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Crystal structure of langbeinite-related $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$

Nataliia Yu. Strutynska,[a]* Marina A. Bondarenko,[a] Ivan V. Ogorodnyk,[a] Vyacheslav N. Baumer[b,c] and Nikolay S. Slobodyanik[a]

[a]Department of Inorganic Chemistry, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., 01601 Kyiv, Ukraine, [b]STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine, and [c]V. N. Karazin National University, 4, Svobody Square, 61001 Kharkiv, Ukraine. *Correspondence e-mail: Strutynska_N@bigmir.net

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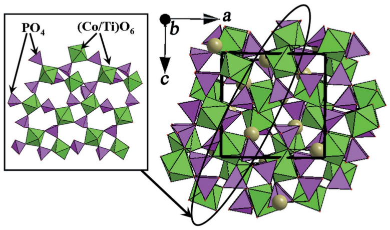
Potassium rubidium cobalt(II)/titanium(IV) tris(orthophosphate), $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$, has been obtained using a high-temperature crystallization method. The obtained compound has a langbeinite-type structure. The three-dimensional framework is built up from mixed-occupied $(Co/Ti^{IV})O_6$ octahedra (point group symmetry .3.) and PO_4 tetrahedra. The K^+ and Rb^+ cations are statistically distributed over two distinct sites (both with site symmetry .3.) in the large cavities of the framework. They are surrounded by 12 O atoms.



1. Chemical context

Nowadays, there are a number of reports on the synthesis and investigation of langbeinite-related complex phosphates, which exhibit interesting properties such as magnetic (Ogorodnyk *et al.*, 2006), luminescence (Zhang *et al.*, 2013; Chawla *et al.*, 2013) and phase transitions (Hikita *et al.*, 1977). It should be noted that compounds with a langbeinite-type structure are prospects for use as a matrix for the storage of nuclear waste (Orlova *et al.*, 2011). Zaripov *et al.* (2009) and Ogorodnyk *et al.* (2007*a*) proved that caesium can be introduced into the cavity of a langbeinite framework that can be used for the immobilization of ^{137}Cs in an inert matrix for safe disposal.

A large number of compounds with a langbeinite framework based on a variety of different valence elements are known. Three major types of substitutions of the elements are known as well as their combinations. They are: metal substitution in octahedra, element substitution in anion tetrahedra, and substitution of ions in cavities. Among these compounds, potassium-containing langbeinites are the most studied (Ogorodnyk *et al.*, 2006, 2007*b*,*c*; Norberg, 2002; Orlova *et al.*, 2003). However, several reports concerning phosphate langbeinites with Rb^+ in the cavities of the framework are known: $Rb_2FeZr(PO_4)_3$ (Trubach *et al.*, 2004), $Rb_2YbTi(PO_4)_3$ (Gustafsson *et al.*, 2005) and $Rb_2TiY(PO_4)_3$ (Gustafsson *et al.*, 2006).

Herein, the structure of $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$, potassium rubidium cobalt(II)/titanium(IV) tris(orthophosphate) is reported.

2. Structural commentary

The asymmetric unit of $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$ consists of two mixed-occupied (Co/Ti^{IV}), two (Rb/K), one P and four oxygen positions (Fig. 1). The structure of the title

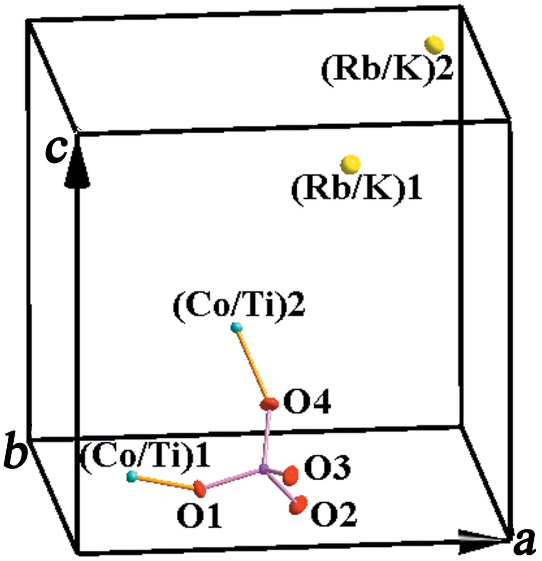


Figure 1
The asymmetric unit of $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$, showing displacement ellipsoids at the 50% probability level.

