

Lamellar crystal structure of the trigonal mixed-metal phosphate $\text{RbCoFe}(\text{PO}_4)_2$

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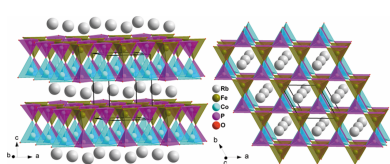
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The title compound, rubidium cobalt iron bis(phosphate), was synthesized by the solid-state method under atmospheric conditions. This phosphate crystallizes with trigonal symmetry in space group $P3m1$ and all atoms lie on special crystallographic positions. In this structure, the $\text{Co}^{\text{II}}\text{O}_4$ tetrahedra alternate with one of the two types of PO_4 tetrahedra, sharing the vertices of their bases and extending along the a - and b -axis directions to form a first tetrahedral layer, lying parallel to the (001) plane. The same alternation is observed between the $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra and the other PO_4 tetrahedra, leading to the formation of a second layer also lying parallel to the (001) plane. In the first layer, all tetrahedra are oriented downwards, while in the second, they are oriented upwards with respect to the c axis. The interconnection between these two layers is ensured by the sharing of the vertices of the CoO_4 and PO_4 tetrahedra, as well as the vertex of the FeO_4 tetrahedra, with those of the other PO_4 tetrahedra. The stacking of these two layers leads to the formation of $[\text{CoFeP}_2\text{O}_8]_\infty$ double layers lying parallel to the (001) plane and creates hexagonal tunnels running parallel to the c -axis direction. The Rb^+ cations are located at the intersection of the tunnels with the interlayer space, thus forming a plane lying perpendicular to the c -axis direction, sandwiched between the double layers. In this structure, each rubidium atom exhibits a coordination number of twelve, whereas in the similar structure of $\text{KMgFe}(\text{PO}_4)_2$, which has monoclinic symmetry, the potassium cation is surrounded by eight oxygen atoms.

1. Chemical context

In solid-state chemistry and materials science, transition-metal (TM) phosphates have been studied extensively, particularly those with open structures. These porous materials are interesting due to their potential industrial and environmental applications, ranging from catalysis to ion exchange and separation (Gier & Stucky, 1991; Maspoch *et al.*, 2007; Lin *et al.*, 2004), electrochemistry (Trad *et al.*, 2010) and magnetism (Ofer *et al.*, 2012; Hadouchi *et al.*, 2019). Among these, iron phosphates are particularly attractive due to their rich crystal chemistry (Moore, 1970; Redrup & Weller, 2009; Lajmi *et al.*, 2009) and variable physical properties (Elbouaanani *et al.*, 2002; Riou-Cavellec *et al.*, 1999). The structural diversity is mainly due to the ability of TM cations to adopt different oxidation states such as $\text{PbMn}^{\text{II}}_2\text{Mn}^{\text{III}}(\text{PO}_4)_3$ (Alhakmi *et al.*, 2013) and coordination geometries, leading to a wide variety of families such as $\text{NaZnAl}(\text{PO}_4)_2$ (Yakubovich, *et al.*, 2019) and $\text{NaCuIn}(\text{PO}_4)_2$ (Benhsina *et al.*, 2020).

Our research team has previously developed and characterized several new phosphates with the general formula $\text{AMM}'(\text{PO}_4)_2$, where A , M , and M' represent alkali or alkaline



earth cations, divalent and trivalent metals, respectively. Most of the compounds were obtained by solid-state reactions and identified by X-ray diffraction. Investigations of these materials reveal the richness and diversity of their structures. The most frequent structural types adopted by these crystals are alluaudite, ABW-zeolite, α -CrPO₄, and others. The following compounds represent an example of each structural type, respectively, Na₂M₂Fe(PO₄)₃ (*M* = Co, Ni) (Bouraima *et al.*, 2015); β -KCoFe(PO₄)₂ (Bouraima *et al.*, 2022); BaNi₂Fe(PO₄)₃ (Ouaatta *et al.*, 2023) and K₃Ni₆Fe(PO₄)₆ (Ouaatta *et al.*, 2019). As part of our ongoing studies in this area, we now describe the synthesis and characterization of the title compound RbCoFe(PO₄)₂ (**I**) (Fig. 1).

