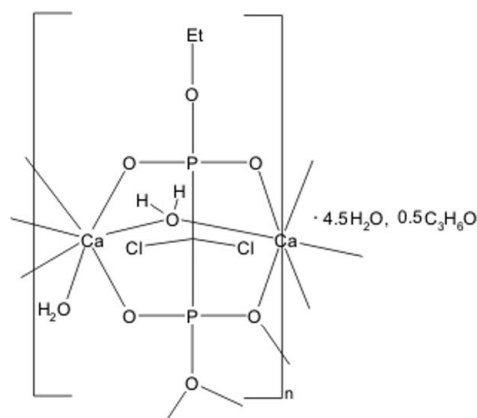
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.030; wR factor = 0.073; data-to-parameter ratio = 19.8.

The title compound, $\{[\text{Ca}_{1.5}(\text{C}_3\text{H}_5\text{Cl}_2\text{O}_6\text{P}_2)(\text{H}_2\text{O})_2] \cdot 0.5\text{CH}_3\text{COCH}_3 \cdot 4.5\text{H}_2\text{O}\}_n$, has a two-dimensional polymeric structure. The asymmetric unit contains two crystallographically independent Ca^{2+} cations connected by a chelating and bridging ethyl (dichloromethylene)diphosphonate(3^-) ligand and an aqua ligand. One of the Ca atoms, lying on a centre of symmetry, has a slightly distorted octahedral geometry, while the other Ca atom is seven-coordinated in a distorted monocapped trigonal-prismatic geometry. The polymeric layers are further connected by extensive $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding into a three-dimensional supramolecular network. The acetone solvent molecule and one uncoordinated water molecule are located on twofold rotation axes.

Related literature

For applications of metal complexes of bisphosphonates, see: Clearfield *et al.* (2001); Clearfield (1998); Fu *et al.* (2007); Serre *et al.* (2006). For calcium bisphosphonate complexes, see: Lin *et al.* (2007); Mathew *et al.* (1998). For metal complexes of bisphosphonate ester derivatives, see: Jokiniemi *et al.* (2007, 2008).



Experimental

Crystal data

$[\text{Ca}_{1.5}(\text{C}_3\text{H}_5\text{Cl}_2\text{O}_6\text{P}_2)(\text{H}_2\text{O})_2] \cdot 0.5\text{C}_3\text{H}_6\text{O} \cdot 4.5\text{H}_2\text{O}$
 $M_r = 476.17$
Monoclinic, $C2/c$
 $a = 31.2205$ (3) Å
 $b = 10.1546$ (1) Å
 $c = 11.6510$ (1) Å

$\beta = 103.107$ (1)°
 $V = 3597.51$ (6) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 1.02$ mm⁻¹
 $T = 150$ K
 $0.25 \times 0.15 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*XPRED* in *SHELXTL*;
Sheldrick, 2008)
 $T_{\text{min}} = 0.823$, $T_{\text{max}} = 0.905$

31118 measured reflections
4209 independent reflections
3617 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.073$
 $S = 1.10$
4209 reflections

213 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.58$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ca1—O1	2.3778 (14)	Ca2—O11 ⁱ	2.4049 (15)
Ca1—O11	2.2278 (14)	Ca2—O12	2.3466 (14)
Ca1—O21	2.3279 (15)	Ca2—O13 ⁱⁱ	2.3320 (15)
Ca2—O1	2.5726 (15)	Ca2—O13 ⁱ	2.5858 (15)
Ca2—O2	2.4024 (15)	Ca2—O22	2.3158 (15)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1—H1B \cdots O3	0.99	1.81	2.794 (2)	171
O1—H1A \cdots O12 ⁱⁱ	0.99	1.83	2.637 (2)	137
O2—H2A \cdots O3	0.84	1.88	2.717 (2)	172
O2—H2B \cdots O21 ⁱⁱⁱ	0.85	1.90	2.746 (2)	177
O3—H3A \cdots O6 ^{iv}	0.86	1.93	2.782 (2)	175
O3—H3B \cdots O4 ⁱⁱⁱ	0.86	1.89	2.734 (2)	169
O4—H4A \cdots O22	0.85	2.00	2.841 (2)	166
O4—H4B \cdots O2 ^{iv}	0.85	1.93	2.754 (2)	163
O5—H5A \cdots O4	0.85	2.02	2.838 (2)	163

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5B \cdots O6	0.85	2.05	2.901 (3)	171
O6—H6A \cdots O8	0.85	2.02	2.831 (2)	161
O6—H6B \cdots O7 ^v	0.84	2.26	2.832 (2)	125
O7—H7 \cdots O5	0.84	1.98	2.799 (2)	166

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

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2487).