compound is built up from mixed $(Co/Ti^{IV})O_6$ octahedra and PO_4 tetrahedra, which are connected *via* common O-atom vertices. Each octahedron is linked to six adjacent tetrahedra and reciprocally, each tetrahedron is connected to four neighboring octahedra into a three-dimensional rigid framework (Fig. 2).

The oxygen environment of the metal atoms in the $(Co/Ti^{IV})1O_6$ octahedra is slightly distorted, with *M*—O bonds of 1.940 (2) and 1.966 (2) Å. These distances are close to the corresponding bond lengths in $K_2Ti_2(PO_4)_3$ [*d*(Ti—O) = 1.877 (10)–1.965 (10) Å; Masse *et al.*, 1972], which could be explained by the small occupancy of cobalt in the mixed $(Co/Ti^{IV})1$ [occupancy = 0.1307 (9)] and $(Co/Ti^{IV})2$ [occupancy = 0.162 (3)] sites. It should be noted that $(Co/Ti^{IV})2$—O distances [1.949 (2) and 1.969 (2) Å] are slightly shorter than those in $K_2Co_{0.5}Ti_{1.5}(PO_4)_3$ (Ogorodnyk *et al.*, 2006).

The orthophosphate tetrahedra are also slightly distorted with P—O bond lengths ranging from 1.525 (2) to 1.531 (2) Å. These distances are almost identical to the corresponding ones in $K_2Co_{0.5}Ti_{1.5}(PO_4)_3$ [*d*(P—O) =1.525 (2)–1.529 (9) Å; Ogorodnyk *et al.*, 2006). A comparison of the corresponding interatomic distances for the octahedra and tetrahedra in $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$ and $K_2Co_{0.5}Ti_{1.5}(PO_4)_3$ shows that partial substitution of K^+ by Rb^+ and decreasing the amount of cobalt slightly influences the distances in the polyhedra for $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$.

The K^+ and Rb^+ cations are located in large cavities of the three-dimensional framework in $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$. They are statistically distributed over two distinct sites in which they have partial occupancies of 0.540 (9) and 0.330 (18) for Rb1 and K1, respectively, and 0.203 (8) and 0.514 (17) for Rb2 and K2, respectively. For the determination of the (Rb/K)1 and (Rb/K)2 coordination numbers (CN), Voronoi–Dirichlet polyhedra (VDP) were built using the *DIRICHLET* program included in the *TOPOS* package (Blatov *et al.*, 1995). Analysis of the solid-angle (Ω) distribution revealed twelve (Rb/K)—O contacts for both the (Rb/K)1 and (Rb/K)2 sites (cut-off distance of 4.0 Å, neglecting those corresponding to Ω < 1.5%; Blatov *et al.*, 1998). The results of the construction of the Voronoi–Dirichlet polyhedra (Blatov *et al.*, 1995) indicated that the coordination scheme for (Rb/K)1 is described as [9 + 3] [nine meaning 'ion–covalent' bonds are in the range 2.896 (2)–3.095 (2) Å which have Ω > 5.0% and three (Rb/K)1—O distances equal to 3.438 (8) Å with Ω = 2.42%]. The (Rb/K)—O distances in the $[(Rb/K)2O_{12}]$-polyhedra are in the range 2.870 (2)–3.219 (2) Å (4.91% < Ω < 9.5%).