2. Structural commentary

In this structure, all atoms occupy special positions of the *P3m1* space group. The asymmetric unit of the new phase consists of one Rb atom in Wyckoff position 1*b* (3*m*), Co1, P2, and O3 atoms in position 1*c* (3*m*), Fe1, P1, and O1 atoms in position 1*a* (3*m*), while O2 and O4 occupy Wyckoff position 3*d* (*m*). However, refining the structure with cobalt in Wyckoff position (1*a*) and iron in (1*c*) leads to inconclusive results. Reversing the positions of Fe in (1*a*) and Co in (1*c*) leads to slightly better results: the Co—O distances (Table 1) are slightly longer than the Fe—O distances, and the bond-valence sums are very close to the expected values. It is also noted that freely refining the occupancies of the Co/Fe sites by a mixture of Co²⁺ and Fe³⁺ leads to unstable refinement, and the refinement diverges. Refining the statistical distribution of the two cations Co²⁺ and Fe³⁺ at the two Wyckoff sites (1*a*) and (1*c*) converged well, with a slight improvement in the values of *R* (0.030) and *R*_w2 (0.077), but with very high standard

Table 1

Selected geometric parameters (Å, °).

Rb1—O2	3.220 (5)	Co1—O2	1.893 (7)
Rb1—O4 ⁱ	3.245 (5)	P1—O2	1.5373 (14)
Fe1—O1 ⁱⁱ	1.844 (9)	P1—O1	1.5398 (15)
Fe1—O4	1.848 (6)	P2—O3	1.500 (9)
Co1—O3 ⁱⁱⁱ	1.870 (13)	P2—O4	1.5374 (14)
P1—O1—Fe1 ^{iv}	180.0	P2—O3—Co1 ^v	180.0
P1—O2—Co1	133.3 (6)	P2—O4—Fe1	137.0 (6)

Symmetry codes: (i) $-y, x - y, z$; (ii) $x, y - 1, z - 1$; (iii) $x, y, z + 1$; (iv) $x, y + 1, z + 1$; (v) $x, y, z - 1$.

deviations in the Co/Fe—O bond lengths. The same results are obtained when refining the structure by fixing different occupancy rates of the two sites by Co²⁺ and Fe³⁺. In light of the preceding analyses, we can conclude that the best model is the one corresponding to Fe³⁺ at (1*a*) and Co²⁺ at (1*c*).

Furthermore, all cations adopt a tetrahedral environment, except for the rubidium ion, which is surrounded by twelve oxygen atoms. The average phosphorus–oxygen bond lengths are 1.538 and 1.528 Å for P1 and P2, respectively. The average bond length for cobalt–oxygen is 1.887 Å, and 1.847 Å for the iron–oxygen distance. The crystal structure is built by two distinct types of sheets lying parallel to the *ab* plane. The CoO₄ tetrahedra alternate with P1O₄ tetrahedra, sharing vertices and extending along both the *a*- and *b*-axis directions to construct a first tetrahedral sheet. All tetrahedra within this layer are oriented upward relative to the *c* axis. These sheets exhibit hexagonal-shaped pores. The same alternation is observed between FeO₄ and P2O₄ tetrahedra, leading to the formation of a second sheet, also encapsulating hexagonal-shaped pores. In this layer, the FeO₄ and P2O₄ tetrahedra are oriented ‘down’ relative to the *c* axis. The interconnection between these two sheets is ensured through vertex-sharing between CoO₄ and P2O₄, and FeO₄ and P1O₄ tetrahedra *via* oxygen atoms (these inter-sheet bonds are constrained to be linear by symmetry). This arrangement leads to a [CoFeP₂O₈][−]_∞ double sheet lying parallel to the *ab* plane. The Rb⁺ cations form a plane sandwiched between the double layers. Each rubidium cation is surrounded by twelve oxygen atoms at the intersection of the tunnels with the interlayer space (Fig. 2).