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Poly[[μ -aqua-aqua[μ_4 -ethyl (dichloromethylene)diphosphonato]sesquicalcium(II)] acetone hemisolvate 4.5-hydrate]

J. Jokiniemi, S. Peräniemi, J. Vepsäläinen and M. Ahlgrén

Comment

Metal bisphosphonates have been attracting closer attention in light of their important applications in industrial processes such as ion-exchange, catalysis and sorption (Clearfield *et al.*, 2001, Clearfield, 1998, Fu *et al.*, 2007). Metal bisphosphonates usually adopt layered or pillared layered structures (Fu *et al.*, 2007, Mathew *et al.*, 1998). Other structural types, such as 1-D and 3-D open networks, have also been prepared in order to study the properties of bisphosphonate solid materials (Lin *et al.*, 2007, Fu *et al.*, 2007). Most of the effective materials consist of open frameworks and microporous structures (Fu *et al.*, 2007, Serre *et al.*, 2006). In recent investigations, we studied the complexing properties of amide ester derivatives of (dichloromethylene)bisphosphonate, Cl₂MBP (Jokiniemi *et al.*, 2007, 2008). The introduction of various ester substituents into phosphonate groups can result in novel structures of metal bisphosphonates and lead to interesting functionalities. Of the numerous metal phosphonate compounds now known, only a small number have been prepared with alkali earth metals. We now present the crystal structure of the Ca(II) complex of the monoethyl ester derivative of Cl₂MBP obtained by gel crystallization.

The title compound consists of two-dimensional layers parallel to the (100) plane. The Ca1 atom lies on the centre of symmetry with two symmetrically chelating (Cl₂CP₂O₆Et)³⁻ ligands and two aqua ligands in axial positions; the geometry is slightly distorted octahedron with Ca1–O bond lengths of 2.228 (1)–2.378 (1) Å (Table 1, Fig. 1). The three *trans* bond angles are 180.0°, while the *cis* bond angles range from 84.12 (5) to 95.88 (5)°. The aqua ligand O1 bridges Ca1 and the adjacent Ca2 atom with Ca...Ca distance of 4.4283 (4) Å. The Ca2 atom is seven-coordinated in distorted monocapped trigonal prismatic geometry and is coordinated by five phosphonate O atoms from three different (Cl₂CP₂O₆Et)³⁻ ligands. The coordination sphere is completed by two aqua ligands. The Ca2–O bond lengths are 2.316 (2)–2.586 (2) Å. The (Cl₂CP₂O₆Et)³⁻ ligand is coordinated to four Ca²⁺ cations through five O atoms forming two six-membered chelate rings with Ca1 and Ca2 atoms, and the P1 atom forms a four-membered chelate ring with the adjacent Ca2D atom (*x*, *-y*, *z* - 1/2). Thus, the two oxygen atoms (O11, O13) act as monoatomic bridges between two Ca atoms.

The layers are further connected by extensive hydrogen bonding (O...O 2.637 (2)–2.901 (3) Å, 125–177°) into a 3-D network with the interlayer distance of 15.2036 (2) Å (Fig. 2, Table 2). The O8 and C2 atoms of the acetone molecule, as well as the water molecule O7, are located on the individual two-fold rotation axis. The ethyl groups and chlorine atoms point out from the layers.

Experimental

Na₃Cl₂CP₂O₆Et (10.0 mg, 0.030 mmol) and CaCl₂·2H₂O (4.3 mg, 0.030 mmol) were dissolved separately in water (2.25 ml), the solutions were mixed, and tetramethoxysilane (TMOS 0.5 ml) was added. The two-phase system was shaken until homogeneous. After gel formation, a precipitant, acetone (1.0 ml), was added above the gel to induce crystallization. After

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about three months, colourless crystals suitable for X-ray analysis were formed uniformly throughout the gel as thin needles. The elemental analyses were performed several times and the results were consistent indicating that the acetone molecule and 3.5 water molecules were evaporated when the crystals were dried in air.

Refinement

H atoms of the ethyl group and acetone molecule were placed at calculated positions in the riding-model approximation with C–H distances of 0.99 Å (methylene) and 0.98 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{C})$. H atoms of the aqua ligands and lattice water molecules were located in a difference map and treated as riding, with O–H bond lengths constrained to 0.84–0.99 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ or $1.2U_{\text{eq}}(\text{O})$.

Figures

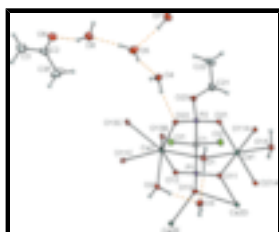


Fig. 1. A part of the polymeric structure of the title compound showing the atomic numbering scheme and 50% probability displacement ellipsoids for non-H atoms. Hydrogen bonds are shown as dashed lines. Atoms labelled with suffixes A–F are at the symmetry positions $(1/2 - x, 1/2 - y, -z)$, $(1/2 - x, 1/2 + y, 1/2 - z)$, $(x, -y, 1/2 + z)$, $(x, -y, z - 1/2)$, $(1/2 - x, y - 1/2, 1/2 - z)$ and $(-x, y, 3/2 - z)$, respectively.

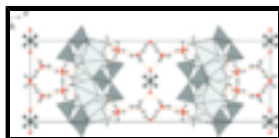


Fig. 2. Packing of the title compound viewed along the *c*-axis showing the hydrogen bond interactions. CaO_6 and CaO_7 polyhedra are presented in light grey and PO_3C tetrahedra in dark grey. Ethyl groups, chlorine atoms and H atoms of the acetone molecules are omitted for clarity.

