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The whitlockite-related phosphate $Ca_9Cr(PO_4)_7$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(P–O) = 0.003 Å; R factor = 0.030; wR factor = 0.073; data-to-parameter ratio = 15.8.

Nonacalcium chromium(III) heptakis(orthophosphate) has been obtained from a melt in the system Cs_2O–CaO–Cr_2O_3 using a polyphosphate flux. The three-dimensional framework is related to the whitlockite structure [β-$Ca_3(PO_4)_3$] and is built up from CaO_8 and CaO_9 polyhedra sharing vertices, edges and faces, further connected by PO_4 tetrahedra and CrO_6 octahedra. The Cr, one P and one O atom are located on threefold rotation axes. $Ca_9Cr(PO_4)_7$ is isotypic with $Ca_9Fe(PO_4)_7$. The crystal studied was an inversion twin.

Related literature

For the structure of whitlockite [β-$Ca_3(PO_4)_2$], see: Dickens *et al.* (1974). For related whitlockite-type phosphates, see: Morozov *et al.* (2002) $Ca_9In(PO_4)_7$; Teterskii *et al.* (2005) $Ca_9RE(PO_4)_7$ (RE = rare earth metals); Lazoryak *et al.* (1996, 2004) $Ca_9Fe(PO_4)_7$; Belik *et al.* (2006) $Sr_{9.2}Co_{1.3}(PO_4)_7$; Legrouri *et al.* (1996) $Ca_{3-x}Co_x(PO_4)_2$; Benarafa *et al.* (2000) $Ca_{3-x}Cu_x(PO_4)_2$.

Experimental

Crystal data

$Ca_9Cr(PO_4)_7$
M_r = 1077.51
Trigonal, $R3c$
a = 10.3272 (5) Å
c = 37.132 (2) Å
V = 3429.6 (3) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 3.14 mm^{-1}
T = 293 (2) K
0.07 × 0.07 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur-3 CCD diffractometer
Absorption correction: multi-scan *MULABS* (Blessing, 1995)
T_{min} = 0.810, T_{max} = 0.859
8460 measured reflections
2161 independent reflections
1814 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.073
S = 1.10
2161 reflections
137 parameters
1 restraint
$\Delta\rho_{max}$ = 1.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}
Absolute structure: Flack (1983), with 1040 Friedel pairs
Flack parameter: 0.59 (4)

Table 1
Selected bond lengths (Å).

Ca1—O8	2.316 (3)	Ca3—O10^{iv}	2.497 (3)
Ca1—O10^{i}	2.352 (3)	Ca3—O1^{vii}	2.5484 (16)
Ca1—O2^{ii}	2.404 (3)	Ca3—O10^{v}	2.577 (3)
Ca1—O7^{iii}	2.477 (3)	Ca3—O3	2.633 (3)
Ca1—O5^{iii}	2.480 (3)	Ca3—O8^{iv}	2.645 (3)
Ca1—O6	2.495 (3)	Ca3—O2^{vii}	2.913 (3)
Ca1—O6^{iii}	2.513 (3)	Cr1—O6^{viii}	2.012 (3)
Ca1—O4	2.716 (3)	Cr1—O9	2.023 (3)
Ca2—O2	2.320 (3)	P1—O2	1.536 (3)
Ca2—O3	2.356 (3)	P1—O1	1.538 (6)
Ca2—O5^{i}	2.386 (3)	P2—O3	1.508 (3)
Ca2—O9^{i}	2.471 (3)	P2—O4	1.530 (3)
Ca2—O4^{iv}	2.474 (3)	P2—O5	1.540 (3)
Ca2—O9^{iv}	2.503 (3)	P2—O6	1.584 (3)
Ca2—O7^{i}	2.590 (3)	P3—O10	1.516 (3)
Ca2—O8^{iv}	2.630 (3)	P3—O8	1.522 (3)
Ca3—O7^{v}	2.398 (3)	P3—O7	1.535 (3)
Ca3—O5	2.417 (3)	P3—O9	1.567 (3)
Ca3—O4^{vi}	2.457 (3)		

Symmetry codes: (i) $-y+\frac{1}{3}, -x+\frac{2}{3}, z+\frac{1}{6}$; (ii) $x-\frac{1}{3}, x-y+\frac{1}{3}, z-\frac{1}{6}$; (iii) $-x+y, -x+1, z$; (iv) $x+\frac{1}{3}, x-y+\frac{2}{3}, z+\frac{1}{6}$; (v) $-x+y+\frac{1}{3}, y-\frac{1}{3}, z+\frac{1}{6}$; (vi) $-x+y, -x, z$; (vii) $-y+\frac{2}{3}, -x+\frac{1}{3}, z-\frac{1}{6}$; (viii) $-x+y-\frac{1}{3}, y-\frac{2}{3}, z-\frac{1}{6}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2144).