The reliability of the structural model was validated using bond-valence-sum (BVS; Altermatt & Brown, 1985) and charge-distribution (CHARDI; Nespolo, 2016) methods. The CHARDI and BVS computations were performed with the CHARDI2015 (Nespolo & Guillot, 2016) and EXPO2014 (Altomare *et al.*, 2013) programs, respectively. The resulting parameters derived from both methods are listed in Table 2. The computed values *V*(*i*) (valence) and *Q*(*i*) (cationic charge) reveal excellent agreement between these values and their corresponding weighted oxidation numbers *q*(*i*)-sof(*i*). In accordance with this charge-distribution scheme, the cationic charge ratio *q*(*i*)/*Q*(*i*) $\simeq 1$ for all species, confirming the accuracy of this structural determination (Nespolo *et al.*, 1999). This model is also corroborated by the low of the mean absolute percentage deviation (MAPD = 2.9%), which assesses the agreement between the calculated CHARDI

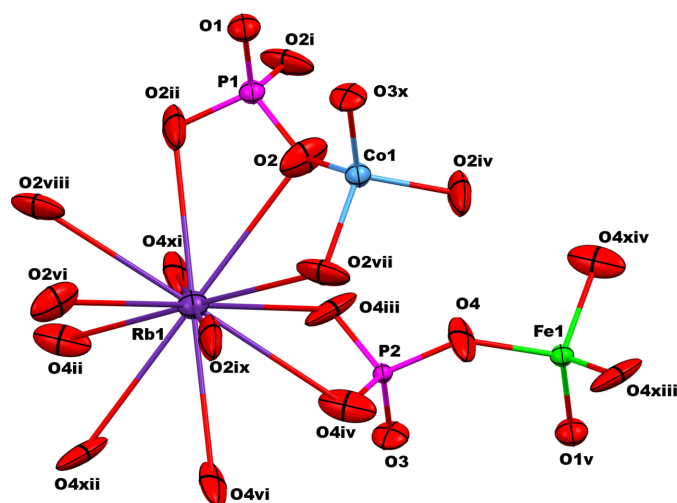


Figure 1

The principal polyhedra constituting the crystal structure of the compound RbCoFe(PO₄)₂, with atomic labels. Displacement ellipsoids are represented at the 50% probability level. Symmetry codes: (i) $-y + 2, x - y + 1, z$; (ii) $-x + y + 1, -x + 2, z$; (iii) $-y + 1, x - y, z$; (iv) $-x + y + 1, -x + 1, z$; (v) $x, y - 1, z - 1$; (vi) $x - 1, y, z$; (vii) $-y + 1, x - y, z$; (viii) $-y + 1, x - y + 1, z$; (ix) $-x + y, -x + 1, z$; (x) $x, y, z + 1$; (xi) $x, y + 1, z$; (xii) $-y, x - y, z$; (xiii) $-y + 1, x - y - 1, z$; (xiv) $-x + y + 2, -x + 1, z$.

Table 2

CHARDI and BVS results for the principal cation species in RbCoFe(PO₄)₂.

$q(i)$ = formal oxidation number; $\text{sof}(i)$ = site occupancy; $\text{CN}(i)$ = classical coordination number; $Q(i)$ = calculated charge; $V(i)$ = calculated valence; $\text{ECoN}(i)$ = effective coordination number.

Cation	$q(i)\text{-sof}(i)$	$\text{CN}(i)$	$\text{ECoN}(i)$	$V(i)$	$Q(i)$	$q(i)/Q(i)$
Rb1	1	12	11.99	0.87	1.00	1.00
Co1	2	4	4.00	2.02	2.00	0.96
Fe1	3	4	4.00	3.17	2.88	1.04
P1	5	4	4.00	4.95	5.17	0.97
P2	5	4	3.98	5.09	4.87	1.03

charges $Q(i)$ and the expected formal ones $q(i)$ (Eon & Nespolo, 2015).

