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The iron phosphate $CaFe_3(PO_4)_3O$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(P–O) = 0.003 Å; R factor = 0.031; wR factor = 0.088; data-to-parameter ratio = 13.2.

A new iron phosphate, calcium triiron(III) tris(phosphate) oxide, $CaFe_3(PO_4)_3O$, has been isolated and shown to exhibit a three-dimensional structure built by FeO_6 octahedra, FeO_5 trigonal bipyramids and PO_4 tetrahedra. The FeO_x (x = 5, 6) polyhedra are linked through common corners and edges, forming $[Fe_6O_{28}]_\infty$ chains with branches running along [010]. Adjacent chains are connected by the phosphate groups *via* common corners and edges, giving rise to a three-dimensional framework analogous to those of the previously reported $SrFe_3(PO_4)_3O$ and $Bi_{0.4}Fe_3(PO_4)_3O$ structures, in which the Ca^{2+} cations occupy a single symmetry non-equivalent cavity.

Related literature

The interest in iron phosphates has increased following the discovery of $LiFePO_4$ with olivine-type structure, which is the most promising electrode material for Li-ion batteries, see: Padhi *et al.* (1997). The title compound is isostructural to the iron phosphates $Bi_{0.4}Fe_3(PO_4)_3$ (Benabad *et al.*, 2000) and $SrFe_3(PO_4)_3O$ (Morozov *et al.*, 2003). For ionic radii, see: Shannon (1976). For P—O distances in orthophosphate groups, see: Baur (1974). For Ca—O distances in hepta-coordinated Ca^{2+} ions in $Ca_3(PO_4)_2$, see: Mathew *et al.* (1977). For Fe—O distances for five-coordinated Fe^{3+} ions in $NaCaFe_3(PO_4)_4$, see: Hidouri *et al.* (2003).The valences of the cations were calculated using the Brown & Altermatt (1985) method.

Experimental

Crystal data

$CaFe_3(PO_4)_3O$ M_r = 508.54
Monoclinic, $P2_1/m$
a = 7.521 (2) Å
b = 6.330 (2) Å
c = 10.160 (2) Å
β = 100.03 (2)°
V = 476.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 5.63 mm^{-1}
T = 293 K
0.36 × 0.22 × 0.22 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.193, T_{max} = 0.293
2072 measured reflections
1493 independent reflections
1412 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
2 standard reflections
frequency: 120 min
intensity decay: 6.0%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.088
S = 1.12
1493 reflections
113 parameters
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −1.59 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2067).

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supplementary materials

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The iron phosphate $CaFe_3(PO_4)_3O$

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Comment

Iron phosphates are extensively studied for their rich structural chemistry owing to the possible occurrence of both +2 and +3 oxidation states for iron and the tendecy of its coordination polyhedra to form with the phosphate groups a variety of frameworks. Such adaptative crystal chemistry provides new and exciting aventures in the exploration of the intrinsic relationship between structure and composition. The interest in these materials is further accentuated since the discovery of $LiFePO_4$ with olivine-type structure the most promising electrode material for Li-ion batteries (Padhi *et al.*, 1997).

As a part of a systematic exploration of the A_2O—MO—Fe_2O_3—P_2O_5 (A = alkali metal, *M* = divalent cation) in a search of new iron phosphates with interesting structures and subsequently intriguing properties, we describe here the structure of $CaFe_3(PO_4)_3O$, extracted from a mixture of nominal composition $LiCaFe_3(PO_4)_4$. This compound is isostructural to the previously reported iron phosphates $Bi_{0.4}Fe_3(PO_4)_3$ (Benabad *et al.*, 2000) and $SrFe_3(PO_4)_3O$ (Morozov *et al.*, 2003). Its structure, shown in figure 1, is built from a three-dimensional arrangement based on two crystallographically distinct FeO_6 octahedra, one symmetry non equivalent FeO_5 polyhedron and three symmetry distinct PO_4 tetrahedra. The Fe polyhedra form $[Fe_6O_{28}]_\infty$ chains with branches running along the [010] direction. In such chains (Fig. 2), each $Fe(1)O_6$ octahedron shares two opposite edges with two equivalent octahedra, one of the equatorial oxo-ligands forming each of the common edges being also shared with one $Fe(2)O_6$ octahedron. The latter is corner-linked with one one $Fe(2)O_5$ polyhedron to form the branches of the chain. The conntection of these chains is ensured by the phosphate tetrahedra in such a way that each PO_4 connects two adjacent chains either by sharing one edge with one chain and one corner with the other ($P(1)O_4$) or by sharing three corners with a same chain and the fourth with the other ($P(2)O_4$ and $P(3)O_4$). The three-dimensional framework constructed in this way delimits a single symmetry non equivalent cavity occupied by the Ca^{2+} cations.