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supplementary materials

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Comment

Partial substitution of alkaline earth metal atoms in $M^{II}{}_3(PO_4)_2$ (M^{II} = Ca, Sr) whitlockite-type structures (Dickens *et al.*, 1974) by monovalent, bivalent and tetravalent metals provides possibilities for obtaining new compounds with useful properties. This group of orthophosphates and their solid solutions have been intensively studied and are interesting in aspects of applications. For example, $Ca_9In(PO_4)_7$ (Morozov *et al.*, 2002), $Ca_9RE(PO_4)_7$ (RE = rare-earth metals) (Teterskii *et al.*, 2005) and $Ca_9Fe(PO_4)_7$ (Lazoryak *et al.*, 2004) exhibit interesting dielectric properties and large second-harmonic generation (SHG) effects; the solid solutions $Sr_{9.2}Co_{1.3}(PO_4)_7$ (Belik *et al.*, 2006), $Ca_{3-x}Co_x(PO_4)_2$ (Legrouri *et al.*, 1996) and $Ca_{3-x}Cu_x(PO_4)_2$ (Benarafa *et al.*, 2000) possess catalytic activity; $Ca_9Fe(PO_4)_7$ (Lazoryak *et al.*, 1996) can be used as a sensor material and for removing H_2 from gas mixtures.

We report here the flux-growth synthesis and structural characterization of the whitlockite-related phosphate $Ca_9Cr(PO_4)_7$, (I), which is isotypic with $Ca_9Fe(PO_4)_7$ (Lazoryak *et al.*, 2004).

The structure of (I) contains three types of layers, which are formed by Ca atoms in positions Ca1, Ca2 and Ca3, respectively (Fig. 1). The $Ca1O_8$, $Ca2O_8$ and $Ca3O_9$ polyhedra, with Ca–O distances ranging from 2.316 (3) to 2.913 (3) Å (Table), are linked together *via* vertices, edges and faces. The polyhedral network is additionally linked by three different corner- or edge-sharing PO_4 tetrahedra and a CrO_6 octahedron. The PO_4 tetrahedra are quite regular with P–O bond lengths ranging from 1.508 (3) to 1.584 (3) Å, and O–P–O angles spreading over the range 104.58 (16)–114.19 (18)°. The coordination of the Cr^{3+} cation is slightly distorted octahedral with two different Cr–O distances of 2.012 (3) and 2.023 (3) Å, respectively (Fig. 3).

Experimental

The title compound was prepared in a flux in the system Cs_2O—P_2O_5—CaO-Cr_2O_3. A mixture of $CsPO_3$ (5.0 g), $CaCO_3$ (0.708 g) and Cr_2O_3 (0.270 g) was ground in an agate mortar, placed into a platinum crucible and heated up to 1273 K. The melt was kept at this temperature until it became homogenous (2 h). The temperature was then decreased to 1053 K at a rate of 30 K h-1, and at this temperature the remaining flux was decantated. Finally, the crucible was cooled down to room temperature. The solidified melt was leached out with deionized water and light-green crystals of $Ca_9Cr(PO_4)_7$ were recovered.

Refinement

The measured crystal was racemically twinned (Flack parameter 0.59 (4)). The highest remaining peak in the final Fourier map is 0.82 Å from atom P1.

Figures

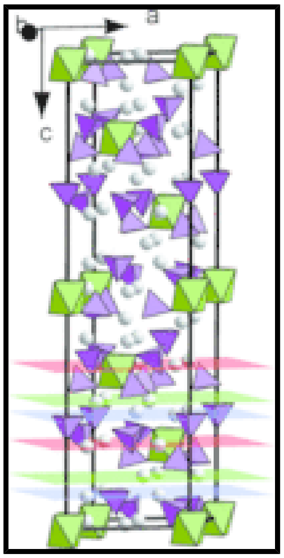

Fig. 1. Unit cell with the three types of calcium layers in the crystal structure of (I). Colour code: Pink plane – Ca1 layer, green plane – Ca2 layer, red plane – Ca3 layer; green octahedra – CrO_6 polyhedra, purple tetrahedra – PO_4).

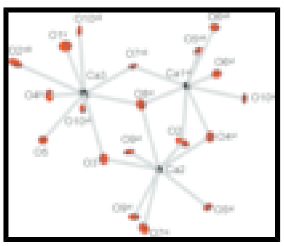

Fig. 2. The Ca^{2+} cations with their oxygen neighbours, displayed with anisotropic displacement ellipsoids at the 70% probability level [Symmetry code: (ii) $-x + y$, $-x$, z; (v) $2/3 - x + y$, $1/3 + y$, $-1/6 + z$; (vi) $1/3 + x$, $2/3 + x$-y, $1/6 + z$; (vii) $1/3 - x + y$, $-1/3 + y$, $1/6 + z$; (viii) $2/3 - y$, $1/3 - x$, $-1/6 + z$; (x) $2/3 - y$, $1/3 + x$-y, $-1/3 + z$; (xi) $1/3 - y$, $2/3 - y$, $1/6 + z$.].

