

Rietveld refinement of $\text{AgCa}_{10}(\text{PO}_4)_7$ from X-ray powder data

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Key indicators: powder X-ray study; $T = 293$ K; mean $\sigma(\text{P}-\text{O}) = 0.050$ Å; R factor = 0.094; wR factor = 0.125; data-to-parameter ratio = 30.3.

Polycrystalline silver(I) decacalcium heptakis(orthophosphate), $\text{AgCa}_{10}(\text{PO}_4)_7$, was obtained by solid-state reaction. It is isotopic with members of the series $\text{M}\text{Ca}_{10}(\text{PO}_4)_7$ ($M = \text{Li}, \text{Na}, \text{K}$ and Cs), and is closely related to the structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$. The crystal structure of the title compound is built up from a framework of $[\text{CaO}_9]$ and two $[\text{CaO}_8]$ polyhedra, one $[\text{CaO}_6]$ octahedron (site symmetry 3.) and three PO_4 tetrahedra (one with site symmetry 3.). The Ag^+ cation is likewise located on a threefold rotation axis and resides in the cavities of the rigid $[\text{Ca}_{10}(\text{PO}_4)_7]^-$ framework. It is surrounded by three O atoms in an almost regular triangular environment.

Related literature

For the structure of the mineral whitlockite, see: Calvo & Gopal (1975); Yashima *et al.* (2003). For powder diffraction studies and Rietveld refinements of phosphate-based whitlockite-related compounds, see: Lazoryak *et al.* (1996); Morozov *et al.* (2000, 2002); Zatonvsky *et al.* (2007, 2010, 2011). For physical properties of these materials, see: Dou *et al.* (2011); Enhai *et al.* (2011); Lazoryak *et al.* (2004); Teterskii *et al.* (2005); Zhang *et al.* (2011). For the crystal structure of isotypic $\text{KCa}_{10}(\text{PO}_4)_7$, see: Sandström & Boström (2006). For bond-valence calculations, see: Brown (2002).

Experimental

Crystal data

$\text{AgCa}_{10}(\text{PO}_4)_7$
 $M_r = 1173.46$
 Trigonal, $R\bar{3}c$
 $a = 10.43723$ (5) Å
 $c = 37.3379$ (7) Å

$V = 3522.50$ (7) Å³
 $Z = 6$
 Cu $K\alpha$ radiation, $\lambda = 1.540560$ Å
 $T = 293$ K
 Flat sheet, 25×25 mm

Data collection

Shimadzu LabX XRD-6000 diffractometer
 Specimen mounting: glass container
 Data collection mode: reflection

Scan method: step
 $2\theta_{\min} = 9.045^\circ$, $2\theta_{\max} = 100.045^\circ$,
 $2\theta_{\text{step}} = 0.020^\circ$

Refinement

$R_p = 0.094$
 $R_{\text{wp}} = 0.125$
 $R_{\text{exp}} = 0.042$
 $R_{\text{Bragg}} = 0.051$
 $R(F) = 0.038$

$\chi^2 = 8.821$
 4551 data points
 150 parameters
 3 restraints

Data collection: *PCXRD* (Shimadzu, 2006); cell refinement: *DICVOL* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodríguez-Carvajal, 2006); program(s) used to solve structure: *FULLPROF* (Rodríguez-Carvajal, 2006); program(s) used to refine structure: *FULLPROF* (Rodríguez-Carvajal, 2006); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2726).

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supplementary materials

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Rietveld refinement of $\text{AgCa}_{10}(\text{PO}_4)_7$ from X-ray powder data

