

Crystal structure of calcium dinickel(II) iron(III) tris(orthophosphate): $\text{CaNi}_2\text{Fe}(\text{PO}_4)_3$

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 α - CrPO_4 structure type.**CCDC reference:** 1551182**Supporting information:** this article has
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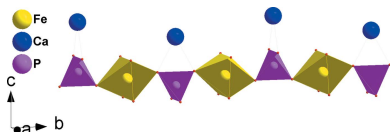
The title compound, $\text{CaNi}_2\text{Fe}(\text{PO}_4)_3$, was synthesized by solid-state reactions. Its structure is closely related to that of α - CrPO_4 in the space group *Imma*. Except for two O atoms in general positions, all atoms are located in special positions. The three-dimensional framework is built up from two types of sheets extending parallel to (100). The first sheet is made up from two edge-sharing $[\text{NiO}_6]$ octahedra, leading to the formation of $[\text{Ni}_2\text{O}_{10}]$ double octahedra that are connected to two PO_4 tetrahedra through a common edge and corners. The second sheet results from rows of corner-sharing $[\text{FeO}_6]$ octahedra and PO_4 tetrahedra forming an infinite linear chain. These layers are linked together through common corners of PO_4 tetrahedra and $[\text{FeO}_6]$ octahedra, resulting in an open three-dimensional framework that delimits two types of channels parallel to [100] and [010] in which the eightfold-coordinated Ca^{II} cations are located.

1. Chemical context

Phosphates belonging to the alluaudite (Moore, 1971) or to the α - CrPO_4 (Attfield *et al.*, 1988) structure type exhibit interesting physical and chemical properties. Consequently, these compounds have many promising applications such as use as positive electrodes in lithium and sodium batteries (Kim *et al.*, 2014; Huang *et al.*, 2015) or as catalysts (Kacimi *et al.*, 2005). Over the last few years, phosphate-based compounds crystallizing in the α - CrPO_4 or alluaudite structure types have been investigated by us. In this context, new phosphates adopting the alluaudite or α - CrPO_4 structure type have been synthesized and structurally characterized. For example, the mixed-valence manganese phosphates $\text{PbMn}^{\text{II}}\text{Mn}^{\text{III}}(\text{PO}_4)_3$ (Alhakmi *et al.*, 2013) and $\text{PbMn}^{\text{II}}\text{Mn}^{\text{III}}(\text{PO}_4)_3$ (Assani *et al.*, 2013), the magnesium phosphate $\text{NaMg}_3(\text{PO}_4)(\text{HPO}_4)_2$ (Ould Saleck *et al.*, 2015) and silver nickel phosphate $\text{Ag}_2\text{Ni}_3(\text{HPO}_4)(\text{PO}_4)_2$ (Assani *et al.*, 2011) were synthesized by hydrothermal methods, while solid-state reactions were applied to synthesize $\text{SrNi}_2\text{Fe}(\text{PO}_4)_3$ (Ouaatta *et al.*, 2015) and $\text{Na}_2\text{Co}_2\text{Fe}(\text{PO}_4)_3$ (Bouraima *et al.*, 2015). In a continuation of the latter preparation route, we have investigated pseudo-quaternary systems $\text{MO-NiO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ (*M* represents a divalent cation) and report here on the synthesis and crystal structure of the title compound, $\text{CaNi}_2\text{Fe}(\text{PO}_4)_3$.

2. Structural commentary

$\text{CaNi}_2\text{Fe}(\text{PO}_4)_3$ crystallizes in the α - CrPO_4 structure type. The principal building units of the crystal structure are one $[\text{CaO}_8]$ polyhedron, $[\text{FeO}_6]$ and $[\text{NiO}_6]$ octahedra and PO_4 tetrahedra,