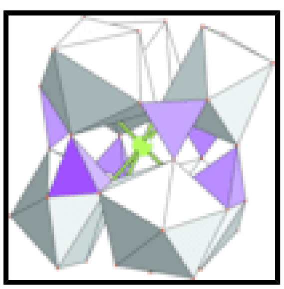

Fig. 3. Fragment of the crystal structure of (I) showing the coordination of the Cr^{3+} cation. The CaO_8 polyhedra are displayed with grey shading, PO_4 tetrahedra with purple shading and Cr atom as green circle.

Nonacalcium chromium(III) heptakis(orthophosphate)

Crystal data

$Ca_9Cr(PO_4)_7$	$Z = 6$
$M_r = 1077.51$	$F_{000} = 3198$
Trigonal, *R*3*c*	$D_x = 3.13$ Mg m^{-3}
Hall symbol: R 3 -2"c	Mo *K*α radiation λ = 0.71073 Å
a = 10.3272 (5) Å	Cell parameters from 8460 reflections
b = 10.3272 (5) Å	θ = 3.2–30.0°
c = 37.132 (2) Å	μ = 3.14 mm^{-1}
α = 90°	*T* = 293 (2) K

$\beta = 90°$	Prism, green
$\gamma = 120°$	0.07 × 0.07 × 0.05 mm
$V = 3429.6$ (3) Å^3	

Data collection

XCalibur-3 CCD (Oxford Diffraction) diffractometer	2161 independent reflections
Radiation source: fine-focus sealed tube	1814 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
$T = 293(2)$ K	$\theta_{max} = 30.0°$
φ and ω scans	$\theta_{min} = 3.2°$
Absorption correction: multi-scan MULABS (Blessing, 1995)	$h = -14\rightarrow14$
$T_{min} = 0.810$, $T_{max} = 0.859$	$k = -14\rightarrow14$
8460 measured reflections	$l = -46\rightarrow52$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$\Delta\rho_{max} = 1.78$ e Å^{-3}
$wR(F^2) = 0.073$	$\Delta\rho_{min} = -0.84$ e Å^{-3}
$S = 1.10$	Extinction correction: none
2161 reflections	Absolute structure: Flack (1983), 1040 Friedel pairs
137 parameters	Flack parameter: 0.59 (4)
1 restraint	

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.

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

	x	y	z	U_{iso}*/U_{eq}
Ca1	0.05547 (9)	0.52061 (10)	0.100572 (19)	0.00617 (17)
Ca2	0.20187 (10)	0.37769 (10)	0.23313 (2)	0.00654 (17)
Ca3	0.38876 (10)	0.20333 (9)	0.16032 (2)	0.01017 (17)
Cr1	0	0	0.00199 (3)	0.00405 (18)
P1	0	0	0.27062 (5)	0.0106 (4)
P2	0.17511 (12)	0.31774 (12)	0.13731 (3)	0.0042 (2)
P3	0.18862 (12)	0.34253 (14)	0.03226 (3)	0.0052 (2)
O1	0	0	0.31204 (16)	0.0148 (11)
O2	0.1360 (3)	0.1467 (3)	0.25799 (8)	0.0111 (6)

O3	0.1821 (4)	0.2731 (4)	0.17561 (8)	0.0121 (6)
O4	0.0164 (3)	0.2525 (4)	0.12245 (8)	0.0103 (6)
O5	0.2744 (3)	0.2782 (3)	0.11421 (7)	0.0076 (6)
O6	0.2502 (4)	0.4937 (3)	0.13402 (8)	0.0083 (6)
O7	0.3479 (3)	0.3948 (3)	0.04562 (8)	0.0097 (6)
O8	0.1122 (3)	0.4133 (3)	0.05284 (8)	0.0101 (6)
O9	0.0940 (3)	0.1692 (3)	0.03804 (8)	0.0076 (6)
O10	0.1937 (3)	0.3779 (3)	−0.00752 (7)	0.0097 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0074 (4)	0.0061 (4)	0.0053 (4)	0.0036 (3)	−0.0003 (3)	−0.0012 (3)
Ca2	0.0062 (4)	0.0071 (4)	0.0060 (3)	0.0032 (4)	0.0011 (3)	0.0020 (3)
Ca3	0.0151 (4)	0.0082 (4)	0.0091 (4)	0.0072 (3)	−0.0035 (3)	0.0001 (3)
Cr1	0.0040 (3)	0.0040 (3)	0.0042 (4)	0.00199 (13)	0	0
P1	0.0060 (5)	0.0060 (5)	0.0199 (10)	0.0030 (2)	0	0
P2	0.0037 (5)	0.0030 (4)	0.0058 (5)	0.0016 (4)	0.0007 (4)	−0.0006 (4)
P3	0.0060 (5)	0.0049 (4)	0.0046 (5)	0.0026 (4)	0.0020 (4)	0.0008 (4)
O1	0.0126 (16)	0.0126 (16)	0.019 (3)	0.0063 (8)	0	0
O2	0.0055 (13)	0.0057 (14)	0.0184 (18)	0.0002 (10)	−0.0037 (11)	0.0035 (11)
O3	0.0149 (15)	0.0126 (15)	0.0095 (15)	0.0075 (12)	0.0002 (12)	0.0003 (11)
O4	0.0080 (15)	0.0141 (15)	0.0080 (15)	0.0050 (12)	0.0004 (11)	0.0001 (11)
O5	0.0073 (14)	0.0053 (13)	0.0098 (14)	0.0028 (11)	−0.0017 (10)	−0.0026 (11)
O6	0.0081 (14)	0.0075 (14)	0.0107 (14)	0.0050 (13)	0.0007 (11)	0.0001 (10)
O7	0.0031 (13)	0.0131 (15)	0.0111 (15)	0.0026 (12)	−0.0008 (11)	0.0012 (12)
O8	0.0142 (15)	0.0103 (14)	0.0099 (14)	0.0091 (13)	0.0025 (11)	−0.0023 (11)
O9	0.0058 (14)	0.0030 (13)	0.0129 (14)	0.0014 (12)	−0.0001 (11)	0.0010 (11)
O10	0.0128 (15)	0.0097 (14)	0.0031 (13)	0.0031 (12)	−0.0016 (11)	0.0005 (10)