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Comment

In recent years phosphates which are isotypic with $\beta\text{-Ca}_3(\text{PO}_4)_2$ (whitlockite; Calvo & Gopal, 1975; Yashima *et al.*, 2003) or whitlockite-related structures have attracted a growing interest due to their ferroelectric (Lazoryak *et al.*, 2004), non-linear optical (Teterskii *et al.*, 2005) or luminescent (Dou *et al.*, 2011; Enhai *et al.*, 2011; Zhang *et al.*, 2011) properties. The structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ contains three phosphorus (P1—P3) and five metal ($M1$ — $M5$) sites, that are amenable to different types of substitutions, thus yielding a large number of closely related compounds. The Ca sites in the $M1$ and $M2$ positions (6a) are prone to substitution by univalent metals under formation of $M\text{Ca}_{10}(\text{PO}_4)_7$ compounds ($M = \text{Li, Na, K, Cs}$; Morozov *et al.*, 2000; Sandström & Boström, 2006; Zatovsky *et al.*, 2011), or by trivalent metals under formation of $\text{Ca}_9M(\text{PO}_4)_7$ ($M = \text{Cr, Fe, In}$; Lazoryak *et al.*, 1996; Morozov *et al.*, 2002; Zatovsky *et al.*, 2007), or combinations of univalent and trivalent metals (Zatovsky *et al.*, 2010; Zatovsky *et al.*, 2011). The new title compound $\text{AgCa}_{10}(\text{PO}_4)_7$ (I), is likewise isotopic to the family of $M\text{Ca}_{10}(\text{PO}_4)_7$ ($M = \text{Li, Na, K, Cs}$) phosphates.

In the crystal structure of (I) four types of Ca sites (three in general positions 18b and one in special position 6a), three P sites (two in 18b one in 6a), ten O atoms (nine in 18b and one in 6a) and one Ag in 6a are present (Fig. 1).

The anionic framework $[\text{Ca}_{10}(\text{PO}_4)_7]^-$ of (I) is formed by interconnection of four types of $[\text{CaO}_x]$ and $[\text{PO}_4]$ tetrahedra (Fig. 2). The silver cations reside in cavities and compensate the charge of the rigid framework.

The Ca—O distances in the three types of $[\text{CaO}_x]$ polyhedra (one $[\text{CaO}_9]$ (Ca4) and two $[\text{CaO}_8]$ (Ca2, Ca3)) are in the range 2.28 (4)–2.97 (4) Å which is close to that in the series of $M\text{Ca}_{10}(\text{PO}_4)_7$ structures ($M = \text{K, Cs}$; Sandström & Boström, 2006; Zatovsky *et al.*, 2011). The polyhedron $[\text{CaO}_6]$ (Ca1) is more irregular with Ca—O distances spread over the range 2.17 (4) to 2.40 (4) Å. In the case of $M\text{Ca}_{10}(\text{PO}_4)_7$ ($M = \text{K, Cs}$), the corresponding distances are 2.23–2.31 Å. The nearest oxygen environment of the Ag site corresponds to an almost regular triangular arrangement. The position of the Ag site is slightly shifted by 0.30 (3) Å from the plane of the O_3 triangle (Fig. 3). On both sides from the central triangular plane two further groups of Ag—O contacts can be observed. Three O2 atoms, which belong to a single orthophosphate tetrahedron, coordinate the Ag atom from one side of the plane and three O9 atoms, which belong to three different orthophosphate tetrahedra, complete the other part of the $[\text{AgO}_9]$ coordination sphere. Such kind of arrangement of O atoms can be described as a distorted three-capped triangular antiprism (Fig. 3). The lengths of Ag—O contacts are 2.476 (19), 3.15 (4) and 3.35 (4) Å. In comparison with $M\text{Ca}_{10}(\text{PO}_4)_7$ ($M = \text{Na, Cs}$) the corresponding M —O distances are: $d(\text{Na—O}) = 2.452, 2.981, 3.362$ (Morozov *et al.*, 2000) and $d(\text{Cs—O}) = 2.803, 3.200, 3.252$ Å (Zatovsky *et al.*, 2011) and the coordination numbers of the alkaline metal are six for Na and nine for Cs (Fig. 4(b,c)). For the Ag atom, the Ag—O2 distance (3.15 (4) Å) significantly exceeds that of Ag—O10 (2.471 (15) Å) thus indicating that the coordination number should rather be described as $[3 + 6]$ (Fig. 4a). Bond valence calculations (Brown, 2002) of the Ag^+ cation resulted in 0.60 valence units considering the three close O atoms, and 0.67 v.u. considering also the six remote O atoms, thus indicating a rather low contribution to the overall bonding of the latter O atoms.