In the crystal structure of RbCoFe(PO₄)₂, the coordination numbers (CN) and effective coordination numbers (ECoN) found for all the cationic sites are entirely consistent with the expected environments. For all crystallographic sites, the CN and ECoN values closely match, indicating well-defined coordination polyhedra, with the exception of the Rb1 atom, which exhibits a very low distortion level. Indeed, the Rb1 site adopts a high coordination number (CN = 12) with an ECoN value of 11.99, reflecting an almost ideal twelvefold coordination environment. This result confirms the existence of weakly directional bonds typical of alkali metal cations, where slight variations in bond lengths have a negligible impact on effective coordination. Both transition-metal sites, Co1 and Fe1, exhibit the same CN and ECoN values (CN = ECoN = 4.00), a feature of regular metal–oxygen bond lengths and consequently well-defined tetrahedral coordination geometries. Similarly, the P1 and P2 sites, each display CN = 4 and ECoN = 4.00, confirming the presence of highly regular PO₄ tetrahedra.

Comparison of BVS results with the nominal valences $V(i)$ confirms that the BVS approach leads to the expected values for the different crystallographic sites in the crystal structure of RbCoFe(PO₄)₂. The global instability index (GII) was also calculated to assess the electrostatic plausibility and the overall stability of the crystal structure (Salinas-Sanchez *et al.*, 1992). The resulting GII value of 0.108 suggests a structurally stable and rigid framework, thereby confirming the reliability of the structural model.

The title compound crystallizes in a non-centrosymmetric space group with a polar axis ($P3m1$), which allows it to be classified among compounds likely to have ferroelectric properties (Abrahams, 2008). The ferroelectric paraelectric phase transition requires a space group change from $P3m1$ to one of its the non-isomorphic supergroups $P\bar{3}m1$, $P\bar{6}m2$, $P6_3mc$, or $P6mm$. Analysis of atomic positions using PLATON (Spek, 2020) shows that the structure could exhibit an approximate/pseudo-inversion symmetry (Marsh, 1994).

3. Database survey

A survey of the Powder Diffraction database (PDF2; version 2023) and of the Inorganic Crystal Structure Database (ICSD; version 5.5.0 from FIZ Karlsruhe) shows that among phosphates of the type $AMM'(\text{PO}_4)_2$ ($A = \text{K}$ or Rb , $M = \text{divalent cation}$ and $M' = \text{trivalent cation}$), to our knowledge only RbCoFe(PO₄)₂ crystallizes in a trigonal symmetry (space group $P3m1$) with $a = 5.4474 \text{ \AA}$ and $c = 8.1547 \text{ \AA}$.

A number of known phosphates show similar unit cells, such as: $\beta\text{-CaZn}_2(\text{PO}_4)_2$ ($a = 5.180 \text{ \AA}$, $c = 7.670 \text{ \AA}$, space group $P3$; Kreidler & Hummel, 1967; Czaya, 1972), $\text{SrMg}_2(\text{PO}_4)_2$ ($a = 5.133 \text{ \AA}$, $c = 8.038 \text{ \AA}$, space group $P3m$; CPDS N 52–1587), and $\text{BaMg}_2(\text{PO}_4)_2$ ($a = 5.236 \text{ \AA}$, $c = 8.201 \text{ \AA}$, space group $P3m$;