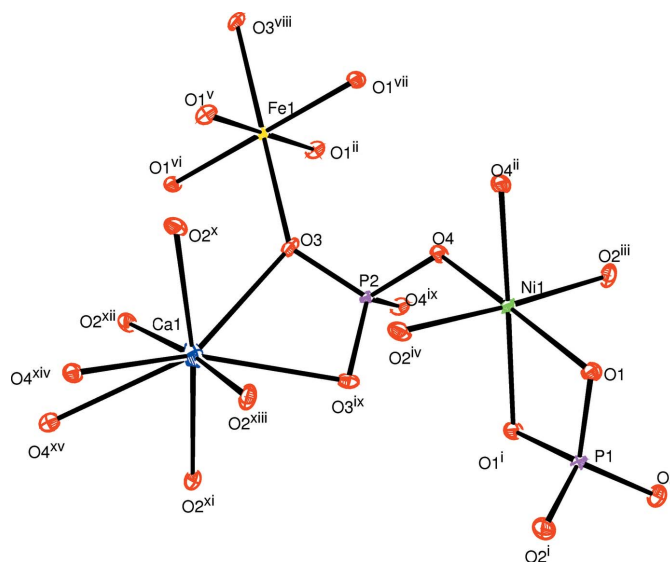


Figure 1
The principal building units in the crystal structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 2, -y + \frac{3}{2}, z + 1$; (ii) $x, y, z + 1$; (iii) $-x + 2, -y + \frac{3}{2}, z$; (iv) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$;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

as shown in Fig. 1. The octahedral coordination sphere of the iron(III) cation is more distorted than that of nickel(II), with Fe–O bond lengths in the range 1.9504 (7)–2.0822 (11) Å and Ni–O bond lengths in the range 2.0498 (8)–2.0841 (8) Å. In the title structure, all atoms are on special positions, except for the two oxygen atoms O1 and O2, which are on general positions. The structure can be described by the stacking of two types of sheets extending parallel to (100). The first sheet is formed by alternating [FeO₆] octahedra and PO₄ tetrahedra sharing corners to build a linear infinite chain surrounding a zigzag chain of Ca^{II} cations (Fig. 2). The second sheet is built up from two edge-sharing [NiO₆] octahedra leading to the formation of [Ni₂O₁₀] double octahedra, which are connected to two PO₄ tetrahedra by a common edge and a common corner, as shown in Fig. 3. The linkage of both layers, through vertices of PO₄ tetrahedra and [FeO₆] octahedra, gives rise to the formation of an open three-dimensional framework that delimits two types of channels parallel to [100] and [010] in which the Ca^{II} cations are located with eight neighbouring O

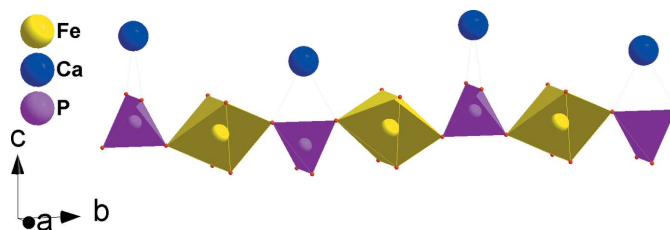


Figure 2
A chain formed by sharing corners of PO₄ tetrahedra and [FeO₆] octahedra, alternating with a zigzag chain of calcium cations.

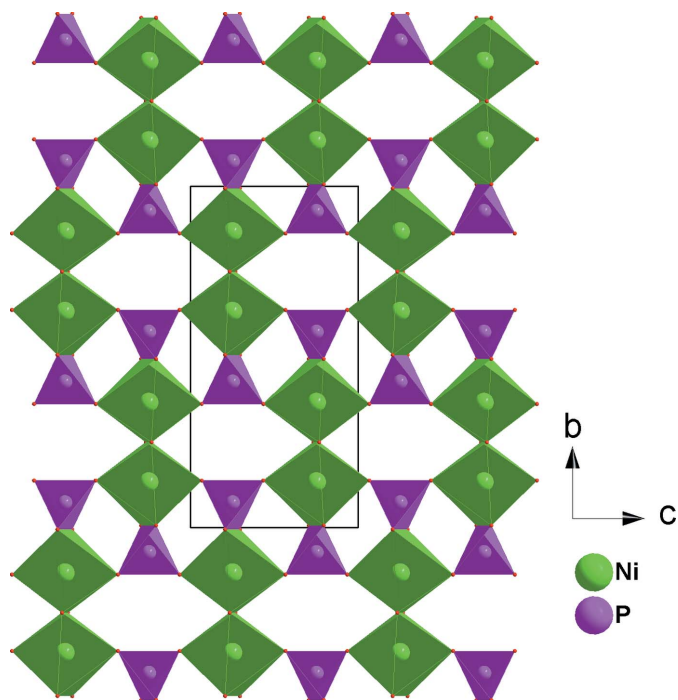


Figure 3
Edge-sharing [NiO₆] octahedra linked by PO₄ tetrahedra, forming a sheet parallel to (100).

atoms, as shown in Fig. 4. The title compound has a stoichiometric composition like that of the related strontium homologue SrNi₂Fe(PO₄)₃.

