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Synthesis and crystal structure of calcium dizinc iron(III) tris(orthophosphate), $CaZn_2Fe(PO_4)_3$

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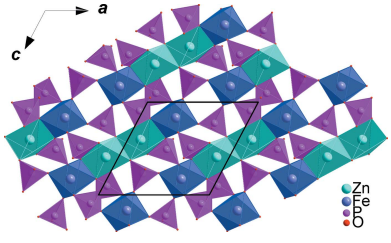
Single crystals of the title compound, $CaZn_2Fe(PO_4)_3$, were synthesized by conventional solid-state reaction. In the asymmetric unit, all atoms are located in fully occupied general positions of the $P2_1/c$ space group. The zinc atoms are located on two crystallographically independent sites with tetrahedral and distorted triangular-based bipyramidal geometries. Two edge-sharing triangular bipyramidal ZnO_5 units form a dimer, which is linked to slightly deformed FeO_6 octahedra *via* a common edge. The resulting chains are interconnected through PO_4 tetrahedra to form a layer perpendicular to the *b* axis. Moreover, the remaining PO_4 and ZnO_4 tetrahedra are linked together through common vertices to form tapes parallel to the *c* axis and surrounding a chain of Ca^{2+} cations to build a sheet, also perpendicular to the *b* axis. The stacking of the two layers along the *b* axis leads to the resulting three-dimensional framework, which defines channels in which the Ca^{2+} cations are located, each cation being coordinated by seven oxygen atoms.

1. Chemical context

Microporous compounds with an open anionic framework containing transition metals have been widely studied during recent years, especially iron phosphates, because of their potential applications in several fields such as gas sensing (Abdurahman *et al.*, 2014), catalysis (Ai, 1999), as cathode materials for rechargeable lithium batteries (Masquelier *et al.*, 1998), biocompatibility of glass fibres for tissue engineering (Ahmed *et al.*, 2004), and immobilization of spent nuclear fuel (Mesko & Day, 1999). Metal phosphates with an open framework can exhibit different architectures such as linear-chain, layered and three-dimensional structures with channels or cavities where a variety of cations with different sizes, ratio and charges are accommodated. The occupancy of the allowed sites by cations can provide different properties such as remarkable flexibility, fast ionic conduction and low thermal expansion, mainly observed in the compounds belonging to the NASICON family with the general formula $MM'_2P_3O_{12}$ (where *M* = alkali metal, alkaline-earth metal or a vacant site and *M*′ = Zr, Ti, Hf, *etc.*; Senbhagaraman *et al.*, 1993). In our previous hydrothermal investigations, a variety of compounds have been synthesized and characterized with different ratios of alkaline earth metal:P, *viz.* $Sr_2Mn_3(HPO_4)_2(PO_4)_2$ (Khmiyas *et al.*, 2013), $BaMn^{II}_2Mn^{III}(PO_4)_3$ (Assani *et al.*, 2013), $Mg_7(PO_4)_2(HPO_4)_4$ (Assani *et al.*, 2011). In this context, our interest is focused on the synthesis of new iron orthophosphates with an open-framework structure. Accordingly, we have succeeded in synthesizing and structurally characterizing a new calcium, zinc and iron-based open-framework phosphate, namely $CaZn_2Fe(PO_4)_3$.



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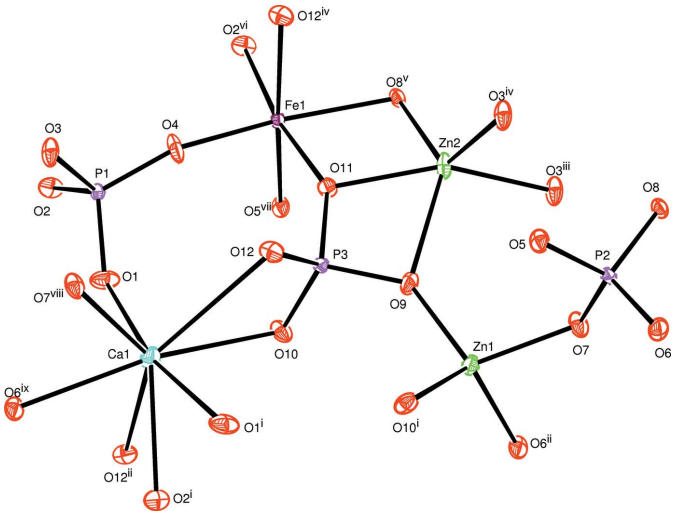