Experimental

The title compound has been prepared by solid state reactions from a mixture of Ag_3PO_4 , CaCO_3 and CaHPO_4 in the stoichiometric molar ratio $\text{Ag}:\text{Ca}:\text{P} = 1:10:7$. The starting components were finely ground in an agate mortar and then placed in a porcelain crucible. The thermal treatment has been carried out in two steps. The first one included preheating to 873 K to decompose the carbonate and calcium hydrogen phosphate. After that, the mixture was annealed at 1173 K for 20 h. The final product was a white powder.

Refinement

Structure refinement was performed using $\text{KCa}_{10}(\text{PO}_4)_7$ (Sandström & Boström, 2006) as a starting model. For profile refinement Pearson VII function was used. For the oxygen atoms of each orthophosphate group the isotropic temperature factors were restrained as equal. The result of the final Rietveld refinement is given in Fig. 5.

Computing details

Data collection: *PCXRD* (Shimadzu, 2006); cell refinement: *Dicvol* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodriguez-Carvajal, 2006); program(s) used to solve structure: *FULLPROF* (Rodriguez-Carvajal, 2006); program(s) used to refine structure: *FULLPROF* (Rodriguez-Carvajal, 2006); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

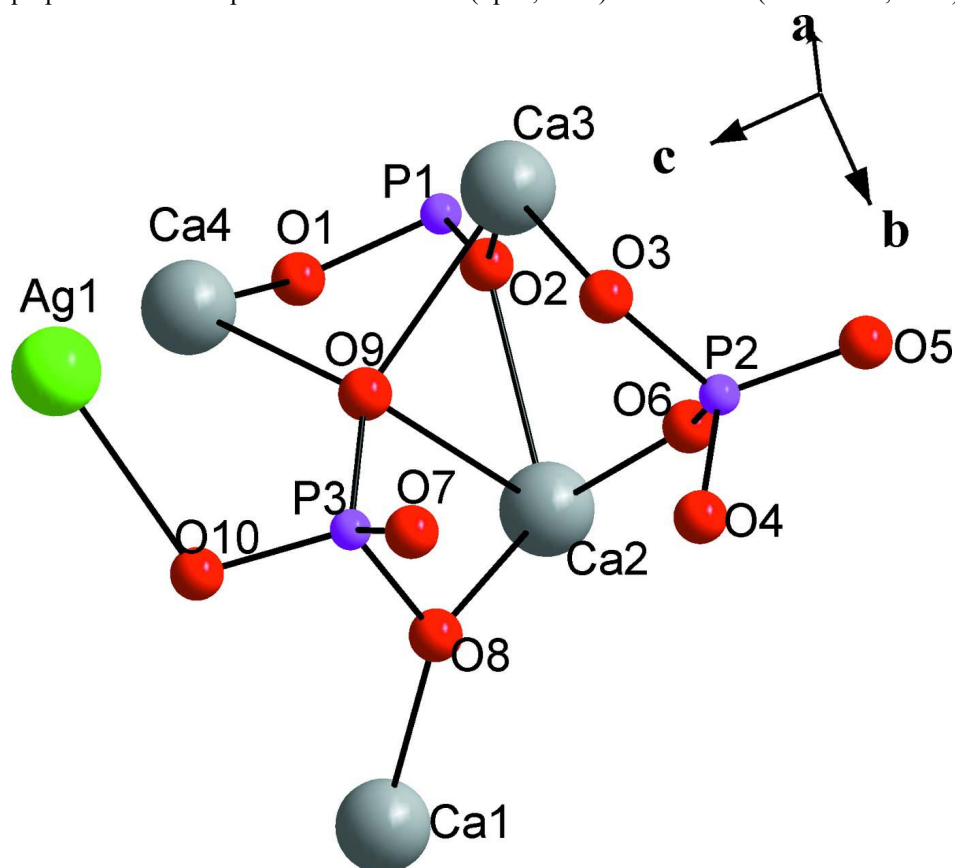


Figure 1

The asymmetric unit of the structure of compound (I).