Poly[[μ -aqua-aqua[μ_4 -ethyl (dichloromethylene)diphosphonato]sesquicalcium(II)] acetone hemisolvate 4.5-hydrate]

Crystal data

$[\text{Ca}_{1.5}(\text{C}_3\text{H}_5\text{Cl}_2\text{O}_6\text{P}_2)(\text{H}_2\text{O})_2] \cdot 0.5\text{C}_3\text{H}_6\text{O} \cdot 4.5\text{H}_2\text{O}$	$F_{000} = 1968$
$M_r = 476.17$	$D_x = 1.758 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
Hall symbol: $-C 2yc$	$\lambda = 0.71073 \text{ \AA}$
$a = 31.2205 (3) \text{ \AA}$	Cell parameters from 31118 reflections
$b = 10.15460 (10) \text{ \AA}$	$\theta = 2.7\text{--}28.0^\circ$
$c = 11.65100 (10) \text{ \AA}$	$\mu = 1.02 \text{ mm}^{-1}$
$\beta = 103.1070 (10)^\circ$	$T = 150 \text{ K}$
$V = 3597.51 (6) \text{ \AA}^3$	Needle, colourless
$Z = 8$	$0.25 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer	4209 independent reflections
Radiation source: fine-focus sealed tube	3617 reflections with $I > 2\sigma(I)$

Monochromator: graphite $R_{\text{int}} = 0.055$
 $T = 150$ K $\theta_{\text{max}} = 28.0^\circ$
 φ scans, and ω scans with κ offsets $\theta_{\text{min}} = 2.7^\circ$
 Absorption correction: multi-scan (XPREP in SHELXTL; Sheldrick, 2008) $h = -40 \rightarrow 40$
 $T_{\text{min}} = 0.823$, $T_{\text{max}} = 0.905$ $k = -13 \rightarrow 13$
 31118 measured reflections $l = -14 \rightarrow 15$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.030$ H-atom parameters constrained
 $wR(F^2) = 0.073$ $w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 12P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.10$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 4209 reflections $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
 213 parameters $\Delta\rho_{\text{min}} = -0.58 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Experimental. These results are supported by the IR spectrum and TG analysis. Anal. Found: C, 9.30; H, 3.06%. Calc. for $\text{C}_3\text{H}_{11}\text{Cl}_2\text{Ca}_{1.5}\text{O}_9\text{P}_2$: C, 9.38; H, 2.89%. Main IR absorptions (KBr pellet, cm^{-1}): 3385 (b,s), 2995 (w), 1648 (b,m), 1389 (m), 1213 (s), 1148 (s), 1105 (*versus*), 1082 (*versus*), 1048 (m), 1008 (m), 959 (m), 871 (m), 852 (w), 760 (m). ^{31}P CP/MAS NMR: δ_{p} 7.4 and 5.1 p.p.m.. TGA (25–700 °C under a synthetic air): 25–180 °C 13.1% (calculated 14.1% for the loss of three water molecules). The observed total weight loss is 40.0% (calculated 41.1% if the final product is assumed to be a mixture of $\text{Ca}(\text{PO}_3)_2$ and CaO in a molar ratio of 2:1).

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ca1	0.2500	0.2500	0.0000	0.00999 (12)
Ca2	0.248223 (14)	0.12782 (4)	0.36375 (3)	0.00930 (9)
Cl1	0.129792 (17)	-0.08747 (5)	0.13650 (4)	0.01375 (11)
Cl2	0.137474 (18)	0.01918 (5)	-0.08762 (4)	0.01548 (11)

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P1	0.218448 (17)	-0.04904 (5)	0.08794 (4)	0.00900 (11)
P2	0.160183 (17)	0.18410 (5)	0.12307 (5)	0.00960 (11)
O1	0.28281 (5)	0.23098 (14)	0.20444 (12)	0.0126 (3)
H1A	0.2911	0.3217	0.2318	0.015*
H1B	0.3108	0.1830	0.2091	0.015*
O2	0.32098 (5)	0.03608 (14)	0.41612 (13)	0.0129 (3)
H2A	0.3353	0.0476	0.3639	0.019*
H2B	0.3198	-0.0467	0.4244	0.019*
O3	0.36311 (5)	0.09774 (16)	0.24321 (14)	0.0178 (3)
H3A	0.3899	0.1215	0.2683	0.027*
H3B	0.3643	0.0198	0.2163	0.027*
O4	0.13454 (5)	0.36331 (16)	0.37057 (14)	0.0180 (3)
H4A	0.1472	0.3000	0.3430	0.027*
H4B	0.1530	0.3864	0.4332	0.027*
O5	0.05044 (6)	0.30916 (18)	0.41409 (16)	0.0269 (4)
H5A	0.0775	0.3154	0.4142	0.040*
H5B	0.0476	0.3118	0.4851	0.040*
O6	0.05040 (6)	0.32700 (17)	0.66254 (16)	0.0238 (4)
H6A	0.0405	0.2579	0.6883	0.036*
H6B	0.0285	0.3765	0.6374	0.036*
O7	0.0000	0.4816 (2)	0.2500	0.0224 (5)
H7	0.0189	0.4385	0.2985	0.034*
O8	0.0000	0.1357 (2)	0.7500	0.0265 (6)
O11	0.24121 (5)	0.03290 (14)	0.00999 (12)	0.0107 (3)
O12	0.23607 (5)	-0.03674 (14)	0.21857 (12)	0.0108 (3)
O13	0.21597 (5)	-0.18636 (14)	0.04307 (12)	0.0103 (3)
O21	0.18181 (5)	0.26929 (14)	0.04781 (13)	0.0116 (3)
O22	0.17957 (5)	0.18469 (14)	0.25168 (12)	0.0115 (3)
O23	0.10987 (5)	0.21652 (15)	0.10779 (13)	0.0132 (3)
C1	0.16168 (7)	0.0176 (2)	0.06555 (17)	0.0104 (4)
C21	0.08235 (8)	0.2669 (2)	0.0003 (2)	0.0196 (5)
H21A	0.0615	0.1982	-0.0384	0.024*
H21B	0.1006	0.2944	-0.0548	0.024*
C22	0.05800 (9)	0.3813 (3)	0.0325 (3)	0.0292 (6)
H22A	0.0416	0.3541	0.0911	0.044*
H22B	0.0374	0.4143	-0.0380	0.044*
H22C	0.0788	0.4511	0.0656	0.044*
C2	0.0000	0.0182 (3)	0.7500	0.0228 (7)
C3	-0.02303 (10)	-0.0568 (3)	0.8273 (3)	0.0394 (7)
H3C	-0.0317	0.0033	0.8837	0.059*
H3D	-0.0033	-0.1244	0.8701	0.059*
H3E	-0.0493	-0.0990	0.7791	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0143 (3)	0.0066 (3)	0.0097 (3)	-0.0003 (2)	0.0041 (2)	0.0006 (2)
Ca2	0.0130 (2)	0.00660 (18)	0.00840 (19)	-0.00024 (15)	0.00261 (15)	0.00003 (14)