Geometric parameters (Å, °)

Ca1—O8	2.316 (3)	Ca3—P3^{vi}	3.0244 (14)
Ca1—O10^{i}	2.352 (3)	Ca3—P2	3.0987 (14)
Ca1—O2^{ii}	2.404 (3)	Ca3—P3^{v}	3.1244 (14)
Ca1—O7^{iii}	2.477 (3)	Cr1—O6^{ix}	2.012 (3)
Ca1—O5^{iii}	2.480 (3)	Cr1—O6^{viii}	2.012 (3)
Ca1—O6	2.495 (3)	Cr1—O6^{ii}	2.012 (3)
Ca1—O6^{iii}	2.513 (3)	Cr1—O9^{x}	2.023 (3)
Ca1—O4	2.716 (3)	Cr1—O9^{vii}	2.023 (3)
Ca1—P2^{iii}	3.1171 (14)	Cr1—O9	2.023 (3)
Ca1—P2	3.2195 (14)	P1—O2^{x}	1.536 (3)
Ca1—P1^{iv}	3.4804 (9)	P1—O2	1.536 (3)
Ca1—Ca2^{ii}	3.4861 (10)	P1—O2^{vii}	1.536 (3)
Ca2—O2	2.320 (3)	P1—O1	1.538 (6)
Ca2—O3	2.356 (3)	P1—Ca3^{i}	3.2507 (15)