The FeO_6 octahedra are both highly distorted as indicated by the Fe—O distances ranging from 1.986 (2) to 2.114 (2) Å for $Fe(1)O_6$ and from 1.870 (2) to 2.183 (3) Å for $Fe(2)O_6$ with average values of 2.037 (2) Å and 2.019 (3) Å, respectively, close to that 2.03 Å, predicted by Shannon for octahedral Fe^{3+} ions (Shannon, 1976). The FeO_5 polyhedron is also very distorted with Fe—O distances ranging from 1.872 (4) to 1.986 (2) Å. The mean distance of 1.940 (4) Å is consistent with those 1.946 Å and 1.956 Å, observed for five-coordinated Fe^{3+} ions in $NaCaFe_3(PO_4)_4$ (Hidouri *et al.*, 2003). The PO_4 tetrahedra have P—O distances in the range 1.513 (3)–1.561 (3) Å with an overall distance of 1.535 (3) Å, close to that 1.537 calculated for the monophosphate groups (Baur, 1974). The Ca^{2+} cations occupy a single non equivalent site delimited by the Fe/P/O network. Its environement (Fig.3) is consisted by seven oxygen atoms with four Ca—O distances included between 2.391 (3) and 2.514 (2) Å showing the CaO_7 polyhedron to be highly distorted. The mean Ca—O distance of 2.462 (2) Å is in the range of those previously reported for heptacoordinated Ca^{2+} ions in $Ca_3(PO_4)_2$ (Mathew *et al.*, 1977). The valences of all the cations were calculated using the Brown & Altermatt method (Brown & Altermatt, 1985). The calculated values of 1.85, 2.86, 3.10, 3.09, 4.94, 5.03 and 5.02 for Ca, Fe(1), Fe(2), Fe(3), P(1), P(2) and P(3), respectively are consistent with their respective oxidation numbers of 2.0, 3.0, 3.0, 3.0, 5.0, 5.0 and 5.0.

The structural similarity between the title compound and the iron phosphates $SrFe_3(PO_4)_3O$ and $Bi_{0.4}Fe_3(PO_4)_3O$ shows the great flexibility of the $[Fe_3P_3O_{13}]_\infty$ framework which seems to accomodate various cations. Further invstigation of the chemical stablity of this structural type by including other cations would be of interest.

Experimental

Single crystals of the title compound were isolated during an attempt to crystallize $LiCaFe_3(PO_4)_4$ in a flux of lithium dimolybdate $Li_2Mo_2O_7$ in an atomic ratio, P: Mo = 8:1. Appropriate amounts of $LiNO_3$, $CaCO_3$, $Fe(NO_3)_3.9H_2O$, $(NH_4)_2HPO_4$ and MoO_3 were firstly dissolved in nitric acid and the solution obtained was dried for 24 h at 353 K. After grinding in an agate mortar to ensure its best homogeneity, the dry residue was heated in a platinum crucible to 673 K for 24 h in order to remove the decomposition products: NO_2, NH_3 and H_2O. The sample was then reground, melted at 1173 K for 1 h and subsequently cooled at a 10 °.h^{-1} rate to 673 K after which the furnace was turned off. The final product was washed with warm water in order to dissolve the flux. From the mixture, dark brown and irregularely shaped crystals of $CaFe_3(PO_4)_3O$ were extracted.

Refinement

The Fe and Ca atoms were loctaed by direct methods and the remaining atoms were found by successive difference Fourier maps. All atomic positions were refined with anisotrop displacement parameterers.

Figures

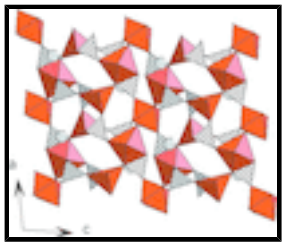

Fig. 1. : The $CaFe_3(PO_4)_3O$ structure as projected along the [010] direction.