Cl1	0.0156 (2)	0.0112 (2)	0.0157 (3)	-0.00233 (19)	0.00603 (19)	0.00042 (18)
Cl2	0.0205 (3)	0.0151 (2)	0.0094 (2)	0.0024 (2)	0.00041 (19)	-0.00142 (18)
P1	0.0129 (3)	0.0059 (2)	0.0088 (3)	0.00034 (19)	0.00368 (19)	0.00012 (18)
P2	0.0122 (3)	0.0072 (2)	0.0097 (3)	0.00102 (19)	0.0030 (2)	0.00008 (18)
O1	0.0177 (8)	0.0088 (7)	0.0112 (7)	-0.0003 (6)	0.0030 (6)	-0.0011 (5)
O2	0.0160 (7)	0.0083 (7)	0.0154 (8)	-0.0001 (6)	0.0054 (6)	0.0010 (6)
O3	0.0171 (8)	0.0164 (8)	0.0199 (8)	0.0005 (6)	0.0045 (6)	0.0000 (6)
O4	0.0205 (8)	0.0176 (8)	0.0152 (8)	0.0029 (6)	0.0027 (6)	-0.0036 (6)
O5	0.0227 (9)	0.0291 (10)	0.0296 (10)	-0.0008 (8)	0.0074 (7)	-0.0014 (8)
O6	0.0200 (9)	0.0214 (9)	0.0297 (10)	-0.0012 (7)	0.0053 (7)	0.0032 (7)
O7	0.0205 (12)	0.0243 (13)	0.0216 (12)	0.000	0.0032 (10)	0.000
O8	0.0306 (14)	0.0174 (12)	0.0344 (15)	0.000	0.0130 (11)	0.000
O11	0.0159 (7)	0.0068 (7)	0.0109 (7)	0.0000 (6)	0.0057 (6)	0.0007 (5)
O12	0.0146 (7)	0.0086 (7)	0.0092 (7)	0.0005 (6)	0.0027 (6)	-0.0010 (5)
O13	0.0137 (7)	0.0072 (7)	0.0103 (7)	0.0009 (5)	0.0030 (6)	-0.0011 (5)
O21	0.0155 (7)	0.0068 (7)	0.0135 (7)	0.0009 (6)	0.0052 (6)	0.0003 (5)
O22	0.0146 (7)	0.0095 (7)	0.0102 (7)	0.0017 (6)	0.0025 (6)	-0.0010 (5)
O23	0.0130 (7)	0.0128 (7)	0.0138 (7)	0.0040 (6)	0.0031 (6)	0.0019 (6)
C1	0.0134 (10)	0.0085 (9)	0.0095 (10)	-0.0008 (8)	0.0031 (8)	0.0006 (7)
C21	0.0190 (11)	0.0221 (12)	0.0155 (11)	0.0052 (9)	-0.0009 (9)	0.0015 (9)
C22	0.0262 (13)	0.0223 (13)	0.0356 (15)	0.0100 (11)	-0.0002 (11)	0.0030 (11)
C2	0.0166 (16)	0.0189 (17)	0.033 (2)	0.000	0.0050 (14)	0.000
C3	0.0362 (16)	0.0276 (15)	0.061 (2)	0.0062 (13)	0.0253 (15)	0.0149 (14)

Geometric parameters (Å, °)