Figure 1
The principal building units in the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+2, -y+1, -z+1$; (vi) $-x+1, -y+1, -z+2$; (vii) $x, y, z+1$; (viii) $x-1, y, z$; (ix) $x-1, -y+\frac{3}{2}, z+\frac{1}{2}$.]

2. Structural commentary

All atoms in asymmetric unit of the title compound occupy general positions of the $P2_1/c$ space group. The refinement of this model was very easy and lead to an ordered structure in which the zinc cations occupy two sites with different environments. The coordination numbers of all cations were confirmed by bond-valence-sum calculations (Brown & Altermatt, 1985). The obtained values for Ca^{II+}, Zn^{II+}, Fe^{III+} and P^{V+} are as expected, *viz*. Ca1 (1.93), Zn1 (2.00), Zn2 (1.91), Fe1 (3.04), P1 (5.11), P2 (4.97) and P3 (4.94). The crystal structure is build up from PO_4 and $Zn1O_4$ tetrahedra, distorted triangular-based bipyramidal $Zn2O_5$ and FeO_6 octahedra, as shown in Fig. 1. The FeO_6 octahedra are slightly deformed with Fe—O distances varying from 1.8908 (8) to 2.1318 (8) Å and share a common edge with the highly distorted $[(Zn2)_2O_8]$ dimer resulting from the edge-sharing of two triangular-based bipyramidal $Zn2O_5$ units. Sequences of these polyhedra build chains interconnected by PO_4 tetrahedra, forming a layer perpendicular to the *b* axis, as shown in Fig. 2. The remaining $Zn1O_4$ tetrahedra are linked to irregular PO_4 groups *via* common corners, forming tapes parallel to the *c* axis, which are linked together by Ca^{2+} cations in sheets perpendicular to the *b* axis (see Fig. 3). The obtained three-dimensional framework shows one type of channel running along the [001] direction in which the Ca^{2+} cations are located, each being coordinated by seven oxygen atoms (Fig. 4).

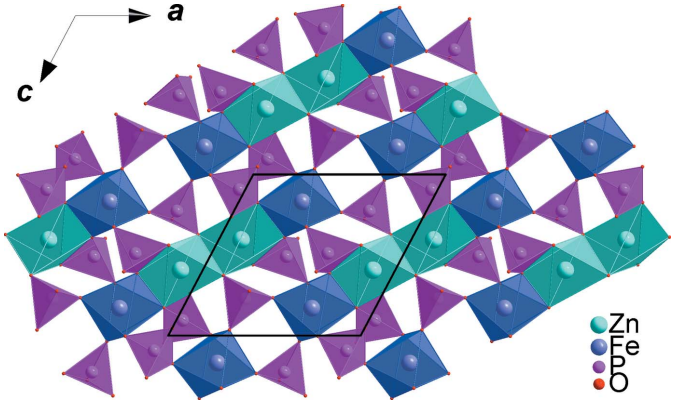

Figure 2
Edge-sharing triangular bipyramidal ZnO_5 units linked to FeO_6 octahedra and to PO_4 tetrahedra, forming a layer perpendicular to the *b* axis.

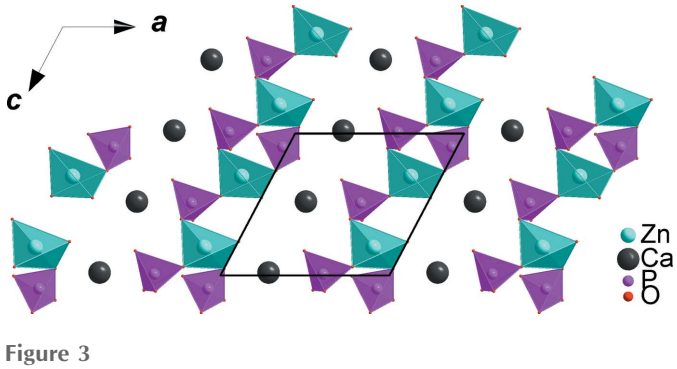

Figure 3
A layer perpendicular to the *b* axis, resulting from the chains connected *via* vertices of the ZnO_4 and PO_4 tetrahedra.