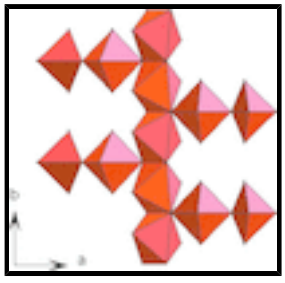

Fig. 2. : A view of the $[Fe_6O_{28}]_\infty$ chain running along the [010] direction.

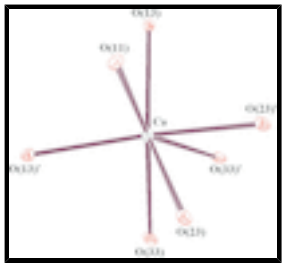

Fig. 3. : The environment of the Ca^{2+} cations showing the anisotropic atomic displacements.

calcium triiron(III) tris(phosphate) oxide

Crystal data

$CaFe_3(PO_4)_3O$	$F_{000} = 494$
$M_r = 508.54$	$D_x = 3.546$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yb	Cell parameters from 25 reflections
$a = 7.521$ (2) Å	$\theta = 8.9$–12.5º
$b = 6.330$ (2) Å	$\mu = 5.63$ mm^{-1}
$c = 10.160$ (2) Å	$T = 293$ K
$\beta = 100.03$ (2)º	Prism, brown
$V = 476.3$ (2) Å^3	0.36 × 0.22 × 0.22 mm
$Z = 2$	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$R_{int} = 0.035$
Radiation source: fine-focus sealed tube	$\theta_{max} = 29.9$º
Monochromator: graphite	$\theta_{min} = 2.0$º
$T = 293$ K	$h = -1 \rightarrow 10$
$\omega/2\theta$ scans	$k = -1 \rightarrow 8$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -14 \rightarrow 14$
$T_{min} = 0.193$, $T_{max} = 0.293$	2 standard reflections
2072 measured reflections	every 120 min
1493 independent reflections	intensity decay: 6.0%
1412 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.6592P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.088$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
$S = 1.12$	$\Delta\rho_{min} = -1.59$ e Å^{-3}
1493 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
113 parameters	Extinction coefficient: 0.173 (7)
Primary atom site location: structure-invariant direct methods	

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.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca	0.66161 (10)	−0.2500	0.19595 (7)	0.00891 (18)
Fe1	0.0000	−0.5000	0.0000	0.00627 (16)
Fe2	−0.64926 (7)	−0.7500	0.20179 (5)	0.00561 (16)
Fe3	−0.21388 (7)	−0.7500	0.43643 (5)	0.00684 (16)
P1	−0.31703 (11)	−0.7500	0.11247 (8)	0.0052 (2)
O11	−0.5087 (3)	−0.7500	0.0310 (2)	0.0081 (5)
O12	−0.3598 (3)	−0.7500	0.2566 (3)	0.0080 (5)
O13	−0.2107 (2)	−0.5489 (3)	0.09386 (18)	0.0083 (3)
P2	0.26341 (12)	−0.2500	0.23940 (9)	0.0054 (2)
O21	0.0855 (3)	−0.2500	0.1340 (3)	0.0084 (5)
O22	0.2123 (4)	−0.2500	0.3770 (3)	0.0130 (5)
O23	0.3790 (2)	−0.4390 (3)	0.21363 (18)	0.0091 (3)
P3	0.21762 (12)	−0.7500	0.48890 (9)	0.0064 (2)
O31	0.0256 (4)	−0.7500	0.4084 (3)	0.0140 (5)
O32	0.3513 (4)	−0.7500	0.3933 (3)	0.0119 (5)
O33	−0.2479 (3)	−1.0599 (3)	0.41460 (18)	0.0116 (4)
O	−0.8765 (3)	−0.7500	0.0924 (2)	0.0070 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	0.0108 (3)	0.0090 (3)	0.0072 (3)	0.000	0.0024 (2)	0.000
Fe1	0.0075 (2)	0.0054 (2)	0.0068 (3)	−0.00023 (16)	0.00379 (17)	0.00011 (17)
Fe2	0.0066 (3)	0.0050 (3)	0.0057 (2)	0.000	0.00243 (17)	0.000
Fe3	0.0111 (3)	0.0060 (3)	0.0036 (3)	0.000	0.00167 (18)	0.000
P1	0.0065 (4)	0.0052 (4)	0.0045 (4)	0.000	0.0028 (3)	0.000
O11	0.0075 (11)	0.0106 (12)	0.0066 (11)	0.000	0.0019 (9)	0.000
O12	0.0096 (11)	0.0097 (12)	0.0058 (10)	0.000	0.0042 (8)	0.000
O13	0.0089 (7)	0.0075 (8)	0.0096 (8)	−0.0013 (6)	0.0048 (6)	0.0000 (6)
P2	0.0077 (4)	0.0049 (4)	0.0038 (4)	0.000	0.0019 (3)	0.000
O21	0.0099 (11)	0.0089 (11)	0.0065 (10)	0.000	0.0011 (9)	0.000
O22	0.0189 (13)	0.0164 (13)	0.0047 (11)	0.000	0.0050 (9)	0.000