Ca2—O5^{i}	2.386 (3)	P1—Ca3^{xi}	3.2507 (16)
Ca2—O9^{i}	2.471 (3)	P1—Ca3^{vi}	3.2508 (15)
Ca2—O4^{v}	2.474 (3)	P1—Ca1^{xii}	3.4803 (9)
Ca2—O9^{v}	2.503 (3)	P1—Ca1^{v}	3.4804 (9)
Ca2—O7^{i}	2.590 (3)	P1—Ca1^{xiii}	3.4804 (9)
Ca2—O8^{v}	2.630 (3)	P2—O3	1.508 (3)
Ca2—P3^{i}	3.1141 (15)	P2—O4	1.530 (3)
Ca2—P3^{v}	3.1424 (14)	P2—O5	1.540 (3)
Ca2—Ca1^{v}	3.4862 (10)	P2—O6	1.584 (3)
Ca2—Cr1^{i}	3.5254 (12)	P2—Ca1^{xiv}	3.1171 (14)
Ca3—O7^{vi}	2.398 (3)	P2—Ca3^{x}	3.5400 (13)
Ca3—O5	2.417 (3)	P3—O10	1.516 (3)
Ca3—O4^{vii}	2.457 (3)	P3—O8	1.522 (3)
Ca3—O10^{v}	2.497 (3)	P3—O7	1.535 (3)
Ca3—O1^{viii}	2.5484 (16)	P3—O9	1.567 (3)
Ca3—O10^{vi}	2.577 (3)	P3—Ca3^{xv}	3.0244 (14)
Ca3—O3	2.633 (3)	P3—Ca2^{viii}	3.1141 (15)
Ca3—O8^{v}	2.645 (3)	P3—Ca3^{ii}	3.1244 (14)
Ca3—O2^{viii}	2.913 (3)	P3—Ca2^{ii}	3.1424 (14)
O8—Ca1—O10^{i}	142.88 (11)	O1^{viii}—Ca3—O2^{viii}	53.59 (14)
O8—Ca1—O2^{ii}	84.88 (11)	O10^{vi}—Ca3—O2^{viii}	65.06 (9)
O10^{i}—Ca1—O2^{ii}	77.14 (10)	O3—Ca3—O2^{viii}	130.12 (10)
O8—Ca1—O7^{iii}	73.68 (10)	O8^{v}—Ca3—O2^{viii}	141.78 (9)
O10^{i}—Ca1—O7^{iii}	138.10 (10)	O6^{ix}—Cr1—O6^{viii}	83.53 (13)
O2^{ii}—Ca1—O7^{iii}	91.57 (10)	O6^{ix}—Cr1—O6^{ii}	83.53 (13)
O8—Ca1—O5^{iii}	141.13 (11)	O6^{viii}—Cr1—O6^{ii}	83.53 (13)
O10^{i}—Ca1—O5^{iii}	74.37 (10)	O6^{ix}—Cr1—O9^{x}	98.93 (13)
O2^{ii}—Ca1—O5^{iii}	98.61 (10)	O6^{viii}—Cr1—O9^{x}	177.54 (15)
O7^{iii}—Ca1—O5^{iii}	67.56 (9)	O6^{ii}—Cr1—O9^{x}	96.57 (12)
O8—Ca1—O6	85.21 (11)	O6^{ix}—Cr1—O9^{vii}	96.57 (12)
O10^{i}—Ca1—O6	79.07 (10)	O6^{viii}—Cr1—O9^{vii}	98.93 (13)
O2^{ii}—Ca1—O6	124.72 (10)	O6^{ii}—Cr1—O9^{vii}	177.54 (15)
O7^{iii}—Ca1—O6	136.30 (10)	O9^{x}—Cr1—O9^{vii}	80.98 (13)
O5^{iii}—Ca1—O6	121.53 (10)	O6^{ix}—Cr1—O9	177.54 (15)
O8—Ca1—O6^{iii}	124.59 (11)	O6^{viii}—Cr1—O9	96.57 (12)
O10^{i}—Ca1—O6^{iii}	77.97 (10)	O6^{ii}—Cr1—O9	98.93 (13)
O2^{ii}—Ca1—O6^{iii}	150.53 (10)	O9^{x}—Cr1—O9	80.98 (13)
O7^{iii}—Ca1—O6^{iii}	96.50 (10)	O9^{vii}—Cr1—O9	80.98 (13)
O5^{iii}—Ca1—O6^{iii}	59.32 (10)	O2^{x}—P1—O2	111.11 (12)
O6—Ca1—O6^{iii}	64.72 (14)	O2^{x}—P1—O2^{vii}	111.11 (12)
O8—Ca1—O4	71.64 (10)	O2—P1—O2^{vii}	111.11 (12)