Ca1—O1 ⁱ	2.3778 (14)	P2—O22	1.4834 (15)
Ca1—O1	2.3778 (14)	P2—O21	1.4972 (15)
Ca1—O11	2.2278 (14)	P2—O23	1.5750 (15)
Ca1—O11 ⁱ	2.2278 (14)	P2—C1	1.823 (2)
Ca1—O21 ⁱ	2.3279 (15)	O1—H1A	0.9900
Ca1—O21	2.3279 (15)	O1—H1B	0.9900
Ca1—P2 ⁱ	3.4915 (5)	O2—H2A	0.8414
Ca1—P2	3.4915 (5)	O2—H2B	0.8477
Ca1—P1 ⁱ	3.4204 (5)	O3—H3A	0.8560
Ca1—P1	3.4204 (5)	O3—H3B	0.8554
Ca1—Ca2 ⁱⁱ	4.1476 (4)	O4—H4A	0.8541
Ca1—Ca2 ⁱⁱⁱ	4.1476 (4)	O4—H4B	0.8536
Ca2—O1	2.5726 (15)	O5—H5A	0.8468
Ca2—O2	2.4024 (15)	O5—H5B	0.8525
Ca2—O11 ^{iv}	2.4049 (15)	O6—H6A	0.8481
Ca2—O12	2.3466 (14)	O6—H6B	0.8448
Ca2—O13 ⁱⁱⁱ	2.3320 (15)	O7—H7	0.8416
Ca2—O13 ^{iv}	2.5858 (15)	O8—C2	1.193 (4)
Ca2—O22	2.3158 (15)	O11—Ca2 ⁱⁱ	2.4049 (15)
Ca2—P1 ^{iv}	3.0705 (6)	O13—Ca2 ^{vi}	2.3320 (15)

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Ca2—P1 ⁱⁱⁱ	3.4498 (6)	O13—Ca2 ⁱⁱ	2.5858 (15)
Ca2—P2	3.4999 (7)	O23—C21	1.442 (3)
Ca2—Ca2 ^v	4.0111 (8)	C21—C22	1.482 (3)
Ca2—Ca1 ^{vi}	4.1476 (4)	C21—H21A	0.9900
Ca2—H2A	2.8382	C21—H21B	0.9900
Ca2—H2B	2.8142	C22—H22A	0.9800
Cl1—C1	1.785 (2)	C22—H22B	0.9800
Cl2—C1	1.773 (2)	C22—H22C	0.9800
P1—O13	1.4851 (15)	C2—C3 ^{vii}	1.484 (3)
P1—O12	1.5016 (15)	C2—C3	1.484 (3)
P1—O11	1.5216 (15)	C3—H3C	0.9800
P1—C1	1.860 (2)	C3—H3D	0.9800
P1—Ca2 ⁱⁱ	3.0705 (6)	C3—H3E	0.9800
P1—Ca2 ^{vi}	3.4498 (6)		
O21 ⁱ —Ca1—O21	180.00 (6)	P2—Ca2—Ca2 ^v	114.135 (18)
O21 ⁱ —Ca1—O11	93.40 (5)	O22—Ca2—Ca1 ^{vi}	112.14 (4)
O21—Ca1—O11	86.60 (5)	O13 ⁱⁱⁱ —Ca2—Ca1 ^{vi}	127.37 (4)
O21 ⁱ —Ca1—O11 ⁱ	86.60 (5)	O2—Ca2—Ca1 ^{vi}	67.31 (4)
O21—Ca1—O11 ⁱ	93.40 (5)	O12—Ca2—Ca1 ^{vi}	66.62 (4)
O11—Ca1—O11 ⁱ	180.00 (8)	O11 ^{iv} —Ca2—Ca1 ^{vi}	25.39 (3)
O21 ⁱ —Ca1—O1 ⁱ	88.67 (5)	O1—Ca2—Ca1 ^{vi}	132.96 (4)
O21—Ca1—O1 ⁱ	91.33 (5)	O13 ^{iv} —Ca2—Ca1 ^{vi}	82.95 (3)
O11—Ca1—O1 ⁱ	95.88 (5)	P1 ^{iv} —Ca2—Ca1 ^{vi}	54.110 (11)
O11 ⁱ —Ca1—O1 ⁱ	84.12 (5)	P1 ⁱⁱⁱ —Ca2—Ca1 ^{vi}	147.146 (14)
O21 ⁱ —Ca1—O1	91.33 (5)	P2—Ca2—Ca1 ^{vi}	113.429 (13)
O21—Ca1—O1	88.67 (5)	Ca2 ^v —Ca2—Ca1 ^{vi}	105.887 (14)
O11—Ca1—O1	84.12 (5)	O22—Ca2—H2A	146.7
O11 ⁱ —Ca1—O1	95.88 (5)	O13 ⁱⁱⁱ —Ca2—H2A	82.8
O1 ⁱ —Ca1—O1	180.00 (11)	O2—Ca2—H2A	15.8
O21 ⁱ —Ca1—P2 ⁱ	19.02 (4)	O12—Ca2—H2A	78.1
O21—Ca1—P2 ⁱ	160.98 (4)	O11 ^{iv} —Ca2—H2A	92.6
O11—Ca1—P2 ⁱ	109.33 (4)	O1—Ca2—H2A	63.8
O11 ⁱ —Ca1—P2 ⁱ	70.67 (4)	O13 ^{iv} —Ca2—H2A	127.9
O1 ⁱ —Ca1—P2 ⁱ	77.10 (4)	P1 ^{iv} —Ca2—H2A	113.6
O1—Ca1—P2 ⁱ	102.90 (4)	P1 ⁱⁱⁱ —Ca2—H2A	91.1
O21 ⁱ —Ca1—P2	160.98 (4)	P2—Ca2—H2A	128.7
O21—Ca1—P2	19.02 (4)	Ca2 ^v —Ca2—H2A	108.8
O11—Ca1—P2	70.67 (4)	Ca1 ^{vi} —Ca2—H2A	78.7
O11 ⁱ —Ca1—P2	109.33 (4)	O22—Ca2—H2B	151.6
O1 ⁱ —Ca1—P2	102.90 (4)	O13 ⁱⁱⁱ —Ca2—H2B	97.1
O1—Ca1—P2	77.10 (4)	O2—Ca2—H2B	16.4
P2 ⁱ —Ca1—P2	180.000 (18)	O12—Ca2—H2B	73.8