O23	0.0106 (8)	0.0055 (7)	0.0114 (8)	0.0007 (6)	0.0028 (6)	−0.0005 (6)
P3	0.0103 (4)	0.0053 (4)	0.0044 (4)	0.000	0.0032 (3)	0.000
O31	0.0114 (12)	0.0208 (14)	0.0093 (12)	0.000	0.0005 (9)	0.000
O32	0.0135 (12)	0.0167 (13)	0.0070 (11)	0.000	0.0057 (9)	0.000
O33	0.0213 (9)	0.0059 (7)	0.0078 (8)	−0.0006 (7)	0.0031 (7)	0.0016 (6)
O	0.0065 (10)	0.0070 (11)	0.0068 (10)	0.000	−0.0005 (8)	0.000

Geometric parameters (Å, °)

Ca—O11^{i}	2.391 (3)	Fe3—O33	1.986 (2)
Ca—O13^{ii}	2.434 (2)	Fe3—O33^{xii}	1.986 (2)
Ca—O13^{iii}	2.434 (2)	P1—O13	1.532 (2)
Ca—O23	2.473 (3)	P1—O13^{xii}	1.532 (2)
Ca—O23^{iv}	2.473 (3)	P1—O11	1.532 (3)
Ca—O33^{v}	2.514 (2)	P1—O12	1.554 (3)
Ca—O33^{vi}	2.514 (2)	P1—Ca^{ix}	3.2878 (10)
Ca—P2	3.102 (4)	P1—Ca^{xiii}	3.2878 (10)
Ca—P3^{vii}	3.1724 (16)	O11—Ca^{i}	2.391 (3)
Ca—P1^{ii}	3.2878 (10)	O13—Ca^{ix}	2.434 (2)
Ca—P1^{v}	3.2878 (10)	P2—O22	1.513 (3)
Fe1—O^{viii}	1.9860 (17)	P2—O23^{iv}	1.528 (2)
Fe1—O^{ii}	1.9860 (17)	P2—O23	1.528 (2)
Fe1—O13	2.011 (2)	P2—O21	1.561 (3)
Fe1—O13^{i}	2.011 (2)	O21—Fe1^{xiv}	2.1135 (18)
Fe1—O21^{i}	2.1135 (18)	O22—Fe3^{xi}	1.894 (3)
Fe1—O21	2.1135 (18)	O23—Fe2^{ii}	1.981 (2)
Fe2—O	1.870 (3)	P3—O32	1.515 (3)
Fe2—O32^{ix}	1.945 (3)	P3—O31	1.530 (3)
Fe2—O23^{ix}	1.981 (2)	P3—O33^{xv}	1.544 (2)
Fe2—O23^{x}	1.981 (2)	P3—O33^{xvi}	1.544 (2)
Fe2—O12	2.151 (4)	P3—Ca^{vii}	3.1724 (16)
Fe2—O11	2.183 (3)	O32—Fe2^{ii}	1.945 (3)
Fe2—P1	2.803 (3)	O33—P3^{xvi}	1.544 (2)
Fe3—O31	1.872 (4)	O33—Ca^{xiii}	2.514 (2)
Fe3—O22^{xi}	1.894 (3)	O—Fe1^{xvii}	1.9860 (17)
Fe3—O12	1.960 (3)	O—Fe1^{ix}	1.9860 (17)
O11^{i}—Ca—O13^{ii}	75.42 (7)	O—Fe2—P1	125.58 (10)
O11^{i}—Ca—O13^{iii}	75.42 (7)	O32^{ix}—Fe2—P1	118.50 (10)
O13^{ii}—Ca—O13^{iii}	102.03 (10)	O23^{ix}—Fe2—P1	85.83 (5)
O11^{i}—Ca—O23	78.17 (9)	O23^{x}—Fe2—P1	85.83 (5)
O13^{ii}—Ca—O23	93.59 (8)	O31—Fe3—O22^{xi}	108.28 (14)
O13^{iii}—Ca—O23	144.58 (7)	O31—Fe3—O12	104.83 (13)