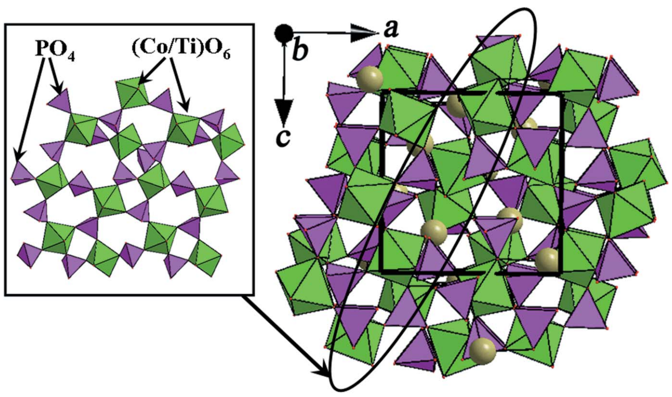


Figure 2
Two-dimensional net and three-dimensional framework for $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$.

The corresponding K1—O contacts in $K_2Co_{0.5}Ti_{1.5}(PO_4)_3$ (Ogorodnyk *et al.*, 2006) are in the range 2.872 (2)–3.231 (3) Å while the K2—O distances in the $K2O_{12}$ polyhedra are in the range 2.855 (2)–3.473 (3) Å, slightly longer than those in $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$. These results indicate that the substitution of K^+ cations by Rb^+ cations in $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$ caused a decrease of the (Rb/K)—O bond length. This fact confirms the rigidity of the framework and the suitability of the cavity dimensions to accommodate different sized ions whose size and nature insignificantly influence the framework.

3. Synthesis and crystallization

The title compound was prepared during crystallization of a self-flux in the Rb_2O–K_2O–P_2O_5–TiO_2–CoO system. The starting components RbH_2PO_4 (4.0 g), KPO_3 (2.4 g), TiO_2 (0.532 g) and CoO (0.50 g) were ground in an agate mortar, placed in a platinum crucible and H_3PO_4 (85%, 0.42 g) was added. The mixture was heated up to 1273 K. The melt was kept at this temperature for one h. After that, the temperature was decreased to 873 K at a rate of 10 K h^{-1}. The crystals of $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$ were separated from the rest flux by washing in hot water. The chemical composition of a single crystal was verified using EDX analysis. Analysis found: K 6.72, Rb 13.85, Co 3.74, Ti 16.86, P 19.96 and O 38.87 at%, while $\mathrm{Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3}$ requires K 6.86, Rb 13.15, Co 3.60, Ti 17.06, P 19.36 and O 39.97 at%.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The O-atom sites were determined from difference Fourier maps. It was assumed that both types of alkaline ions occupy cavity sites while the transition metals occupy framework sites. The occupancies were refined using linear combinations of free variables taking into account the total charge of the cell.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\mathrm{Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3}$
M_r	480.40
Crystal system, space group	Cubic, $P2_13$
Temperature (K)	293
a (Å)	9.8527 (1)
V (Å^3)	956.46 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.63
Crystal size (mm)	0.10 × 0.07 × 0.05
Data collection	
Diffractometer	Oxford Diffraction Xcalibur-3
Absorption correction	Multi-scan (Blessing, 1995)
$T_{\min}$, $T_{\max}$	0.559, 0.734
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1414, 1414, 1312
R_{int}	0.025
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.804
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.051, 1.05
No. of reflections	1414
No. of parameters	67
No. of restraints	3
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.37, −0.36
Absolute structure	Flack (1983), 612 Friedel pairs
Absolute structure parameter	0.024 (10)

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2006), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999), *WinGX* (Farrugia, 2012) and *enCIFer* (Allen *et al.*, 2004).

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Crystal structure of langbeinite-related $Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$

Nataliia Yu. Strutynska, Marina A. Bondarenko, Ivan V. Ogorodnyk, Vyacheslav N. Baumer and Nikolay S. Slobodyanik

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *enCIFer* (Allen *et al.*, 2004).