O21 ⁱ —Ca1—P1 ⁱ	70.24 (4)	O11 ^{iv} —Ca2—H2B	65.8
O21—Ca1—P1 ⁱ	109.76 (4)	O1—Ca2—H2B	89.9
O11—Ca1—P1 ⁱ	160.29 (4)	O13 ^{iv} —Ca2—H2B	112.0
O11 ⁱ —Ca1—P1 ⁱ	19.71 (4)	P1 ^{iv} —Ca2—H2B	89.9
O1 ⁱ —Ca1—P1 ⁱ	73.49 (4)	P1 ⁱⁱⁱ —Ca2—H2B	111.4
O1—Ca1—P1 ⁱ	106.51 (4)	P2—Ca2—H2B	137.6
P2 ⁱ —Ca1—P1 ⁱ	52.709 (12)	Ca2 ^v —Ca2—H2B	108.2
P2—Ca1—P1 ⁱ	127.291 (12)	Ca1 ^{vi} —Ca2—H2B	51.7
O21 ⁱ —Ca1—P1	109.76 (4)	H2A—Ca2—H2B	27.5
O21—Ca1—P1	70.24 (4)	O13—P1—O12	114.38 (8)
O11—Ca1—P1	19.71 (4)	O13—P1—O11	107.30 (8)
O11 ⁱ —Ca1—P1	160.29 (4)	O12—P1—O11	116.49 (8)
O1 ⁱ —Ca1—P1	106.51 (4)	O13—P1—C1	108.70 (9)
O1—Ca1—P1	73.49 (4)	O12—P1—C1	103.32 (9)
P2 ⁱ —Ca1—P1	127.291 (12)	O11—P1—C1	106.05 (9)
P2—Ca1—P1	52.709 (12)	O13—P1—Ca2 ⁱⁱ	57.15 (6)
P1 ⁱ —Ca1—P1	180.000 (17)	O12—P1—Ca2 ⁱⁱ	140.52 (6)
O21 ⁱ —Ca1—Ca2 ⁱⁱ	76.36 (4)	O11—P1—Ca2 ⁱⁱ	50.37 (6)
O21—Ca1—Ca2 ⁱⁱ	103.64 (4)	C1—P1—Ca2 ⁱⁱ	116.00 (7)
O11—Ca1—Ca2 ⁱⁱ	27.57 (4)	O12—P1—Ca2 ^{vi}	83.46 (6)
O11 ⁱ —Ca1—Ca2 ⁱⁱ	152.43 (4)	O11—P1—Ca2 ^{vi}	116.94 (6)
O1 ⁱ —Ca1—Ca2 ⁱⁱ	74.12 (4)	C1—P1—Ca2 ^{vi}	127.72 (7)
O1—Ca1—Ca2 ⁱⁱ	105.88 (4)	Ca2 ⁱⁱ —P1—Ca2 ^{vi}	75.679 (16)
P2 ⁱ —Ca1—Ca2 ⁱⁱ	87.845 (10)	O13—P1—Ca1	136.36 (6)
P2—Ca1—Ca2 ⁱⁱ	92.155 (10)	O12—P1—Ca1	99.53 (6)
P1 ⁱ —Ca1—Ca2 ⁱⁱ	133.342 (10)	C1—P1—Ca1	87.98 (6)
P1—Ca1—Ca2 ⁱⁱ	46.658 (10)	Ca2 ⁱⁱ —P1—Ca1	79.232 (14)
O21 ⁱ —Ca1—Ca2 ⁱⁱⁱ	103.64 (4)	Ca2 ^{vi} —P1—Ca1	142.808 (18)
O21—Ca1—Ca2 ⁱⁱⁱ	76.36 (4)	O22—P2—O21	117.03 (9)
O11—Ca1—Ca2 ⁱⁱⁱ	152.43 (4)	O22—P2—O23	106.35 (8)
O11 ⁱ —Ca1—Ca2 ⁱⁱⁱ	27.57 (4)	O21—P2—O23	112.56 (8)
O1 ⁱ —Ca1—Ca2 ⁱⁱⁱ	105.88 (4)	O22—P2—C1	109.66 (9)
O1—Ca1—Ca2 ⁱⁱⁱ	74.12 (4)	O21—P2—C1	105.54 (9)
P2 ⁱ —Ca1—Ca2 ⁱⁱⁱ	92.155 (10)	O23—P2—C1	105.09 (9)
P2—Ca1—Ca2 ⁱⁱⁱ	87.845 (10)	O22—P2—Ca1	103.43 (6)
P1 ⁱ —Ca1—Ca2 ⁱⁱⁱ	46.658 (10)	O23—P2—Ca1	141.89 (6)
P1—Ca1—Ca2 ⁱⁱⁱ	133.342 (10)	C1—P2—Ca1	86.38 (7)
Ca2 ⁱⁱ —Ca1—Ca2 ⁱⁱⁱ	180.000 (14)	O21—P2—Ca2	100.78 (6)
O22—Ca2—O13 ⁱⁱⁱ	110.21 (5)	O23—P2—Ca2	134.96 (6)
O22—Ca2—O2	160.19 (5)	C1—P2—Ca2	93.57 (7)
O13 ⁱⁱⁱ —Ca2—O2	82.51 (5)	Ca1—P2—Ca2	78.603 (13)