O11^{i}—Ca—O23^{iv}	78.17 (9)	O22^{xi}—Fe3—O12	146.89 (12)
O13^{ii}—Ca—O23^{iv}	144.58 (7)	O31—Fe3—O33	95.26 (6)
O13^{iii}—Ca—O23^{iv}	93.59 (8)	O22^{xi}—Fe3—O33	95.17 (6)
O23—Ca—O23^{iv}	57.88 (11)	O12—Fe3—O33	81.70 (6)
O11^{i}—Ca—O33^{v}	149.65 (5)	O31—Fe3—O33^{xii}	95.26 (6)
O13^{ii}—Ca—O33^{v}	133.04 (8)	O22^{xi}—Fe3—O33^{xii}	95.17 (6)
O13^{iii}—Ca—O33^{v}	86.46 (7)	O12—Fe3—O33^{xii}	81.70 (6)
O23—Ca—O33^{v}	105.74 (8)	O33—Fe3—O33^{xii}	162.15 (12)
O23^{iv}—Ca—O33^{v}	78.93 (9)	O13—P1—O13^{xii}	112.33 (16)
O11^{i}—Ca—O33^{vi}	149.65 (5)	O13—P1—O11	113.29 (9)
O13^{ii}—Ca—O33^{vi}	86.46 (7)	O13^{xii}—P1—O11	113.29 (9)
O13^{iii}—Ca—O33^{vi}	133.04 (8)	O13—P1—O12	108.34 (9)
O23—Ca—O33^{vi}	78.93 (9)	O13^{xii}—P1—O12	108.34 (9)
O23^{iv}—Ca—O33^{vi}	105.74 (8)	O11—P1—O12	100.34 (15)
O33^{v}—Ca—O33^{vi}	57.20 (9)	O13—P1—Fe2	123.62 (8)
O11^{i}—Ca—P2	79.81 (9)	O13^{xii}—P1—Fe2	123.62 (8)
O13^{ii}—Ca—P2	121.53 (5)	O11—P1—Fe2	50.73 (11)
O13^{iii}—Ca—P2	121.53 (5)	O12—P1—Fe2	49.61 (11)
O33^{v}—Ca—P2	89.64 (8)	O13—P1—Ca^{ix}	44.13 (8)
O33^{vi}—Ca—P2	89.64 (8)	O13^{xii}—P1—Ca^{ix}	151.82 (9)
O11^{i}—Ca—P3^{vii}	168.11 (7)	O11—P1—Ca^{ix}	93.19 (4)
O13^{ii}—Ca—P3^{vii}	111.42 (6)	O12—P1—Ca^{ix}	74.294 (19)
O13^{iii}—Ca—P3^{vii}	111.42 (6)	Fe2—P1—Ca^{ix}	80.22 (2)
O23—Ca—P3^{vii}	91.45 (7)	O13—P1—Ca^{xiii}	151.82 (9)
O23^{iv}—Ca—P3^{vii}	91.45 (7)	O13^{xii}—P1—Ca^{xiii}	44.13 (8)
P2—Ca—P3^{vii}	88.29 (7)	O11—P1—Ca^{xiii}	93.19 (4)
O11^{i}—Ca—P1^{ii}	77.77 (2)	O12—P1—Ca^{xiii}	74.294 (19)
O13^{ii}—Ca—P1^{ii}	25.99 (5)	Fe2—P1—Ca^{xiii}	80.22 (2)
O13^{iii}—Ca—P1^{ii}	126.71 (6)	Ca^{ix}—P1—Ca^{xiii}	148.58 (4)
O23—Ca—P1^{ii}	68.54 (6)	P1—O11—Fe2	96.36 (14)
O23^{iv}—Ca—P1^{ii}	124.46 (6)	P1—O11—Ca^{i}	140.38 (15)
O33^{v}—Ca—P1^{ii}	132.14 (5)	Fe2—O11—Ca^{i}	123.26 (13)
O33^{vi}—Ca—P1^{ii}	75.48 (5)	P1—O12—Fe3	134.77 (17)
P2—Ca—P1^{ii}	97.38 (2)	P1—O12—Fe2	97.02 (14)
P3^{vii}—Ca—P1^{ii}	104.01 (2)	Fe3—O12—Fe2	128.22 (14)
O11^{i}—Ca—P1^{v}	77.77 (2)	P1—O13—Fe1	131.13 (12)
O13^{ii}—Ca—P1^{v}	126.71 (6)	P1—O13—Ca^{ix}	109.88 (10)
O23—Ca—P1^{v}	124.46 (6)	Fe1—O13—Ca^{ix}	118.97 (9)
O23^{iv}—Ca—P1^{v}	68.54 (6)	O22—P2—O23^{iv}	113.70 (10)
O33^{v}—Ca—P1^{v}	75.48 (5)	O22—P2—O23	113.70 (10)
O33^{vi}—Ca—P1^{v}	132.14 (5)	O23^{iv}—P2—O23	103.06 (16)