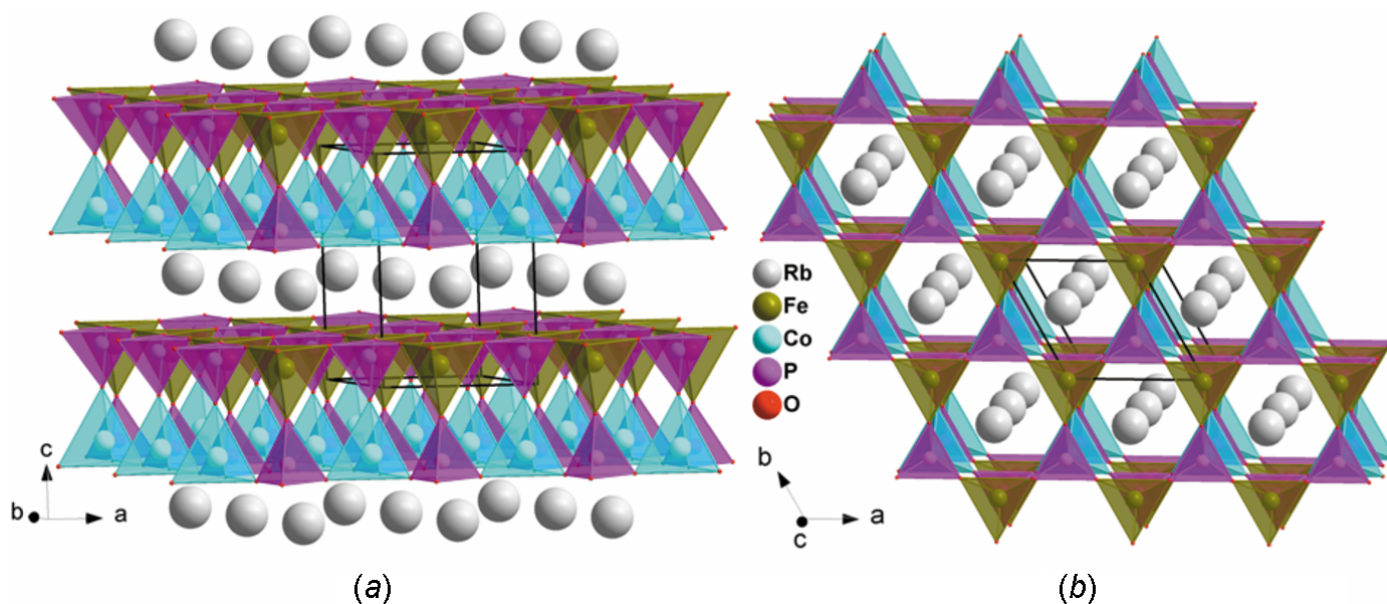


Figure 2

(a) Perspective view of the crystal structure of RbCoFe(PO₄)₂, showing the plane of Rb⁺ ions sandwiched between the double layers of tetrahedra. (b) The Rb⁺ ions are located at the intersection of the channels extending along the [001] direction with the interlayer space.

Table 3
Experimental details.

Crystal data	
Chemical formula	RbCoFe(PO ₄) ₂
M_r	390.19
Crystal system, space group	Trigonal, $P3m1$
Temperature (K)	293
a, c (Å)	5.4474 (2), 8.1547 (3)
V (Å ³)	209.56 (2)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	9.87
Crystal size (mm)	0.25 × 0.21 × 0.14
Data collection	
Diffractometer	Bruker X8 APEX Diffractometer
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}$, $T_{\max}$	0.507, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14543, 945, 844
R_{int}	0.039
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.862
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.079, 1.11
No. of reflections	945
No. of parameters	35
No. of restraints	4
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.30, -0.95
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.50 (7)

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXT2014/4 (Sheldrick, 2015a), SHELXL2019/3 (Sheldrick, 2015b), WinGX (Farrugia, 2012), DIAMOND (Brandenburg, 2006) and publCIF (Westrip, 2010).