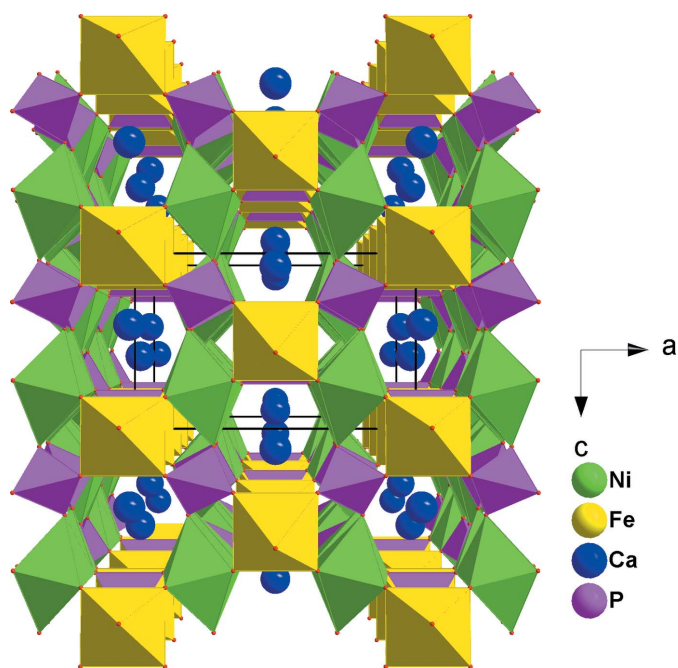


Figure 4
Polyhedral representation of CaNiO₂Fe(PO₄)₃, showing channels running parallel to [100].

3. Synthesis and crystallization

CaNi₂Fe(PO₄)₃ was prepared by solid-state reactions in air. Stoichiometric mixtures of calcium, nickel and iron precursors were dissolved in water to which 85%_{wt} phosphoric acid was added. The obtained mixture was stirred without heating for 24 h and was subsequently evaporated to dryness at 343 K. The resulting dry residue was ground in an agate mortar until homogeneity, progressively heated in a platinum crucible up to 873 K to remove the volatile decomposition products, and then melted at 1433 K. The molten product was cooled down slowly with a 5 K h⁻¹ rate and then to room temperature. The crystals obtained after washing with water were orange with parallelepipedal forms.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The maximum and minimum remaining electron densities are 0.68 and 0.41 Å⁻³, respectively, away from the Ni1 site.

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Table 1
Experimental details.

Crystal data	
Chemical formula	CaNi ₂ Fe(PO ₄) ₃
<i>M_r</i>	498.26
Crystal system, space group	Orthorhombic, <i>Imma</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3126 (3), 13.1138 (3), 6.4405 (2)
<i>V</i> (Å ³)	871.00 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	7.14
Crystal size (mm)	0.30 × 0.27 × 0.21
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.596, 0.748
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8446, 1171, 1153
<i>R_{int}</i>	0.020
(sin θ/λ) _{max} (Å ⁻¹)	0.840
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.017, 0.044, 1.17
No. of reflections	1171
No. of parameters	54
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.76, -0.63

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

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Crystal structure of calcium dinickel(II) iron(III) tris(orthophosphate): CaNi₂Fe(PO₄)₃

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Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXT2014* (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: *pubCIF* (Westrip, 2010).

Calcium dinickel(II) iron(III) tris(orthophosphate)

Crystal data

CaNi ₂ Fe(PO ₄) ₃	$D_x = 3.800 \text{ Mg m}^{-3}$
$M_r = 498.26$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Imma</i>	Cell parameters from 1171 reflections
$a = 10.3126 (3) \text{ \AA}$	$\theta = 3.1\text{--}36.6^\circ$
$b = 13.1138 (3) \text{ \AA}$	$\mu = 7.14 \text{ mm}^{-1}$
$c = 6.4405 (2) \text{ \AA}$	$T = 296 \text{ K}$
$V = 871.00 (4) \text{ \AA}^3$	Parallelepiped, orange
$Z = 4$	$0.30 \times 0.27 \times 0.21 \text{ mm}$
$F(000) = 972$	