P2—Ca—P1^{v}	97.38 (2)	O22—P2—O21	107.95 (17)
P3^{vii}—Ca—P1^{v}	104.01 (2)	O23^{iv}—P2—O21	109.13 (10)
P1^{ii}—Ca—P1^{v}	148.58 (4)	O23—P2—O21	109.13 (10)
O^{viii}—Fe1—O^{ii}	180.0	O22—P2—Ca	122.57 (13)
O^{viii}—Fe1—O13	90.27 (10)	O23^{iv}—P2—Ca	51.94 (8)
O^{ii}—Fe1—O13	89.73 (10)	O23—P2—Ca	51.94 (8)
O^{viii}—Fe1—O13^{i}	89.73 (10)	O21—P2—Ca	129.47 (12)
O^{ii}—Fe1—O13^{i}	90.27 (10)	P2—O21—Fe1	124.75 (8)
O13—Fe1—O13^{i}	180.0	P2—O21—Fe1^{xiv}	124.75 (8)
O^{viii}—Fe1—O21^{i}	103.14 (9)	Fe1—O21—Fe1^{xiv}	96.97 (11)
O^{ii}—Fe1—O21^{i}	76.86 (9)	P2—O22—Fe3^{xi}	165.2 (2)
O13—Fe1—O21^{i}	90.79 (9)	P2—O23—Fe2^{ii}	136.88 (12)
O13^{i}—Fe1—O21^{i}	89.21 (9)	P2—O23—Ca	98.94 (11)
O^{viii}—Fe1—O21	76.86 (9)	Fe2^{ii}—O23—Ca	124.12 (9)
O^{ii}—Fe1—O21	103.14 (9)	O32—P3—O31	109.09 (17)
O13—Fe1—O21	89.21 (9)	O32—P3—O33^{xv}	111.49 (11)
O13^{i}—Fe1—O21	90.79 (9)	O31—P3—O33^{xv}	111.12 (11)
O21^{i}—Fe1—O21	180.0	O32—P3—O33^{xvi}	111.49 (11)
O—Fe2—O32^{ix}	115.92 (13)	O31—P3—O33^{xvi}	111.12 (11)
O—Fe2—O23^{ix}	96.52 (5)	O33^{xv}—P3—O33^{xvi}	102.43 (16)
O32^{ix}—Fe2—O23^{ix}	87.58 (6)	O32—P3—Ca^{vii}	122.83 (13)
O—Fe2—O23^{x}	96.52 (5)	O31—P3—Ca^{vii}	128.08 (12)
O32^{ix}—Fe2—O23^{x}	87.58 (6)	O33^{xv}—P3—Ca^{vii}	51.28 (8)
O23^{ix}—Fe2—O23^{x}	166.93 (11)	O33^{xvi}—P3—Ca^{vii}	51.28 (8)
O—Fe2—O12	158.95 (11)	P3—O31—Fe3	139.66 (19)
O32^{ix}—Fe2—O12	85.13 (12)	P3—O32—Fe2^{ii}	139.08 (19)
O23^{ix}—Fe2—O12	83.75 (5)	P3^{xvi}—O33—Fe3	134.20 (12)
O23^{x}—Fe2—O12	83.75 (5)	P3^{xvi}—O33—Ca^{xiii}	100.10 (10)
O—Fe2—O11	92.67 (12)	Fe3—O33—Ca^{xiii}	125.55 (9)
O32^{ix}—Fe2—O11	151.41 (11)	Fe2—O—Fe1^{xvii}	125.79 (7)
O23^{ix}—Fe2—O11	89.23 (6)	Fe2—O—Fe1^{ix}	125.79 (7)
O23^{x}—Fe2—O11	89.23 (6)	Fe1^{xvii}—O—Fe1^{ix}	105.66 (12)
O12—Fe2—O11	66.28 (11)		