O10^{i}—Ca1—O4	71.58 (10)	O2^{x}—P1—O1	107.78 (13)
O2^{ii}—Ca1—O4	68.34 (10)	O2—P1—O1	107.78 (13)
O7^{iii}—Ca1—O4	141.05 (10)	O2^{vii}—P1—O1	107.78 (13)
O5^{iii}—Ca1—O4	145.46 (10)	O3—P2—O4	114.19 (18)
O6—Ca1—O4	56.93 (10)	O3—P2—O5	107.73 (17)
O6^{iii}—Ca1—O4	117.61 (10)	O4—P2—O5	113.00 (17)
O8—Ca1—P2^{iii}	143.40 (9)	O3—P2—O6	110.64 (18)
O2—Ca2—O3	88.61 (11)	O4—P2—O6	106.27 (17)
O2—Ca2—O5^{i}	84.27 (11)	O5—P2—O6	104.58 (16)
O3—Ca2—O5^{i}	142.23 (11)	P1—O1—Ca3^{i}	102.58 (13)
O2—Ca2—O9^{i}	157.39 (11)	P1—O1—Ca3^{xi}	102.58 (13)
O3—Ca2—O9^{i}	88.49 (11)	Ca3^{i}—O1—Ca3^{xi}	115.40 (9)
O5^{i}—Ca2—O9^{i}	84.36 (10)	P1—O1—Ca3^{vi}	102.58 (13)
O2—Ca2—O4^{v}	73.98 (10)	Ca3^{i}—O1—Ca3^{vi}	115.39 (9)
O3—Ca2—O4^{v}	139.97 (12)	Ca3^{xi}—O1—Ca3^{vi}	115.39 (9)
O5^{i}—Ca2—O4^{v}	72.72 (11)	P1—O2—Ca2	142.12 (19)
O9^{i}—Ca2—O4^{v}	120.70 (11)	P1—O2—Ca1^{v}	122.56 (17)
O2—Ca2—O9^{v}	137.71 (11)	Ca2—O2—Ca1^{v}	95.10 (10)
O3—Ca2—O9^{v}	81.44 (10)	P1—O2—Ca3^{i}	88.21 (14)
O5^{i}—Ca2—O9^{v}	126.71 (10)	Ca2—O2—Ca3^{i}	86.29 (9)
O9^{i}—Ca2—O9^{v}	63.75 (14)	Ca1^{v}—O2—Ca3^{i}	92.17 (9)
O4^{v}—Ca2—O9^{v}	87.73 (10)	P2—O3—Ca2	136.17 (19)
O2—Ca2—O7^{i}	98.25 (10)	P2—O3—Ca3	92.84 (15)
O3—Ca2—O7^{i}	77.37 (11)	Ca2—O3—Ca3	115.12 (13)
O5^{i}—Ca2—O7^{i}	67.12 (10)	P2—O4—Ca3^{x}	123.57 (16)
O9^{i}—Ca2—O7^{i}	59.26 (10)	P2—O4—Ca2^{ii}	142.26 (17)
O4^{v}—Ca2—O7^{i}	139.70 (10)	Ca3^{x}—O4—Ca2^{ii}	93.97 (11)
O9^{v}—Ca2—O7^{i}	119.04 (10)	P2—O4—Ca1	94.49 (15)
O2—Ca2—O8^{v}	79.84 (10)	Ca3^{x}—O4—Ca1	95.96 (11)
O3—Ca2—O8^{v}	70.70 (11)	Ca2^{ii}—O4—Ca1	84.28 (9)
O5^{i}—Ca2—O8^{v}	143.05 (10)	P2—O5—Ca2^{viii}	147.59 (18)
O9^{i}—Ca2—O8^{v}	120.07 (10)	P2—O5—Ca3	100.77 (14)
O4^{v}—Ca2—O8^{v}	70.88 (10)	Ca2^{viii}—O5—Ca3	97.29 (11)
O9^{v}—Ca2—O8^{v}	58.03 (9)	P2—O5—Ca1^{xiv}	98.99 (14)
O7^{i}—Ca2—O8^{v}	148.04 (10)	Ca2^{viii}—O5—Ca1^{xiv}	103.64 (11)
O7^{vi}—Ca3—O5	153.05 (12)	Ca3—O5—Ca1^{xiv}	101.18 (11)
O7^{vi}—Ca3—O4^{vii}	94.92 (11)	P2—O6—Cr1^{i}	135.74 (18)
O5—Ca3—O4^{vii}	72.50 (10)	P2—O6—Ca1	101.92 (15)
O7^{vi}—Ca3—O10^{v}	123.00 (10)	Cr1^{i}—O6—Ca1	103.22 (13)
O5—Ca3—O10^{v}	72.96 (10)	P2—O6—Ca1^{xiv}	96.44 (15)
O4^{vii}—Ca3—O10^{v}	142.08 (10)	Cr1^{i}—O6—Ca1^{xiv}	102.60 (13)

O7^{vi}—Ca3—O1^{viii}	100.65 (13)	Ca1—O6—Ca1^{xiv}	118.58 (12)
O5—Ca3—O1^{viii}	106.20 (13)	P3—O7—Ca3^{xv}	98.15 (14)
O4^{vii}—Ca3—O1^{viii}	113.31 (12)	P3—O7—Ca1^{xiv}	130.55 (17)
O10^{v}—Ca3—O1^{viii}	62.91 (7)	Ca3^{xv}—O7—Ca1^{xiv}	109.05 (12)
O7^{vi}—Ca3—O10^{vi}	59.84 (9)	P3—O7—Ca2^{viii}	94.56 (14)
O5—Ca3—O10^{vi}	133.01 (9)	Ca3^{xv}—O7—Ca2^{viii}	130.06 (13)
O4^{vii}—Ca3—O10^{vi}	72.52 (10)	Ca1^{xiv}—O7—Ca2^{viii}	98.01 (10)
O10^{v}—Ca3—O10^{vi}	123.73 (12)	P3—O8—Ca1	158.44 (19)
O1^{viii}—Ca3—O10^{vi}	61.84 (7)	P3—O8—Ca2^{ii}	94.58 (15)
O7^{vi}—Ca3—O3	101.93 (11)	Ca1—O8—Ca2^{ii}	89.39 (10)
O5—Ca3—O3	58.15 (10)	P3—O8—Ca3^{ii}	93.18 (14)
O4^{vii}—Ca3—O3	98.18 (11)	Ca1—O8—Ca3^{ii}	106.09 (12)
O10^{v}—Ca3—O3	76.22 (10)	Ca2^{ii}—O8—Ca3^{ii}	105.99 (11)
O1^{viii}—Ca3—O3	139.12 (8)	P3—O9—Cr1	130.69 (17)
O10^{vi}—Ca3—O3	157.60 (11)	P3—O9—Ca2^{viii}	98.43 (14)
O7^{vi}—Ca3—O8^{v}	69.36 (10)	Cr1—O9—Ca2^{viii}	102.88 (13)
O5—Ca3—O8^{v}	112.01 (10)	P3—O9—Ca2^{ii}	98.45 (14)
O4^{vii}—Ca3—O8^{v}	153.80 (11)	Cr1—O9—Ca2^{ii}	101.80 (12)
O10^{v}—Ca3—O8^{v}	57.68 (9)	Ca2^{viii}—O9—Ca2^{ii}	128.60 (12)
O1^{viii}—Ca3—O8^{v}	90.72 (13)	P3—O10—Ca1^{viii}	145.17 (19)
O10^{vi}—Ca3—O8^{v}	113.31 (9)	P3—O10—Ca3^{ii}	99.33 (15)
O3—Ca3—O8^{v}	66.48 (10)	Ca1^{viii}—O10—Ca3^{ii}	102.53 (10)
O7^{vi}—Ca3—O2^{viii}	124.77 (10)	P3—O10—Ca3^{xv}	91.55 (13)
O5—Ca3—O2^{viii}	71.97 (10)	Ca1^{viii}—O10—Ca3^{xv}	102.52 (11)
O4^{vii}—Ca3—O2^{viii}	64.38 (9)	Ca3^{ii}—O10—Ca3^{xv}	116.21 (12)
O10^{v}—Ca3—O2^{viii}	90.31 (9)		