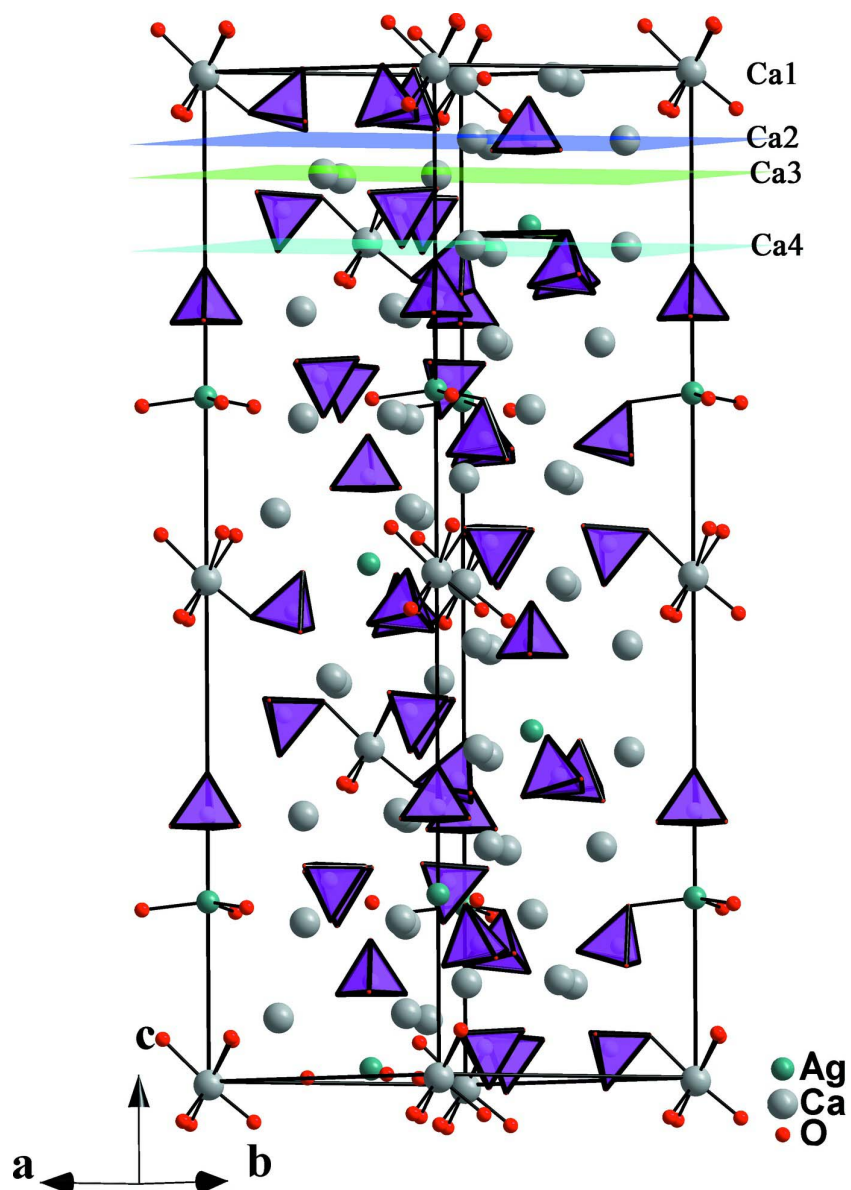


Figure 2

The environment of the four different Ca sites (violet plane corresponds to Ca2 sites, the green plane to Ca3 sites and the blue plane to Ca4 sites) and the Ag⁺ cation in the structure of (I). PO₄ groups are represented as purple tetrahedra.