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

Fig. 1

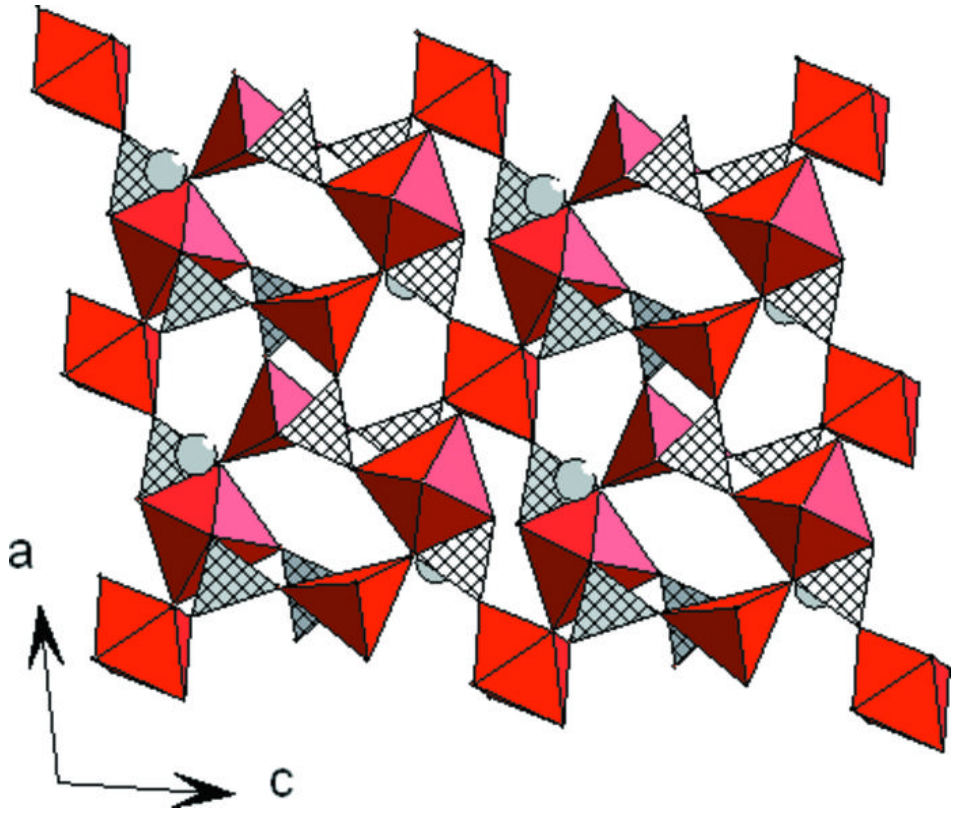