Potassium rubidium cobalt(II)/titanium(IV) tris(orthophosphate)

Crystal data

$Rb_{0.743}K_{0.845}Co_{0.293}Ti_{1.707}(PO_4)_3$
M_r = 480.40
Cubic, $P2_13$
Hall symbol: P 2ac 2ab 3
a = 9.8527 (1) Å
V = 956.46 (2) Å^3
Z = 4
F(000) = 920
D_x = 3.336 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1414 reflections
θ = 2.9–34.9°
μ = 6.63 mm^{-1}
T = 293 K
Tetrahedron, dark red
0.1 × 0.07 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur-3 diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.559, T_{max} = 0.734
1414 measured reflections
1414 independent reflections
1312 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 34.9°, θ_{min} = 2.9°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = 1 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.051
S = 1.05
1414 reflections
67 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.051
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.0026 (6)
Absolute structure: Flack (1983), 612 Friedel pairs
Absolute structure parameter: 0.024 (10)

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 (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Rb1	0.71155 (4)	0.71155 (4)	0.71155 (4)	0.02169 (18)	0.540 (9)
K1	0.71155 (4)	0.71155 (4)	0.71155 (4)	0.02169 (18)	0.330 (18)
Rb2	0.93045 (5)	0.93045 (5)	0.93045 (5)	0.0199 (3)	0.203 (8)
K2	0.93045 (5)	0.93045 (5)	0.93045 (5)	0.0199 (3)	0.514 (17)
Ti1	0.14135 (4)	0.14135 (4)	0.14135 (4)	0.00760 (12)	0.8693 (9)
Co1	0.14135 (4)	0.14135 (4)	0.14135 (4)	0.00760 (12)	0.1307 (9)
Ti2	0.41386 (3)	0.41386 (3)	0.41386 (3)	0.00709 (12)	0.838 (3)
Co2	0.41386 (3)	0.41386 (3)	0.41386 (3)	0.00709 (12)	0.162 (3)
P1	0.45604 (5)	0.22826 (5)	0.12582 (5)	0.00682 (10)	
O1	0.30739 (16)	0.23395 (16)	0.08086 (17)	0.0141 (3)	
O2	0.54329 (18)	0.29756 (17)	0.01814 (17)	0.0179 (3)	
O3	0.50157 (16)	0.08190 (16)	0.14744 (18)	0.0168 (3)	
O4	0.47835 (17)	0.30686 (19)	0.25786 (18)	0.0190 (4)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.02169 (18)	0.02169 (18)	0.02169 (18)	0.00120 (13)	0.00120 (13)	0.00120 (13)
K1	0.02169 (18)	0.02169 (18)	0.02169 (18)	0.00120 (13)	0.00120 (13)	0.00120 (13)
Rb2	0.0199 (3)	0.0199 (3)	0.0199 (3)	−0.00172 (19)	−0.00172 (19)	−0.00172 (19)
K2	0.0199 (3)	0.0199 (3)	0.0199 (3)	−0.00172 (19)	−0.00172 (19)	−0.00172 (19)
Ti1	0.00760 (12)	0.00760 (12)	0.00760 (12)	0.00051 (11)	0.00051 (11)	0.00051 (11)
Co1	0.00760 (12)	0.00760 (12)	0.00760 (12)	0.00051 (11)	0.00051 (11)	0.00051 (11)
Ti2	0.00709 (12)	0.00709 (12)	0.00709 (12)	−0.00033 (11)	−0.00033 (11)	−0.00033 (11)
Co2	0.00709 (12)	0.00709 (12)	0.00709 (12)	−0.00033 (11)	−0.00033 (11)	−0.00033 (11)
P1	0.0059 (2)	0.0076 (2)	0.0070 (2)	−0.00019 (16)	0.00100 (16)	−0.00054 (17)
O1	0.0088 (7)	0.0167 (8)	0.0169 (8)	0.0001 (5)	−0.0032 (6)	0.0021 (6)
O2	0.0183 (9)	0.0185 (8)	0.0170 (8)	0.0001 (7)	0.0075 (6)	0.0049 (6)
O3	0.0160 (8)	0.0130 (8)	0.0214 (8)	0.0064 (6)	0.0022 (6)	0.0034 (6)
O4	0.0196 (9)	0.0229 (10)	0.0146 (8)	−0.0027 (7)	0.0001 (7)	−0.0099 (6)