3. Database Survey

The formula of the title compound, $CaZn_2Fe(PO_4)_3$, is similar to some compounds with alluaudite structures, space group $C2/c$ or the α-$CrPO_4$ structure, space group *Imma*. However, its structure is different and to our knowledge there is no known isotypic structure. Crystals of $CaM_2Fe(PO_4)_3$ (M = Mg,

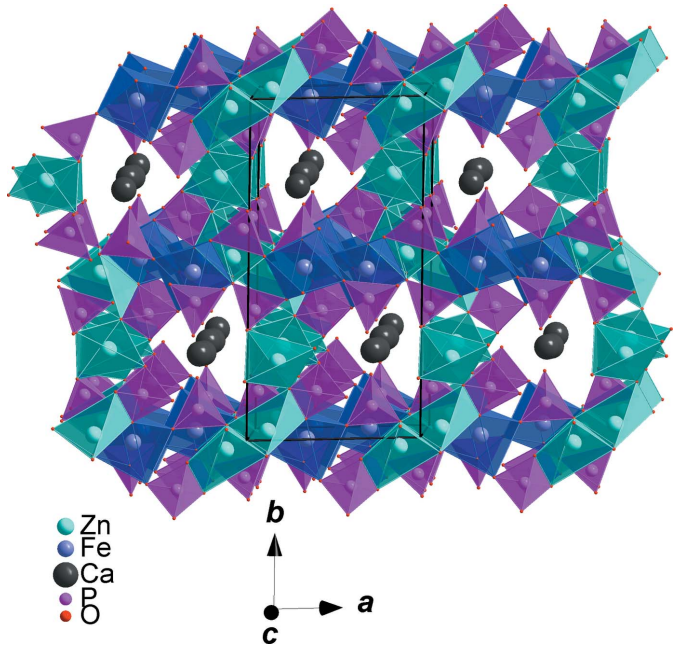

Figure 4
Polyhedral representation of $CaZn_2Fe(PO_4)_3$, showing the channels running along the [001] direction.

Table 1
Experimental details.

Crystal data	
Chemical formula	$CaZn_2Fe(PO_4)_3$
M_r	511.58
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	8.5619 (3), 15.2699 (5), 8.1190 (3)
β (°)	117.788 (2)
V (Å^3)	939.06 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.72
Crystal size (mm)	0.30 × 0.26 × 0.18
Data collection	
Diffractometer	Bruker X8 *APEX*
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.600, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	54053, 4985, 4493
R_{int}	0.033
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.859
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.041, 1.04
No. of reflections	4985
No. of parameters	172
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.07, −0.78

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

Co, Ni, Cu) compounds, which are predicted to have the same structures or isotypes are in preparation, while the structures of $SrM_2Fe(PO_4)_3$ (M = Co, Ni) compounds are isotypic with α-$CrPO_4$ (Bouraima *et al.*, 2016; Ouaatta *et al.*, 2015). Mention may also be made of other similar compounds, for example the phosphates $Na_2Co_2Fe(PO_4)_3$, $NaCr_2Zn(PO_4)_3$ and $Na_{1.66}Zn_{1.66}Fe_{1.34}(PO_4)_3$ (Bouraima *et al.*, 2015; Souiwa *et al.*, 2015; Khmiyas *et al.*, 2015) adopting the alluaudite structure type. In conclusion, we can say that the structure of this phosphate is similar to the alluaudite structure but with lower symmetry.