Fig. 2

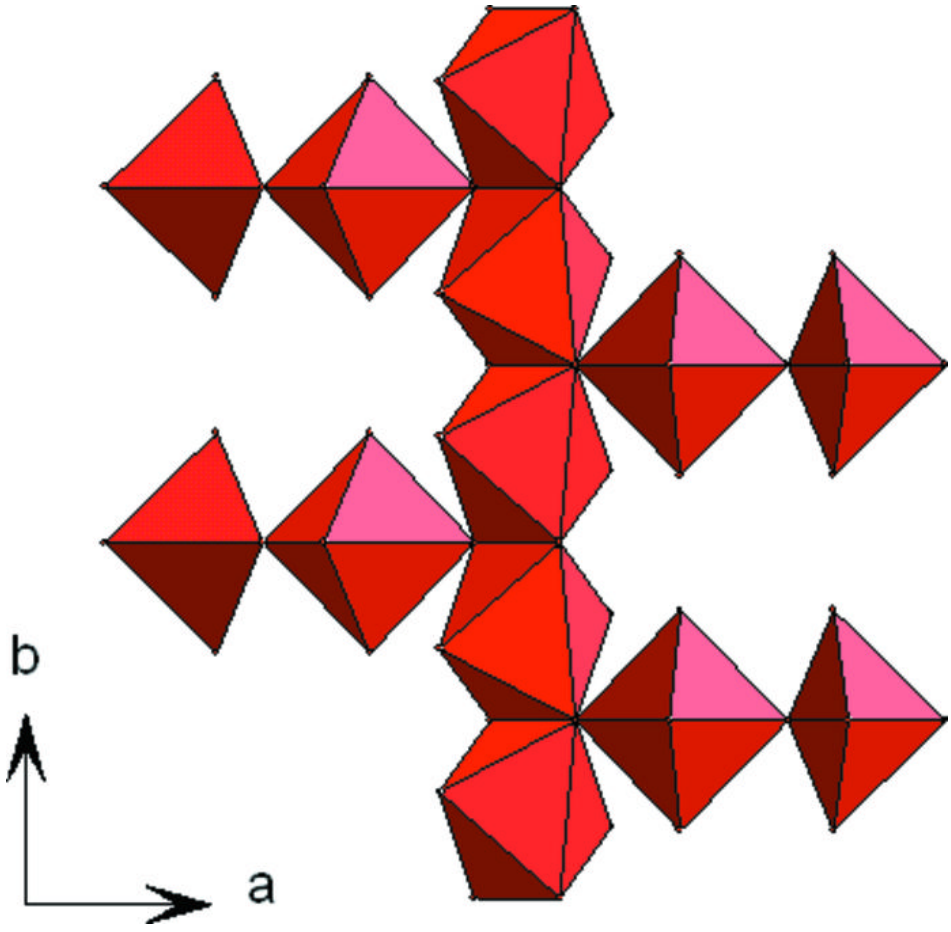
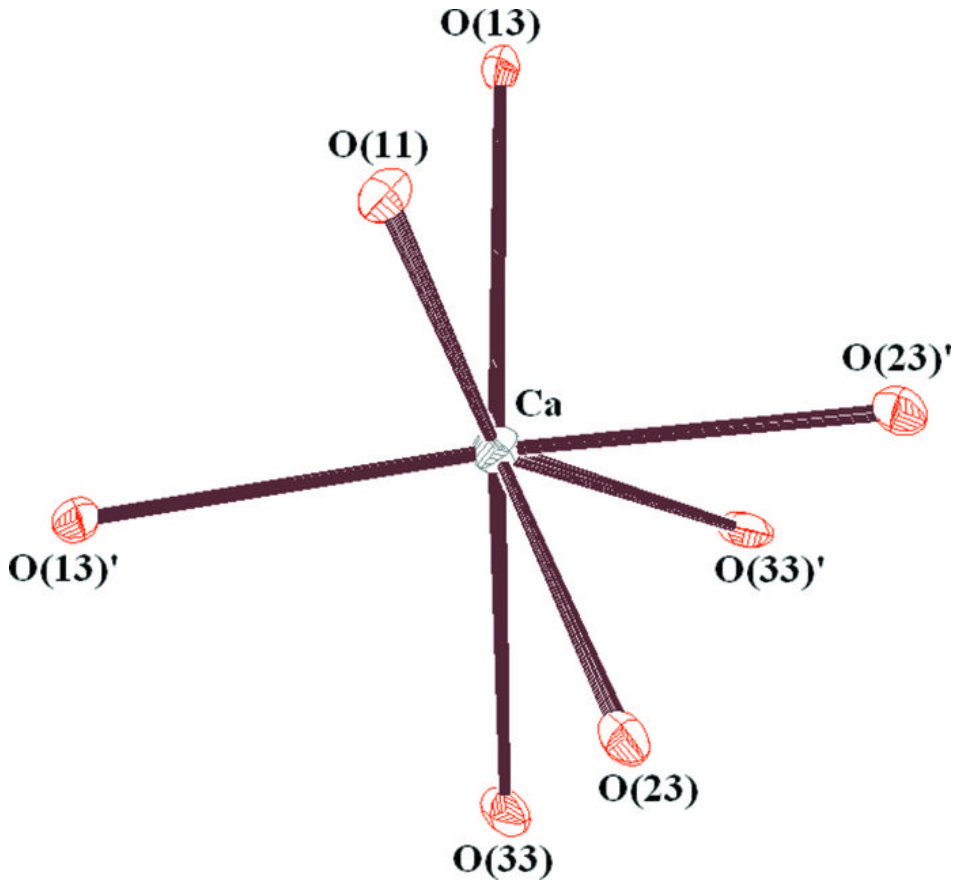
Fig. 3