Geometric parameters (Å, º)

Rb1—O1$^{\rm i}$	2.8956 (17)	Rb2—O4$^{\rm ix}$	3.219 (2)
Rb1—O1$^{\rm ii}$	2.8956 (17)	Rb2—O4$^{\rm viii}$	3.219 (2)
Rb1—O1$^{\rm iii}$	2.8956 (17)	Ti1—O2$^{\rm x}$	1.9404 (17)

Rb1—O2^{iv}	3.0780 (19)	Ti1—O2^{xi}	1.9404 (17)
Rb1—O2^{v}	3.0780 (19)	Ti1—O2^{xii}	1.9404 (17)
Rb1—O2^{vi}	3.0780 (19)	Ti1—O1^{xiii}	1.9657 (16)
Rb1—O4^{iv}	3.0945 (18)	Ti1—O1	1.9657 (16)
Rb1—O4^{vi}	3.0945 (18)	Ti1—O1^{xiv}	1.9657 (16)
Rb1—O4^{v}	3.0945 (18)	Ti2—O3^{ii}	1.9494 (16)
Rb2—O3^{iv}	2.8703 (18)	Ti2—O3^{iii}	1.9494 (16)
Rb2—O3^{vi}	2.8703 (18)	Ti2—O3^{i}	1.9494 (16)
Rb2—O3^{v}	2.8703 (18)	Ti2—O4^{xiii}	1.9691 (17)
Rb2—O2^{vii}	2.9452 (19)	Ti2—O4	1.9691 (17)
Rb2—O2^{viii}	2.9452 (19)	Ti2—O4^{xiv}	1.9691 (17)
Rb2—O2^{ix}	2.9452 (19)	P1—O3	1.5252 (17)
Rb2—O4^{iv}	3.028 (2)	P1—O2	1.5266 (17)
Rb2—O4^{vi}	3.028 (2)	P1—O4	1.5299 (17)
Rb2—O4^{v}	3.028 (2)	P1—O1	1.5312 (16)
Rb2—O4^{vii}	3.219 (2)		