4. Synthesis and crystallization

Single crystals of $CaZn_2Fe(PO_4)_3$ were synthesized by a conventional solid-state method. Appropriate amounts of metal nitrate reagents, in the presence of H_3PO_4 85 wt%, were first dissolved in deionized water in the molar ratio Ca:Zn:Fe:P = 2:2:1:3 for 24 h. Then, the resulting solution was evaporated to dryness. The powder residue was ground in an agate mortar and progressively heated in a platinum crucible at a heating rate of 141 K h^{-1} until melting occurred at 1283 K. The melted product was cooled down at a rate of 5 K h^{-1}. As result of the reaction, we obtained transparent crystals corresponding to the title compound $CaZn_2Fe(PO_4)_3$.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The reflections (202) and (330) probably affected by the beam-stop were omitted from the refinement. The maximum and minimum electron densities in the final Fourier map are at 0.56 and 0.44 Å from Ca1 and Zn2, respectively.

Acknowledgements

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Synthesis and crystal structure of calcium dizinc iron(III) tris(orthophosphate), $CaZn_2Fe(PO_4)_3$

Jamal Khmiyas, Abderrazzak Assani, Mohamed Saadi and Lahcen El Ammari

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Calcium dizinc iron(III) tris(orthophosphate)

Crystal data

$CaZn_2Fe(PO_4)_3$
M_r = 511.58
Monoclinic, $P2_1/c$
a = 8.5619 (3) Å
b = 15.2699 (5) Å
c = 8.1190 (3) Å
β = 117.788 (2)°
V = 939.06 (6) Å^3
Z = 4
$F(000)$ = 988
D_x = 3.618 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4985 reflections
θ = 2.7–37.6°
μ = 7.72 mm^{-1}
T = 296 K
Block, black
0.30 × 0.26 × 0.18 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.600, T_{max} = 0.747
54053 measured reflections
4985 independent reflections
4493 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 37.6°, θ_{min} = 2.7°
h = −14→14
k = −26→26
l = −10→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.041
S = 1.04
4985 reflections
172 parameters
0 restraints
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 0.7655P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 1.07 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.81685 (2)	0.73588 (2)	0.30142 (2)	0.00740 (3)
Zn2	0.88412 (2)	0.52265 (2)	0.59417 (2)	0.01026 (3)
Fe1	0.67075 (2)	0.49009 (2)	0.83003 (2)	0.00500 (3)
Ca1	0.27619 (3)	0.75762 (2)	0.47919 (3)	0.01070 (4)
P1	0.29665 (3)	0.58370 (2)	0.77261 (4)	0.00503 (4)
P2	0.96807 (3)	0.62244 (2)	0.09438 (4)	0.00499 (4)
P3	0.60325 (3)	0.64096 (2)	0.49014 (4)	0.00491 (4)
O1	0.29942 (13)	0.67932 (6)	0.72349 (13)	0.01271 (15)
O2	0.30273 (12)	0.58596 (6)	0.96463 (12)	0.01006 (14)
O3	0.12207 (10)	0.54161 (6)	0.62684 (12)	0.01114 (15)
O4	0.43948 (11)	0.52893 (6)	0.76475 (14)	0.01312 (16)
O5	0.77926 (10)	0.58832 (5)	0.00379 (12)	0.00895 (13)
O6	1.00136 (11)	0.67493 (6)	−0.04745 (13)	0.01045 (14)
O7	1.00262 (11)	0.68143 (6)	0.26134 (13)	0.01055 (14)
O8	1.09932 (10)	0.54481 (5)	0.17408 (12)	0.00724 (13)
O9	0.75426 (11)	0.65280 (6)	0.43941 (13)	0.01160 (15)
O10	0.59377 (10)	0.71947 (6)	0.60355 (12)	0.00974 (14)
O11	0.66602 (11)	0.55677 (5)	0.61102 (12)	0.00822 (13)
O12	0.41993 (10)	0.62799 (6)	0.32620 (12)	0.01012 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.00645 (5)	0.00817 (5)	0.00801 (6)	0.00013 (4)	0.00374 (4)	0.00104 (4)
Zn2	0.00760 (5)	0.01471 (6)	0.01073 (6)	0.00042 (4)	0.00616 (4)	−0.00080 (5)
Fe1	0.00454 (5)	0.00602 (6)	0.00488 (6)	0.00044 (4)	0.00256 (4)	0.00061 (4)
Ca1	0.01029 (8)	0.01095 (9)	0.01178 (10)	0.00175 (6)	0.00591 (7)	0.00601 (7)
P1	0.00467 (9)	0.00607 (10)	0.00452 (10)	0.00011 (7)	0.00229 (8)	−0.00022 (8)
P2	0.00441 (9)	0.00482 (10)	0.00581 (11)	0.00038 (7)	0.00243 (8)	−0.00009 (8)
P3	0.00448 (9)	0.00500 (10)	0.00483 (10)	0.00004 (7)	0.00182 (8)	0.00031 (8)
O1	0.0222 (4)	0.0076 (3)	0.0109 (4)	−0.0001 (3)	0.0098 (3)	0.0019 (3)
O2	0.0169 (3)	0.0093 (3)	0.0063 (3)	0.0009 (3)	0.0073 (3)	0.0011 (3)
O3	0.0051 (3)	0.0176 (4)	0.0102 (4)	−0.0030 (3)	0.0030 (3)	−0.0063 (3)
O4	0.0065 (3)	0.0172 (4)	0.0157 (4)	0.0026 (3)	0.0052 (3)	−0.0045 (3)
O5	0.0056 (3)	0.0100 (3)	0.0101 (3)	−0.0016 (2)	0.0028 (2)	−0.0034 (3)
O6	0.0097 (3)	0.0107 (3)	0.0132 (4)	0.0029 (3)	0.0072 (3)	0.0061 (3)
O7	0.0079 (3)	0.0122 (3)	0.0115 (4)	−0.0005 (2)	0.0045 (3)	−0.0062 (3)
O8	0.0065 (3)	0.0073 (3)	0.0088 (3)	0.0026 (2)	0.0043 (2)	0.0020 (2)
O9	0.0111 (3)	0.0118 (3)	0.0161 (4)	0.0008 (3)	0.0098 (3)	0.0042 (3)