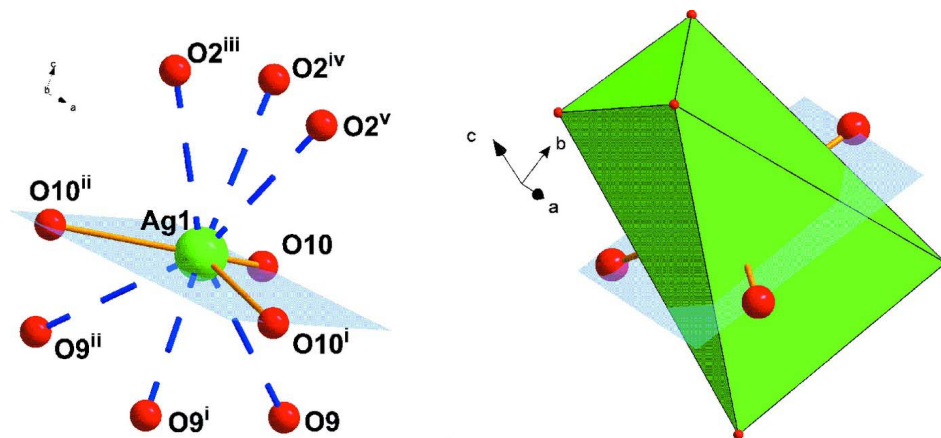


Figure 3

The coordination environment of the Ag^+ cation. [Symmetry codes: (i) $-x + y, -x, z$; (ii) $-y, x - y, z$; (iii) $-2/3 + x, -1/3 + x - y, 1/6 + z$; (iv) $1/3 - y, 2/3 - x, 1/6 + z$; (v) $1/3 - x + y, -1/3 + y, 1/6 + z$].

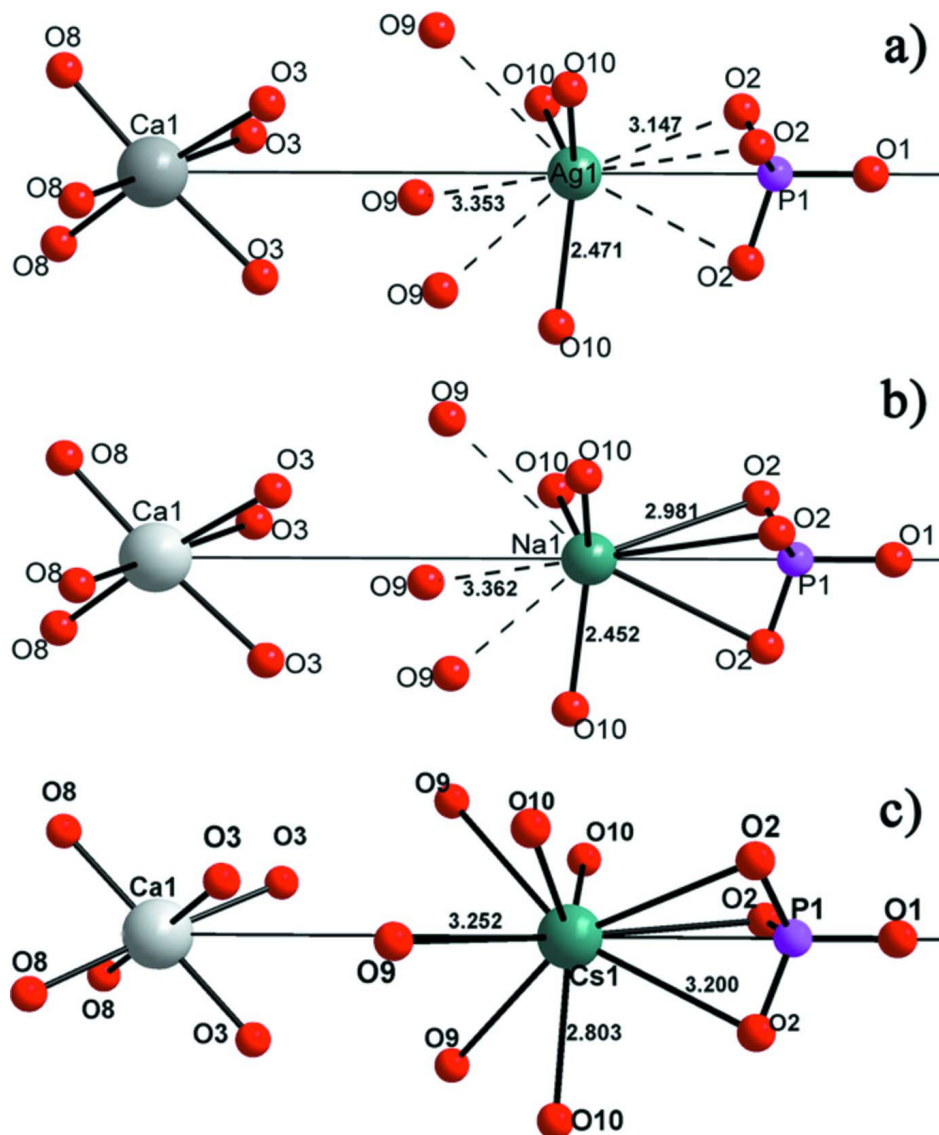


Figure 4

Comparison of the coordination environment of M^I in the series $MCa_{10}(PO_4)_7$; a) $M = Ag$; b) $M = Na$; c) $M = Cs$.