JCPDS N 52-1587), space group $P3m1$), β -NaZnPO₄ ($a = 5.101$ Å, $c = 8.365$ Å, space group $P6_3$; JCPDS N 52-0483) and NaBaPO₄ ($a = 5.622$ Å, $c = 7.259$ Å, space group $P3m1$; Calvo & Faggiani, 1975; Launay *et al.*, 1992). Despite these similarities, the structures of these compounds differ from that studied here. In these materials, the polyhedra form rings around the large cations, whereas in the structure of RbCoFe(PO₄)₂, the tetrahedra are ordered and form a double layer surrounding the rubidium plane. It may be noted that this lamellar structure is adopted by $M\text{Fe}(\text{PO}_4)_2$ phosphates ($M = \text{Mg}, \text{Co}, \text{Zn}$ and $A = \text{K}$ or Rb), although the latter crystallize in the monoclinic system, space group $C2/c$.

4. Synthesis and crystallization

The title compound was synthesized by mixing cobalt nitrate [Co(NO₃)₆·6H₂O], iron nitrate [Fe(NO₃)₃·9H₂O], orthophosphoric acid (H₃PO₄) and rubidium carbonate (Rb₂CO₃) in the molar ratio 1:1:1:2. The mixture was placed in a small beaker containing distilled water, stirred for 24 h at room temperature, and subsequently evaporated to dryness. The resulting reaction mixture was heat-treated at 573 K and 773 K before being thoroughly ground in an agate mortar. The resulting solid was then transferred into a platinum crucible and heated to the melting temperature of 1233 K. After holding this temperature for 15 min, the molten product was cooled gradually to 1073 K at a rate of 5 K h⁻¹, and then quickly to room temperature by shutting off the furnace. The

final product comprised purple single crystals of suitable size for X-ray diffraction analysis, corresponding to the title phosphate.

5. Refinement

Crystal data, data collection and structure refinement details are given in Table 3. The crystal structure was refined as an inversion twin using the TWIN/BASF instructions in SHELXL. The refined Flack parameter is 0.50 (7), indicating a near-perfect two-component inversion twin. The largest residual electron-density peak and the deepest hole in the last difference-Fourier map are located 0.53 and 0.17 Å from atoms O2 and O4, respectively.

Acknowledgements

The authors would like to express their sincere gratitude to the Technical and Scientific Research Support Unit (UATRS, CNRST) for the X-ray measurements and to Mohammed V University in Rabat, Morocco, for the financial support.

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supporting information

Acta Cryst. (2026). E82 [https://doi.org/10.1107/S2056989026007632]

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Computing details

Rubidium cobalt iron bis(phosphate)

Crystal data

$\text{RbCoFe}(\text{PO}_4)_2$

$M_r = 390.19$

Trigonal, $P3m1$

$a = 5.4474(2) \text{ \AA}$

$c = 8.1547(3) \text{ \AA}$

$V = 209.56(2) \text{ \AA}^3$

$Z = 1$

$F(000) = 184$

$D_x = 3.092 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 945 reflections

$\theta = 2.5\text{--}37.8^\circ$

$\mu = 9.87 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, purple

$0.25 \times 0.21 \times 0.14 \text{ mm}$

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)

$T_{\min} = 0.507$, $T_{\max} = 0.748$

14543 measured reflections

945 independent reflections

844 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 37.8^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.079$

$S = 1.11$

945 reflections

35 parameters

4 restraints

Primary atom site location: dual

$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 0.4865P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.30 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.95 \text{ e \AA}^{-3}$

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.50 (7)