O10	0.0076 (3)	0.0091 (3)	0.0103 (3)	0.0006 (2)	0.0024 (3)	−0.0040 (3)
O11	0.0100 (3)	0.0080 (3)	0.0082 (3)	0.0028 (2)	0.0055 (3)	0.0039 (3)
O12	0.0068 (3)	0.0086 (3)	0.0097 (3)	−0.0002 (2)	−0.0006 (3)	−0.0020 (3)

Geometric parameters (Å, º)

Zn1—O9	1.9266 (9)	Ca1—O2^{i}	2.4075 (9)
Zn1—O7	1.9518 (8)	Ca1—O7^{viii}	2.4709 (9)
Zn1—O10^{i}	1.9578 (8)	Ca1—O6^{ix}	2.4840 (9)
Zn1—O6^{ii}	2.0120 (8)	Ca1—O10	2.4885 (8)
Zn2—O3^{iii}	1.9496 (8)	Ca1—O12	2.8984 (9)
Zn2—O11	2.0038 (8)	P1—O4	1.5073 (9)
Zn2—O3^{iv}	2.0241 (9)	P1—O1	1.5166 (9)
Zn2—O8^{v}	2.0911 (8)	P1—O2	1.5358 (9)
Zn2—O9	2.3371 (9)	P1—O3	1.5487 (8)
Fe1—O4	1.8908 (8)	P2—O5	1.5222 (8)
Fe1—O2^{vi}	1.9561 (9)	P2—O6	1.5348 (9)
Fe1—O5^{vii}	1.9700 (8)	P2—O7	1.5371 (9)
Fe1—O11	2.0330 (8)	P2—O8	1.5519 (8)
Fe1—O8^{v}	2.0547 (8)	P3—O12	1.5253 (8)
Fe1—O12^{iv}	2.1318 (8)	P3—O10	1.5365 (9)
Ca1—O1	2.2439 (9)	P3—O9	1.5396 (9)
Ca1—O1^{i}	2.3795 (10)	P3—O11	1.5534 (8)
O9—Zn1—O7	106.60 (4)	O2^{i}—Ca1—O6^{ix}	72.04 (3)
O9—Zn1—O10^{i}	106.09 (4)	O7^{viii}—Ca1—O6^{ix}	65.76 (3)
O7—Zn1—O10^{i}	124.80 (4)	O1—Ca1—O10	83.50 (3)
O9—Zn1—O6^{ii}	116.31 (4)	O1^{i}—Ca1—O10	85.92 (3)
O7—Zn1—O6^{ii}	85.46 (3)	O2^{i}—Ca1—O10	98.16 (3)
O10^{i}—Zn1—O6^{ii}	116.93 (4)	O7^{viii}—Ca1—O10	132.22 (3)
O3^{iii}—Zn2—O11	154.16 (4)	O6^{ix}—Ca1—O10	160.73 (3)
O3^{iii}—Zn2—O3^{iv}	77.67 (4)	O1—Ca1—O12	97.73 (3)
O11—Zn2—O3^{iv}	123.13 (3)	O1^{i}—Ca1—O12	71.19 (3)
O3^{iii}—Zn2—O8^{v}	108.82 (4)	O2^{i}—Ca1—O12	126.00 (3)