O1^{i}—Rb1—O1^{ii}	90.95 (5)	O2^{ix}—Rb2—O4^{v}	94.29 (5)
O1^{i}—Rb1—O1^{iii}	90.95 (5)	O4^{iv}—Rb2—O4^{v}	87.83 (5)
O1^{ii}—Rb1—O1^{iii}	90.95 (5)	O4^{vi}—Rb2—O4^{v}	87.83 (5)
O1^{i}—Rb1—O2^{iv}	145.70 (5)	O3^{iv}—Rb2—O4^{vii}	86.01 (4)
O1^{ii}—Rb1—O2^{iv}	82.60 (4)	O3^{vi}—Rb2—O4^{vii}	55.94 (4)
O1^{iii}—Rb1—O2^{iv}	55.72 (4)	O3^{v}—Rb2—O4^{vii}	157.18 (5)
O1^{i}—Rb1—O2^{v}	55.72 (4)	O2^{vii}—Rb2—O4^{vii}	46.55 (5)
O1^{ii}—Rb1—O2^{v}	145.70 (5)	O2^{viii}—Rb2—O4^{vii}	86.90 (5)
O1^{iii}—Rb1—O2^{v}	82.60 (4)	O2^{ix}—Rb2—O4^{vii}	101.29 (5)
O2^{iv}—Rb1—O2^{v}	119.386 (9)	O4^{iv}—Rb2—O4^{vii}	53.03 (6)
O1^{i}—Rb1—O2^{vi}	82.60 (4)	O4^{vi}—Rb2—O4^{vii}	104.695 (9)
O1^{ii}—Rb1—O2^{vi}	55.72 (4)	O4^{v}—Rb2—O4^{vii}	137.38 (4)
O1^{iii}—Rb1—O2^{vi}	145.70 (5)	O3^{iv}—Rb2—O4^{ix}	55.94 (4)
O2^{iv}—Rb1—O2^{vi}	119.386 (9)	O3^{vi}—Rb2—O4^{ix}	157.18 (5)
O2^{v}—Rb1—O2^{vi}	119.386 (9)	O3^{v}—Rb2—O4^{ix}	86.01 (4)
O1^{i}—Rb1—O4^{iv}	165.33 (5)	O2^{vii}—Rb2—O4^{ix}	86.90 (5)
O1^{ii}—Rb1—O4^{iv}	82.87 (5)	O2^{viii}—Rb2—O4^{ix}	101.29 (5)
O1^{iii}—Rb1—O4^{iv}	102.41 (5)	O2^{ix}—Rb2—O4^{ix}	46.55 (5)
O2^{iv}—Rb1—O4^{iv}	46.75 (5)	O4^{iv}—Rb2—O4^{ix}	104.695 (9)
O2^{v}—Rb1—O4^{iv}	131.42 (5)	O4^{vi}—Rb2—O4^{ix}	137.38 (4)
O2^{vi}—Rb1—O4^{iv}	82.92 (5)	O4^{v}—Rb2—O4^{ix}	53.03 (6)
O1^{i}—Rb1—O4^{vi}	82.87 (5)	O4^{vii}—Rb2—O4^{ix}	115.47 (2)
O1^{ii}—Rb1—O4^{vi}	102.41 (5)	O3^{iv}—Rb2—O4^{viii}	157.18 (5)
O1^{iii}—Rb1—O4^{vi}	165.33 (5)	O3^{vi}—Rb2—O4^{viii}	86.01 (4)
O2^{iv}—Rb1—O4^{vi}	131.42 (5)	O3^{v}—Rb2—O4^{viii}	55.94 (4)
O2^{v}—Rb1—O4^{vi}	82.92 (5)	O2^{vii}—Rb2—O4^{viii}	101.29 (5)
O2^{vi}—Rb1—O4^{vi}	46.75 (5)	O2^{viii}—Rb2—O4^{viii}	46.55 (5)
O4^{iv}—Rb1—O4^{vi}	85.47 (6)	O2^{ix}—Rb2—O4^{viii}	86.90 (5)
O1^{i}—Rb1—O4^{v}	102.41 (5)	O4^{iv}—Rb2—O4^{viii}	137.38 (4)
O1^{ii}—Rb1—O4^{v}	165.33 (5)	O4^{vi}—Rb2—O4^{viii}	53.03 (6)
O1^{iii}—Rb1—O4^{v}	82.87 (5)	O4^{v}—Rb2—O4^{viii}	104.695 (9)