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O22—Ca2—O12	78.08 (5)	Ca1—O1—Ca2	126.86 (6)
O13 ⁱⁱⁱ —Ca2—O12	153.36 (5)	Ca1—O1—H1A	105.6
O2—Ca2—O12	84.02 (5)	Ca2—O1—H1A	105.6
O22—Ca2—O11 ^{iv}	110.33 (5)	Ca1—O1—H1B	105.6
O13 ⁱⁱⁱ —Ca2—O11 ^{iv}	109.29 (5)	Ca2—O1—H1B	105.6
O2—Ca2—O11 ^{iv}	77.85 (5)	H1A—O1—H1B	106.1
O12—Ca2—O11 ^{iv}	90.09 (5)	Ca2—O2—H2A	112.9
O22—Ca2—O1	88.74 (5)	Ca2—O2—H2B	110.5
O13 ⁱⁱⁱ —Ca2—O1	76.76 (5)	H2A—O2—H2B	105.3
O2—Ca2—O1	79.26 (5)	H3A—O3—H3B	105.4
O12—Ca2—O1	78.20 (5)	H4A—O4—H4B	104.4
O11 ^{iv} —Ca2—O1	155.24 (5)	H5A—O5—H5B	108.6
O22—Ca2—O13 ^{iv}	85.30 (5)	H6A—O6—H6B	106.6
O13 ⁱⁱⁱ —Ca2—O13 ^{iv}	70.81 (6)	P1—O11—Ca1	130.70 (8)
O2—Ca2—O13 ^{iv}	113.76 (5)	P1—O11—Ca2 ⁱⁱ	100.46 (7)
O12—Ca2—O13 ^{iv}	135.83 (5)	Ca1—O11—Ca2 ⁱⁱ	127.05 (6)
O11 ^{iv} —Ca2—O13 ^{iv}	57.92 (5)	P1—O12—Ca2	138.76 (9)
O1—Ca2—O13 ^{iv}	142.51 (5)	P1—O13—Ca2 ^{vi}	127.93 (8)
O22—Ca2—P1 ^{iv}	97.16 (4)	P1—O13—Ca2 ⁱⁱ	94.01 (7)
O13 ⁱⁱⁱ —Ca2—P1 ^{iv}	91.17 (4)	Ca2 ^{vi} —O13—Ca2 ⁱⁱ	109.19 (6)
O2—Ca2—P1 ^{iv}	97.71 (4)	P2—O21—Ca1	130.53 (8)
O12—Ca2—P1 ^{iv}	113.39 (4)	P2—O22—Ca2	133.01 (9)
O11 ^{iv} —Ca2—P1 ^{iv}	29.16 (3)	C21—O23—P2	123.71 (14)
O1—Ca2—P1 ^{iv}	167.82 (4)	Cl2—C1—Cl1	108.43 (11)
O13 ^{iv} —Ca2—P1 ^{iv}	28.85 (3)	Cl2—C1—P1	108.63 (11)
O22—Ca2—P1 ⁱⁱⁱ	93.51 (4)	Cl1—C1—P1	109.34 (11)
O13 ⁱⁱⁱ —Ca2—P1 ⁱⁱⁱ	19.85 (4)	Cl2—C1—P2	108.74 (11)
O2—Ca2—P1 ⁱⁱⁱ	95.43 (4)	Cl1—C1—P2	108.71 (11)
O12—Ca2—P1 ⁱⁱⁱ	142.04 (4)	P1—C1—P2	112.90 (11)
O11 ^{iv} —Ca2—P1 ⁱⁱⁱ	127.05 (4)	O23—C21—C22	107.30 (19)
O1—Ca2—P1 ⁱⁱⁱ	64.53 (3)	O23—C21—H21A	110.3
O13 ^{iv} —Ca2—P1 ⁱⁱⁱ	78.92 (3)	C22—C21—H21A	110.3
P1 ^{iv} —Ca2—P1 ⁱⁱⁱ	104.321 (16)	O23—C21—H21B	110.3
O22—Ca2—P2	18.06 (4)	C22—C21—H21B	110.3
O13 ⁱⁱⁱ —Ca2—P2	116.57 (4)	H21A—C21—H21B	108.5
O2—Ca2—P2	142.41 (4)	C21—C22—H22A	109.5
O12—Ca2—P2	64.50 (4)	C21—C22—H22B	109.5
O11 ^{iv} —Ca2—P2	119.83 (4)	H22A—C22—H22B	109.5
O1—Ca2—P2	74.77 (4)	C21—C22—H22C	109.5
O13 ^{iv} —Ca2—P2	103.35 (3)	H22A—C22—H22C	109.5
P1 ^{iv} —Ca2—P2	112.947 (18)	H22B—C22—H22C	109.5
P1 ⁱⁱⁱ —Ca2—P2	97.378 (15)	O8—C2—C3 ^{vii}	120.89 (17)