Data collection

Bruker X8 APEX diffractometer	8446 measured reflections
Radiation source: fine-focus sealed tube	1171 independent reflections
Graphite monochromator	1153 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 36.6^\circ$, $\theta_{\text{min}} = 3.1^\circ$
$T_{\text{min}} = 0.596$, $T_{\text{max}} = 0.748$	$h = -16 \rightarrow 17$
	$k = -20 \rightarrow 22$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 1.467P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.017$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$wR(F^2) = 0.044$	$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
$S = 1.17$	$\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$
1171 reflections	Extinction correction: <i>SHELXL2014</i>
54 parameters	(Sheldrick, 2015b),
0 restraints	$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0033 (2)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.7500	0.36655 (2)	0.7500	0.00475 (5)
Fe1	0.5000	0.0000	0.5000	0.00372 (6)
Ca1	0.5000	0.2500	0.08981 (7)	0.01187 (8)
P1	0.7500	0.57298 (3)	0.7500	0.00385 (7)
P2	0.5000	0.2500	0.58291 (8)	0.00327 (8)
O1	0.86146 (7)	0.49415 (6)	0.79418 (13)	0.00590 (12)
O4	0.61754 (11)	0.2500	0.73284 (17)	0.00587 (16)
O3	0.5000	0.15625 (8)	0.44256 (18)	0.00672 (17)
O2	0.70724 (8)	0.63786 (6)	0.93385 (12)	0.00762 (13)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00486 (9)	0.00326 (8)	0.00613 (9)	0.000	-0.00056 (5)	0.000
Fe1	0.00264 (10)	0.00397 (11)	0.00455 (11)	0.000	0.000	-0.00016 (8)
Ca1	0.01508 (18)	0.01319 (18)	0.00735 (16)	0.000	0.000	0.000
P1	0.00450 (14)	0.00307 (14)	0.00398 (14)	0.000	-0.00041 (9)	0.000
P2	0.00320 (17)	0.00246 (17)	0.00414 (18)	0.000	0.000	0.000
O1	0.0045 (3)	0.0054 (3)	0.0079 (3)	0.0006 (2)	-0.0021 (2)	-0.0004 (2)
O4	0.0049 (4)	0.0057 (4)	0.0070 (4)	0.000	-0.0023 (3)	0.000
O3	0.0082 (4)	0.0045 (4)	0.0075 (4)	0.000	0.000	-0.0024 (3)
O2	0.0102 (3)	0.0069 (3)	0.0057 (3)	0.0018 (2)	0.0001 (2)	-0.0020 (2)

Geometric parameters (\AA , $^\circ$)

Ni1—O1	2.0498 (8)	Ca1—O2 ^{xi}	2.5987 (8)
Ni1—O1 ⁱ	2.0499 (8)	Ca1—O2 ^{xii}	2.5987 (8)
Ni1—O4	2.0529 (8)	Ca1—O2 ^{xiii}	2.5987 (8)
Ni1—O4 ⁱⁱ	2.0529 (8)	Ca1—O4 ^{xiv}	2.5990 (12)
Ni1—O2 ⁱⁱⁱ	2.0841 (8)	Ca1—O4 ^{xv}	2.5990 (12)
Ni1—O2 ^{iv}	2.0841 (8)	Ca1—P2	3.1758 (7)
Fe1—O1 ⁱⁱ	1.9504 (7)	Ca1—P2 ^{xv}	3.2647 (7)
Fe1—O1 ^v	1.9504 (7)	P1—O2 ⁱ	1.5233 (8)
Fe1—O1 ^{vi}	1.9504 (7)	P1—O2	1.5233 (8)
Fe1—O1 ^{vii}	1.9504 (7)	P1—O1 ⁱ	1.5719 (8)
Fe1—O3 ^{viii}	2.0822 (11)	P1—O1	1.5719 (8)
Fe1—O3	2.0822 (11)	P2—O3	1.5259 (11)
Ca1—O3	2.5832 (12)	P2—O3 ^{ix}	1.5259 (11)
Ca1—O3 ^{ix}	2.5832 (12)	P2—O4 ^{ix}	1.5498 (11)