O2^{iv}—Rb1—O4^{v}	82.92 (5)	O4^{vii}—Rb2—O4^{viii}	115.47 (2)
O2^{v}—Rb1—O4^{v}	46.75 (5)	O4^{ix}—Rb2—O4^{viii}	115.47 (2)
O2^{vi}—Rb1—O4^{v}	131.42 (5)	O2^{x}—Ti1—O2^{xi}	90.14 (7)
O4^{iv}—Rb1—O4^{v}	85.47 (6)	O2^{x}—Ti1—O2^{xii}	90.14 (7)
O4^{vi}—Rb1—O4^{v}	85.47 (6)	O2^{xi}—Ti1—O2^{xii}	90.14 (7)
O3^{iv}—Rb2—O3^{vi}	101.27 (5)	O2^{x}—Ti1—O1^{xiii}	91.43 (7)
O3^{iv}—Rb2—O3^{v}	101.27 (5)	O2^{xi}—Ti1—O1^{xiii}	88.09 (7)
O3^{vi}—Rb2—O3^{v}	101.27 (5)	O2^{xii}—Ti1—O1^{xiii}	177.64 (7)
O3^{iv}—Rb2—O2^{vii}	99.30 (5)	O2^{x}—Ti1—O1	88.09 (7)
O3^{vi}—Rb2—O2^{vii}	96.75 (5)	O2^{xi}—Ti1—O1	177.64 (7)
O3^{v}—Rb2—O2^{vii}	149.30 (5)	O2^{xii}—Ti1—O1	91.43 (7)
O3^{iv}—Rb2—O2^{viii}	149.30 (5)	O1^{xiii}—Ti1—O1	90.39 (7)
O3^{vi}—Rb2—O2^{viii}	99.30 (5)	O2^{x}—Ti1—O1^{xiv}	177.64 (7)
O3^{v}—Rb2—O2^{viii}	96.75 (5)	O2^{xi}—Ti1—O1^{xiv}	91.43 (7)
O2^{vii}—Rb2—O2^{viii}	55.61 (6)	O2^{xii}—Ti1—O1^{xiv}	88.09 (7)
O3^{iv}—Rb2—O2^{ix}	96.75 (5)	O1^{xiii}—Ti1—O1^{xiv}	90.39 (7)
O3^{vi}—Rb2—O2^{ix}	149.30 (5)	O1—Ti1—O1^{xiv}	90.39 (7)
O3^{v}—Rb2—O2^{ix}	99.30 (5)	O3^{ii}—Ti2—O3^{iii}	91.87 (7)
O2^{vii}—Rb2—O2^{ix}	55.61 (6)	O3^{ii}—Ti2—O3^{i}	91.87 (7)
O2^{viii}—Rb2—O2^{ix}	55.61 (6)	O3^{iii}—Ti2—O3^{i}	91.87 (7)
O3^{iv}—Rb2—O4^{iv}	49.64 (5)	O3^{ii}—Ti2—O4^{xiii}	94.30 (7)
O3^{vi}—Rb2—O4^{iv}	52.65 (5)	O3^{iii}—Ti2—O4^{xiii}	172.63 (8)
O3^{v}—Rb2—O4^{iv}	116.41 (6)	O3^{i}—Ti2—O4^{xiii}	83.90 (7)
O2^{vii}—Rb2—O4^{iv}	94.29 (5)	O3^{ii}—Ti2—O4	83.90 (7)
O2^{viii}—Rb2—O4^{iv}	138.73 (5)	O3^{iii}—Ti2—O4	94.30 (7)
O2^{ix}—Rb2—O4^{iv}	133.42 (5)	O3^{i}—Ti2—O4	172.63 (8)
O3^{iv}—Rb2—O4^{vi}	116.41 (6)	O4^{xiii}—Ti2—O4	90.39 (7)
O3^{vi}—Rb2—O4^{vi}	49.64 (5)	O3^{ii}—Ti2—O4^{xiv}	172.63 (8)
O3^{v}—Rb2—O4^{vi}	52.65 (5)	O3^{iii}—Ti2—O4^{xiv}	83.90 (7)
O2^{vii}—Rb2—O4^{vi}	133.42 (5)	O3^{i}—Ti2—O4^{xiv}	94.30 (7)
O2^{viii}—Rb2—O4^{vi}	94.29 (5)	O4^{xiii}—Ti2—O4^{xiv}	90.39 (7)
O2^{ix}—Rb2—O4^{vi}	138.73 (5)	O4—Ti2—O4^{xiv}	90.39 (7)
O4^{iv}—Rb2—O4^{vi}	87.83 (5)	O3—P1—O2	110.75 (9)
O3^{iv}—Rb2—O4^{v}	52.65 (5)	O3—P1—O4	108.52 (11)
O3^{vi}—Rb2—O4^{v}	116.41 (6)	O2—P1—O4	106.48 (10)
O3^{v}—Rb2—O4^{v}	49.64 (5)	O3—P1—O1	110.87 (9)
O2^{vii}—Rb2—O4^{v}	138.73 (5)	O2—P1—O1	108.74 (10)
O2^{viii}—Rb2—O4^{v}	133.42 (5)	O4—P1—O1	111.40 (10)

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