O22—Ca2—Ca2 ^v	98.51 (4)	O8—C2—C3	120.89 (17)
O13 ⁱⁱⁱ —Ca2—Ca2 ^v	37.50 (4)	C3 ^{vii} —C2—C3	118.2 (3)
O2—Ca2—Ca2 ^v	100.60 (4)	C2—C3—H3C	109.5
O12—Ca2—Ca2 ^v	169.12 (4)	C2—C3—H3D	109.5
O11 ^{iv} —Ca2—Ca2 ^v	81.36 (4)	H3C—C3—H3D	109.5
O1—Ca2—Ca2 ^v	112.23 (4)	C2—C3—H3E	109.5
O13 ^{iv} —Ca2—Ca2 ^v	33.30 (3)	H3C—C3—H3E	109.5
P1 ^{iv} —Ca2—Ca2 ^v	56.443 (13)	H3D—C3—H3E	109.5
P1 ⁱⁱⁱ —Ca2—Ca2 ^v	47.877 (12)		

Symmetry codes: (i) $-x+1/2, -y+1/2, -z$; (ii) $x, -y, z-1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $x, -y, z+1/2$; (v) $-x+1/2, -y+1/2, -z+1$; (vi) $-x+1/2, y-1/2, -z+1/2$; (vii) $-x, y, -z+3/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1B \cdots O3	0.99	1.81	2.794 (2)	171
O1—H1A \cdots O12 ⁱⁱⁱ	0.99	1.83	2.637 (2)	137
O2—H2A \cdots O3	0.84	1.88	2.717 (2)	172
O2—H2B \cdots O21 ^{vi}	0.85	1.90	2.746 (2)	177
O3—H3A \cdots O6 ^v	0.86	1.93	2.782 (2)	175
O3—H3B \cdots O4 ^{vi}	0.86	1.89	2.734 (2)	169
O4—H4A \cdots O22	0.85	2.00	2.841 (2)	166
O4—H4B \cdots O2 ^v	0.85	1.93	2.754 (2)	163
O5—H5A \cdots O4	0.85	2.02	2.838 (2)	163
O5—H5B \cdots O6	0.85	2.05	2.901 (3)	171
O6—H6A \cdots O8	0.85	2.02	2.831 (2)	161
O6—H6B \cdots O7 ^{viii}	0.84	2.26	2.832 (2)	125
O7—H7 \cdots O5	0.84	1.98	2.799 (2)	166

Symmetry codes: (iii) $-x+1/2, y+1/2, -z+1/2$; (vi) $-x+1/2, y-1/2, -z+1/2$; (v) $-x+1/2, -y+1/2, -z+1$; (viii) $-x, -y+1, -z+1$.

Fig. 1

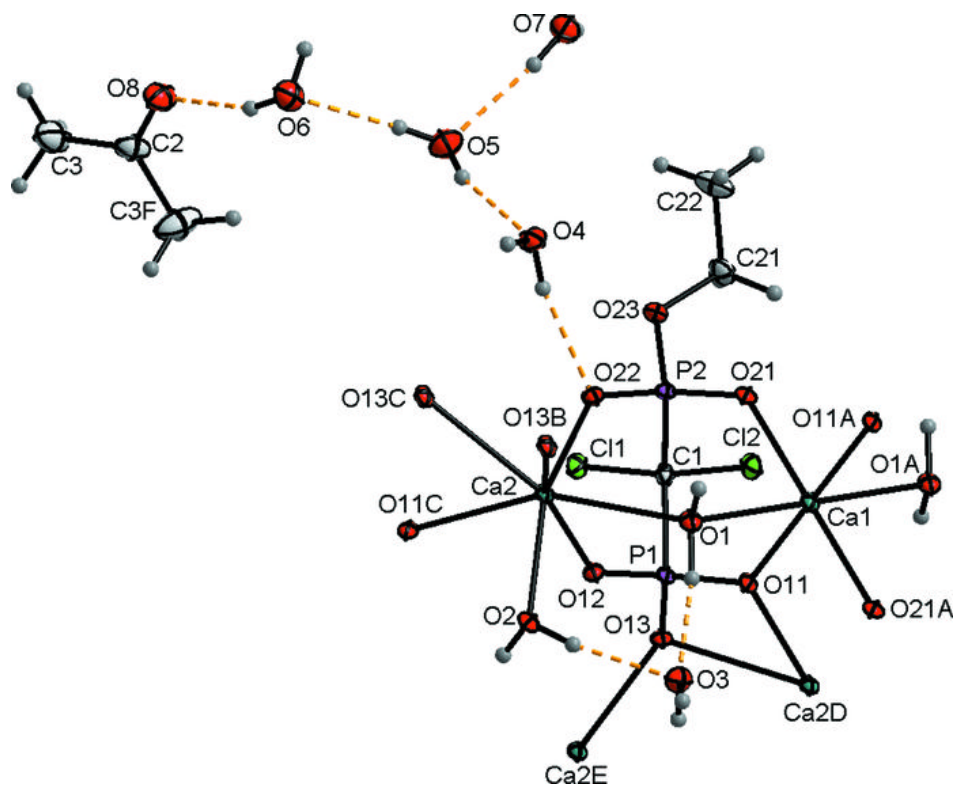


Fig. 2