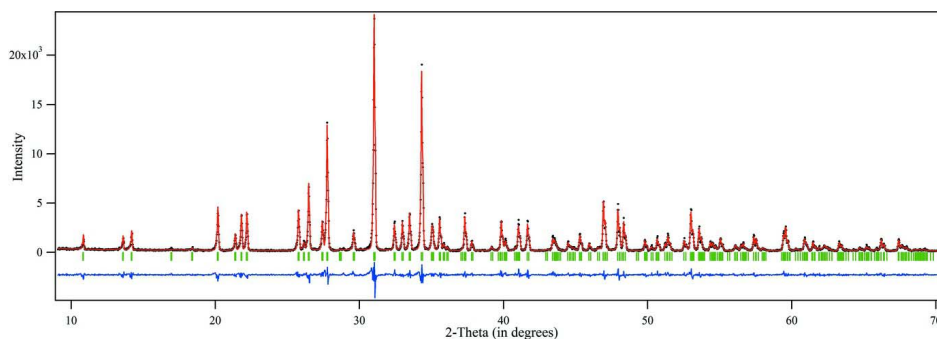


Figure 5

Rietveld refinement of $AgCa_{10}(PO_4)_7$. Experimental (dots), calculated (red curve) and difference (blue curve) data for 2θ range $9-72^\circ$.

Silver(I) decacalcium heptakis(orthophosphate)

Crystal data

AgCa₁₀(PO₄)₇

M_r = 1173.46

Trigonal, *R*3c

Hall symbol: R 3 -2" c

a = 10.43723 (5) Å

c = 37.3379 (7) Å

V = 3522.50 (7) Å³

Z = 6

D_x = 3.319 Mg m⁻³

Cu *Kα* radiation, λ = 1.540560 Å

T = 293 K

Particle morphology: isometric
white

flat sheet, 25 × 25 mm

Specimen preparation: Prepared at 293 K and
101.3 kPa

Data collection

Shimadzu LabX XRD-6000

diffractometer

Radiation source: X-ray tube, X-ray

Graphite monochromator

Specimen mounting: glass container

Data collection mode: reflection

Scan method: step

2θ_{min} = 9.045°, 2θ_{max} = 100.045°, 2θ_{step} = 0.020°

Refinement

R_p = 0.094

R_{wp} = 0.125

R_{exp} = 0.042

R_{Bragg} = 0.051

R(F) = 0.038

χ² = 8.821

4551 data points

Profile function: Pearson VII

150 parameters

3 restraints

3 constraints

Standard least squares refinement

(Δ/σ)_{max} = 0.001

Background function: Linear Interpolation
between a set background points with refinable
heights

Preferred orientation correction: March-Dollase

Numeric Multiaxial Function

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Ag1	0.00000	0.00000	0.1780 (8)	0.042 (2)*
Ca1	0.33333	0.66667	0.1632 (9)	0.002 (2)*
Ca2	0.4650 (10)	0.5260 (11)	0.0955 (8)	0.0044 (14)*
Ca3	0.2864 (7)	0.1558 (12)	0.0625 (8)	0.004 (2)*
Ca4	0.3992 (5)	0.1876 (9)	0.1565 (8)	0.0044 (14)*
P1	0.66667	0.33333	0.0976 (8)	0.002 (4)*
P2	0.1577 (14)	0.3495 (13)	0.0288 (8)	0.009 (3)*
P3	0.1366 (11)	0.3111 (7)	0.1306 (8)	0.003 (3)*
O1	0.66667	0.33333	0.1387 (11)	0.006 (11)*
O2	0.5229 (16)	0.325 (2)	0.0860 (9)	0.006 (6)*
O3	0.082 (3)	0.1873 (15)	0.0421 (9)	0.005 (3)*
O4	0.051 (2)	0.394 (3)	0.0420 (10)	0.005 (3)*
O5	0.173 (2)	0.3689 (18)	-0.0111 (9)	0.005 (3)*
O6	0.316 (2)	0.440 (2)	0.0462 (10)	0.005 (3)*
O7	-0.0093 (19)	0.267 (3)	0.1100 (9)	0.006 (4)*
O8	0.241 (3)	0.4824 (13)	0.1261 (9)	0.006 (4)*

O9	0.221 (2)	0.243 (3)	0.1161 (10)	0.006 (4)*
O10	0.0887 (18)	0.267 (2)	0.1700 (10)	0.006 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
?	?	?	?	?	?	?