Ca1—O2 ^x	2.5987 (8)	P2—O4	1.5498 (11)
O1—Ni1—O1 ⁱ	70.58 (4)	O2 ^x —Ca1—O2 ^{xi}	173.27 (4)
O1—Ni1—O4	171.24 (3)	O3—Ca1—O2 ^{xii}	77.42 (2)
O1 ⁱ —Ni1—O4	103.13 (3)	O3 ^{ix} —Ca1—O2 ^{xii}	108.72 (2)
O1—Ni1—O4 ⁱⁱ	103.13 (3)	O2 ^x —Ca1—O2 ^{xii}	110.65 (3)
O1 ⁱ —Ni1—O4 ⁱⁱ	171.24 (3)	O2 ^{xi} —Ca1—O2 ^{xii}	68.92 (3)
O4—Ni1—O4 ⁱⁱ	83.76 (5)	O3—Ca1—O2 ^{xiii}	108.72 (2)
O1—Ni1—O2 ⁱⁱⁱ	90.33 (3)	O3 ^{ix} —Ca1—O2 ^{xiii}	77.42 (2)
O1 ⁱ —Ni1—O2 ⁱⁱⁱ	92.27 (3)	O2 ^x —Ca1—O2 ^{xiii}	68.92 (3)
O4—Ni1—O2 ⁱⁱⁱ	83.75 (4)	O2 ^{xi} —Ca1—O2 ^{xiii}	110.65 (3)
O4 ⁱⁱ —Ni1—O2 ⁱⁱⁱ	93.87 (4)	O2 ^{xii} —Ca1—O2 ^{xiii}	173.27 (4)
O1—Ni1—O2 ^{iv}	92.27 (3)	O3—Ca1—O4 ^{xiv}	141.08 (2)
O1 ⁱ —Ni1—O2 ^{iv}	90.33 (3)	O3 ^{ix} —Ca1—O4 ^{xiv}	141.08 (2)
O4—Ni1—O2 ^{iv}	93.87 (4)	O2 ^x —Ca1—O4 ^{xiv}	64.19 (3)
O4 ⁱⁱ —Ni1—O2 ^{iv}	83.75 (4)	O2 ^{xi} —Ca1—O4 ^{xiv}	109.37 (3)
O2 ⁱⁱⁱ —Ni1—O2 ^{iv}	176.81 (4)	O2 ^{xii} —Ca1—O4 ^{xiv}	109.37 (3)
O1 ⁱⁱ —Fe1—O1 ^v	180.0	O2 ^{xiii} —Ca1—O4 ^{xiv}	64.19 (3)
O1 ⁱⁱ —Fe1—O1 ^{vi}	85.81 (5)	O3—Ca1—O4 ^{xv}	141.08 (2)
O1 ^v —Fe1—O1 ^{vi}	94.19 (5)	O3 ^{ix} —Ca1—O4 ^{xv}	141.08 (2)
O1 ⁱⁱ —Fe1—O1 ^{vii}	94.19 (5)	O2 ^x —Ca1—O4 ^{xv}	109.37 (3)
O1 ^v —Fe1—O1 ^{vii}	85.81 (5)	O2 ^{xi} —Ca1—O4 ^{xv}	64.19 (3)
O1 ^{vi} —Fe1—O1 ^{vii}	180.0	O2 ^{xii} —Ca1—O4 ^{xv}	64.19 (3)
O1 ⁱⁱ —Fe1—O3 ^{viii}	85.29 (3)	O2 ^{xiii} —Ca1—O4 ^{xv}	109.37 (3)
O1 ^v —Fe1—O3 ^{viii}	94.71 (3)	O4 ^{xiv} —Ca1—O4 ^{xv}	55.60 (5)
O1 ^{vi} —Fe1—O3 ^{viii}	94.71 (3)	O2 ⁱ —P1—O2	112.08 (6)
O1 ^{vii} —Fe1—O3 ^{viii}	85.29 (3)	O2 ⁱ —P1—O1 ⁱ	116.00 (4)
O1 ⁱⁱ —Fe1—O3	94.71 (3)	O2—P1—O1 ⁱ	107.24 (4)
O1 ^v —Fe1—O3	85.29 (3)	O2 ⁱ —P1—O1	107.24 (4)
O1 ^{vi} —Fe1—O3	85.29 (3)	O2—P1—O1	116.00 (4)
O1 ^{vii} —Fe1—O3	94.71 (3)	O1 ⁱ —P1—O1	97.76 (6)
O3 ^{viii} —Fe1—O3	180.000 (10)	O3—P2—O3 ^{ix}	107.35 (9)
O3—Ca1—O3 ^{ix}	56.84 (5)	O3—P2—O4 ^{ix}	111.66 (3)
O3—Ca1—O2 ^x	77.42 (2)	O3 ^{ix} —P2—O4 ^{ix}	111.66 (3)
O3 ^{ix} —Ca1—O2 ^x	108.72 (2)	O3—P2—O4	111.66 (3)
O3—Ca1—O2 ^{xi}	108.72 (2)	O3 ^{ix} —P2—O4	111.66 (3)
O3 ^{ix} —Ca1—O2 ^{xi}	77.42 (2)	O4 ^{ix} —P2—O4	102.91 (9)

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