O11—Zn2—O8^{v}	75.00 (3)	O7^{viii}—Ca1—O12	79.74 (3)
O3^{iv}—Zn2—O8^{v}	121.44 (4)	O6^{ix}—Ca1—O12	145.10 (3)
O3^{iii}—Zn2—O9	98.73 (4)	O10—Ca1—O12	53.99 (3)
O11—Zn2—O9	65.84 (3)	O1—Ca1—O12^{ii}	69.93 (3)
O3^{iv}—Zn2—O9	97.26 (4)	O1^{i}—Ca1—O12^{ii}	114.39 (3)
O8^{v}—Zn2—O9	135.92 (3)	O2^{i}—Ca1—O12^{ii}	57.96 (3)
O4—Fe1—O2^{vi}	96.63 (4)	O7^{viii}—Ca1—O12^{ii}	140.52 (3)
O4—Fe1—O5^{vii}	92.55 (4)	O6^{ix}—Ca1—O12^{ii}	78.49 (3)
O2^{vi}—Fe1—O5^{vii}	90.75 (4)	O10—Ca1—O12^{ii}	82.24 (3)
O4—Fe1—O11	90.37 (4)	O12—Ca1—O12^{ii}	135.98 (3)
O2^{vi}—Fe1—O11	171.82 (3)	O4—P1—O1	114.24 (6)
O5^{vii}—Fe1—O11	93.18 (4)	O4—P1—O2	114.28 (5)
O4—Fe1—O8^{v}	164.34 (4)	O1—P1—O2	104.36 (5)
O2^{vi}—Fe1—O8^{v}	97.38 (3)	O4—P1—O3	104.50 (5)

O5^{vii}—Fe1—O8^{v}	94.22 (3)	O1—P1—O3	109.05 (5)
O11—Fe1—O8^{v}	75.18 (3)	O2—P1—O3	110.42 (5)
O4—Fe1—O12^{iv}	93.16 (4)	O5—P2—O6	110.07 (5)
O2^{vi}—Fe1—O12^{iv}	82.55 (4)	O5—P2—O7	110.55 (5)
O5^{vii}—Fe1—O12^{iv}	171.65 (3)	O6—P2—O7	109.20 (5)
O11—Fe1—O12^{iv}	92.86 (4)	O5—P2—O8	109.84 (5)
O8^{v}—Fe1—O12^{iv}	81.77 (3)	O6—P2—O8	111.11 (5)
O1—Ca1—O1^{i}	167.91 (4)	O7—P2—O8	106.00 (5)
O1—Ca1—O2^{i}	126.91 (3)	O12—P3—O10	107.69 (5)
O1^{i}—Ca1—O2^{i}	60.49 (3)	O12—P3—O9	115.63 (5)
O1—Ca1—O7^{viii}	92.62 (3)	O10—P3—O9	110.75 (5)
O1^{i}—Ca1—O7^{viii}	90.17 (3)	O12—P3—O11	110.86 (5)
O2^{i}—Ca1—O7^{viii}	120.77 (3)	O10—P3—O11	111.50 (5)
O1—Ca1—O6^{ix}	89.31 (3)	O9—P3—O11	100.36 (5)
O1^{i}—Ca1—O6^{ix}	102.55 (3)		

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