Symmetry codes: (i) −*y*+1/3, −*x*+2/3, *z*+1/6; (ii) *x*−1/3, *x*−*y*+1/3, *z*−1/6; (iii) −*x*+*y*, −*x*+1, *z*; (iv) −*y*−1/3, −*x*+1/3, *z*−1/6; (v) *x*+1/3, *x*−*y*+2/3, *z*+1/6; (vi) −*x*+*y*+1/3, *y*−1/3, *z*+1/6; (vii) −*x*+*y*, −*x*, *z*; (viii) −*y*+2/3, −*x*+1/3, *z*−1/6; (ix) −*x*+*y*−1/3, *y*−2/3, *z*−1/6; (x) −*y*, *x*−*y*, *z*; (xi) *x*−2/3, *x*−*y*−1/3, *z*+1/6; (xii) −*x*+*y*−2/3, *y*−1/3, *z*+1/6; (xiii) −*y*+1/3, −*x*−1/3, *z*+1/6; (xiv) −*y*+1, *x*−*y*+1, *z*; (xv) −*x*+*y*+2/3, *y*+1/3, *z*−1/6.

Fig. 1

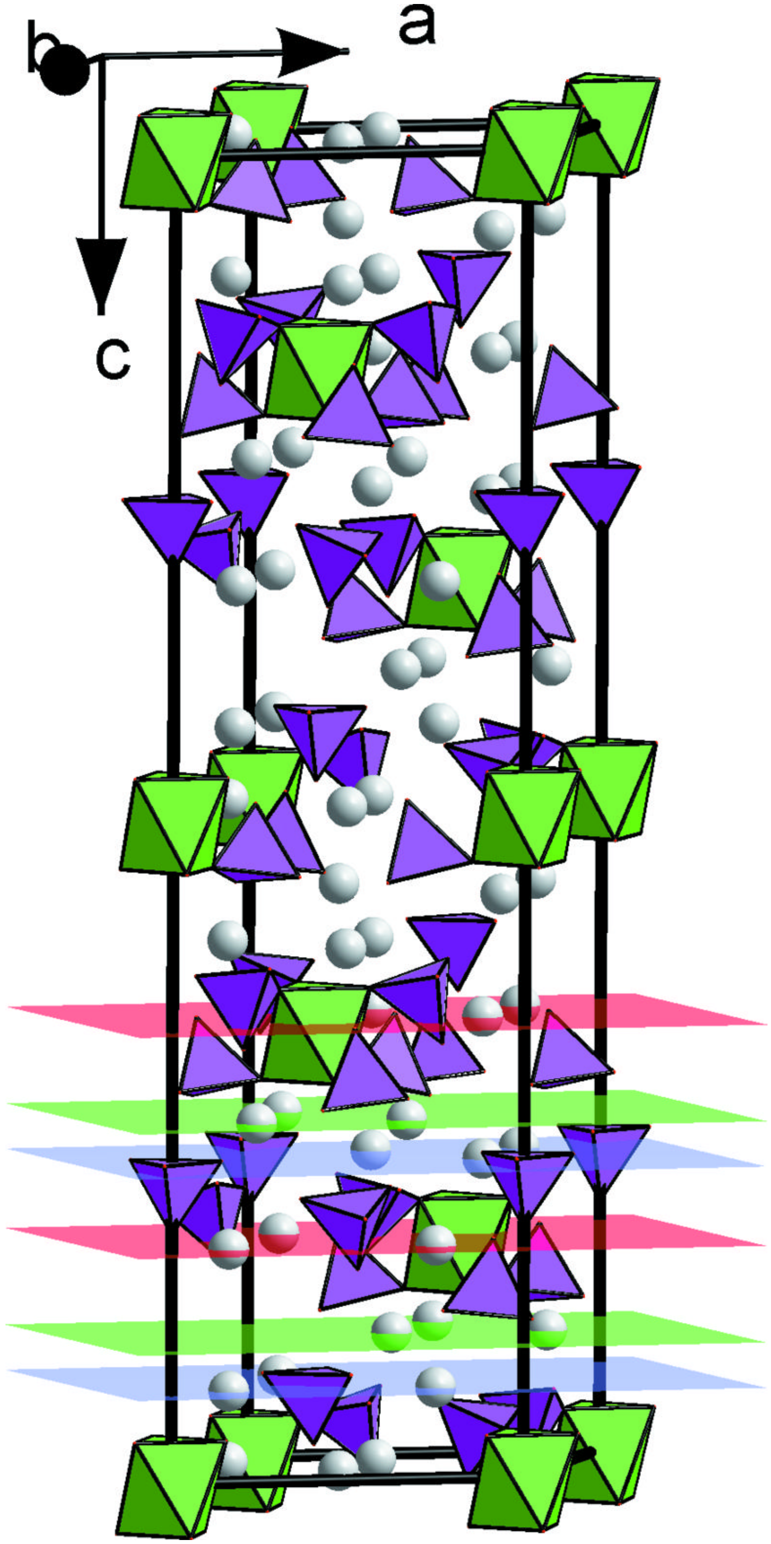

Fig. 2

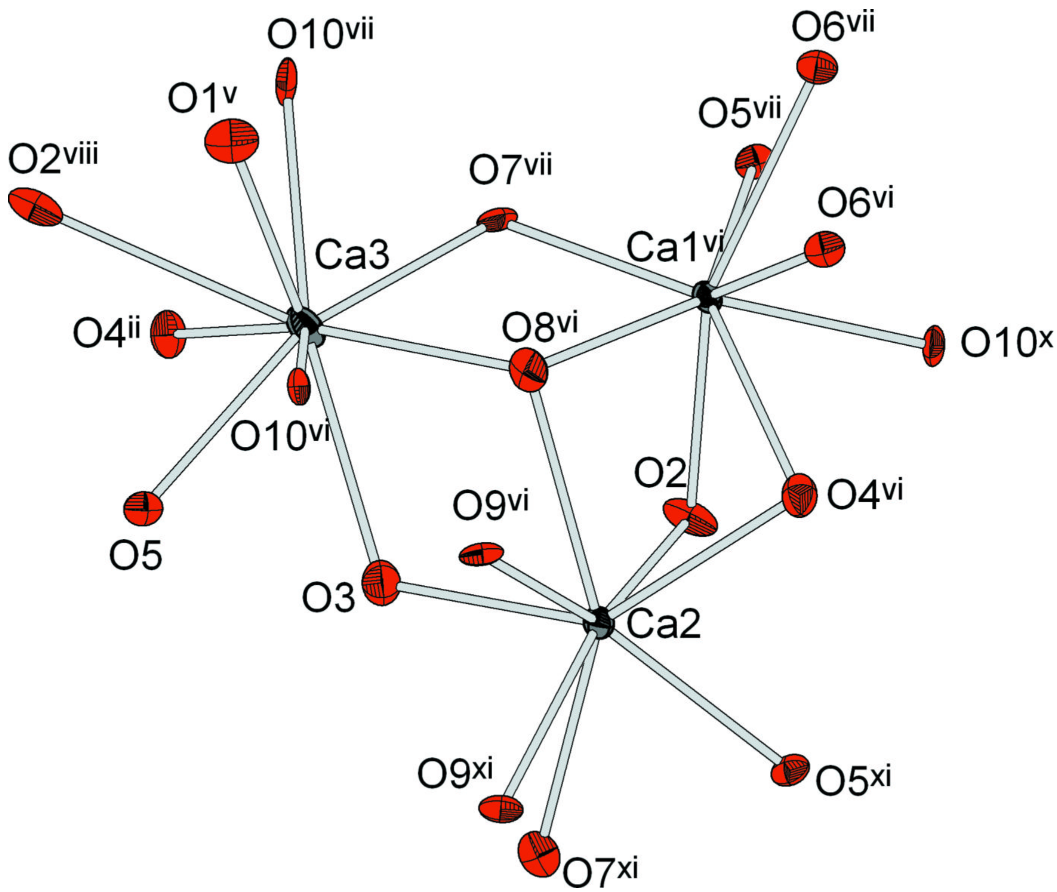
O10vii
O1v
O2viii
O7vii
O6vii
O5vii
O6vi
Ca3
Ca1vi
O4ii
O8vi
O10x
O10vi
O2
O9vi
O4vi
O5
O3
Ca2
O9xi
O5xi
O7xi

Fig. 3