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

Ag1—O10	2.476 (19)	Ca3—O4 ⁱⁱ	2.62 (4)
Ag1—O10 ⁱ	2.476 (19)	Ca3—O6	2.89 (3)
Ag1—O10 ⁱⁱ	2.476 (19)	Ca4—O7 ⁱⁱ	2.40 (4)
Ca1—O8	2.17 (4)	Ca4—O6 ^{ix}	2.45 (4)
Ca1—O8 ⁱⁱⁱ	2.17 (4)	Ca4—O4 ^{vi}	2.46 (4)
Ca1—O8 ^{iv}	2.17 (4)	Ca4—O1	2.510 (14)
Ca1—O3 ^v	2.40 (4)	Ca4—O5 ^{ix}	2.55 (3)
Ca1—O3 ^{vi}	2.40 (4)	Ca4—O5 ^{vi}	2.59 (2)
Ca1—O3 ^{vii}	2.40 (4)	Ca4—O9	2.67 (4)
Ca2—O6	2.28 (4)	Ca4—O10 ⁱⁱ	2.692 (18)
Ca2—O5 ^{vi}	2.41 (4)	Ca4—O2	2.97 (4)
Ca2—O8	2.43 (4)	P1—O1	1.54 (5)
Ca2—O4 ⁱⁱⁱ	2.45 (4)	P1—O2	1.52 (2)
Ca2—O2	2.48 (3)	P1—O2 ^x	1.52 (2)
Ca2—O8 ⁱⁱⁱ	2.48 (3)	P1—O2 ^{xi}	1.52 (2)
Ca2—O7 ⁱⁱⁱ	2.57 (2)	P2—O3	1.55 (2)
Ca2—O9	2.88 (3)	P2—O4	1.49 (3)
Ca3—O7 ⁱⁱ	2.31 (4)	P2—O5	1.50 (4)
Ca3—O3 ⁱⁱ	2.37 (2)	P2—O6	1.58 (3)
Ca3—O2	2.37 (2)	P3—O7	1.56 (3)
Ca3—O9	2.43 (4)	P3—O8	1.570 (15)
Ca3—O3	2.44 (4)	P3—O9	1.48 (3)
Ca3—O10 ^{viii}	2.46 (4)	P3—O10	1.55 (5)
O10—Ag1—O10 ⁱ	118.5 (9)	O1—P1—O2 ^x	106.6 (17)
O10—Ag1—O10 ⁱⁱ	118.6 (7)	O2 ^x —P1—O2 ^{xi}	112.3 (18)
O10 ⁱ —Ag1—O10 ⁱⁱ	118.6 (8)	O2—P1—O2 ^x	112.2 (16)
O7—P3—O8	107.7 (19)	O2—P1—O2 ^{xi}	112.2 (17)
O7—P3—O9	114 (2)	O3—P2—O4	101 (2)
O7—P3—O10	105.0 (17)	O4—P2—O5	109 (2)
O8—P3—O9	105.5 (18)	O3—P2—O5	115.3 (19)
O8—P3—O10	112 (2)	O3—P2—O6	109 (2)
O9—P3—O10	112.7 (19)	O4—P2—O6	114 (2)
O1—P1—O2 ^{xi}	106.5 (16)	O5—P2—O6	108.6 (19)
O1—P1—O2	106.5 (16)	Ag1—O10—P3	109.4 (15)

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-y+1, x-y+1, z$; (iv) $-x+y, -x+1, z$; (v) $-y+1/3, -x+2/3, z+1/6$; (vi) $x+1/3, x-y+2/3, z+1/6$; (vii) $-x+y+1/3, y+2/3, z+1/6$; (viii) $-y+2/3, -x+1/3, z-1/6$; (ix) $-x+y+1/3, y-1/3, z+1/6$; (x) $-y+1, x-y, z$; (xi) $-x+y+1, -x+1, z$.