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.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb1	0.333333	0.666667	0.4375 (7)	0.02836 (19)
Fe1	1.000000	0.000000	0.1327 (6)	0.0167 (6)
Co1	0.666667	0.333333	0.7444 (6)	0.0204 (6)
P1	1.000000	1.000000	0.7177 (5)	0.0198 (11)
P2	0.666667	0.333333	0.1577 (4)	0.0127 (8)
O1	1.000000	1.000000	0.9066 (5)	0.029 (5)
O2	0.8489 (5)	0.6978 (9)	0.6473 (11)	0.052 (4)
O3	0.666667	0.333333	−0.0263 (12)	0.033 (6)
O4	0.8199 (4)	0.1801 (4)	0.2218 (10)	0.055 (4)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0310 (3)	0.0310 (3)	0.0230 (3)	0.01552 (13)	0.000	0.000
Fe1	0.0175 (9)	0.0175 (9)	0.0153 (13)	0.0087 (4)	0.000	0.000
Co1	0.0207 (9)	0.0207 (9)	0.0198 (14)	0.0104 (4)	0.000	0.000
P1	0.0211 (15)	0.0211 (15)	0.017 (2)	0.0106 (7)	0.000	0.000
P2	0.0121 (11)	0.0121 (11)	0.0139 (18)	0.0061 (5)	0.000	0.000
O1	0.033 (7)	0.033 (7)	0.020 (7)	0.016 (4)	0.000	0.000
O2	0.083 (9)	0.018 (5)	0.035 (5)	0.009 (2)	0.0034 (18)	0.007 (4)
O3	0.044 (9)	0.044 (9)	0.011 (5)	0.022 (4)	0.000	0.000
O4	0.099 (10)	0.099 (10)	0.019 (3)	0.088 (10)	−0.0049 (17)	0.0049 (17)

Geometric parameters ($\text{\AA}$, $^\circ$)

Rb1—O2 ⁱ	3.220 (5)	Fe1—O4 ^{xi}	1.848 (6)
Rb1—O2 ⁱⁱ	3.220 (5)	Fe1—O4	1.848 (6)
Rb1—O2 ⁱⁱⁱ	3.220 (5)	Co1—O3 ^{xii}	1.870 (13)
Rb1—O2	3.220 (5)	Co1—O2 ^{vi}	1.893 (7)
Rb1—O2 ^{iv}	3.220 (5)	Co1—O2 ^v	1.893 (7)
Rb1—O2 ^v	3.220 (5)	Co1—O2	1.893 (7)
Rb1—O4 ^{vi}	3.245 (5)	P1—O2	1.5373 (14)
Rb1—O4 ^v	3.245 (5)	P1—O2 ^{xiii}	1.5373 (15)
Rb1—O4 ⁱⁱⁱ	3.245 (5)	P1—O2 ⁱ	1.5373 (14)
Rb1—O4 ^{vii}	3.245 (5)	P1—O1	1.5398 (15)
Rb1—O4 ^{viii}	3.245 (5)	P2—O3	1.500 (9)
Rb1—O4 ⁱ	3.245 (5)	P2—O4	1.5374 (14)
Fe1—O1 ^{ix}	1.844 (9)	P2—O4 ^v	1.5374 (14)
Fe1—O4 ^x	1.848 (6)	P2—O4 ^{vi}	1.5374 (14)
O2 ⁱ —Rb1—O2 ⁱⁱ	55.1 (2)	O4 ^x —Fe1—Rb1 ^{xvi}	52.81 (12)
O2 ⁱ —Rb1—O2 ⁱⁱⁱ	94.4 (2)	O4 ^{xi} —Fe1—Rb1 ^{xvi}	52.81 (12)
O2 ⁱⁱ —Rb1—O2 ⁱⁱⁱ	45.10 (12)	O4—Fe1—Rb1 ^{xvi}	118.5 (2)
O2 ⁱ —Rb1—O2	45.10 (12)	Rb1 ^{xiv} —Fe1—Rb1 ^{xvi}	85.60 (7)
O2 ⁱⁱ —Rb1—O2	94.4 (2)	Rb1 ^{xv} —Fe1—Rb1 ^{xvi}	85.60 (7)

O2 ⁱⁱⁱ —Rb1—O2	115.6 (3)	O3 ^{xii} —Co1—O2 ^{vi}	114.7 (2)
O2 ⁱ —Rb1—O2 ^{iv}	115.6 (3)	O3 ^{xii} —Co1—O2 ^v	114.7 (2)
O2 ⁱⁱ —Rb1—O2 ^{iv}	94.4 (2)	O2 ^{vi} —Co1—O2 ^v	103.7 (3)
O2 ⁱⁱⁱ —Rb1—O2 ^{iv}	55.1 (2)	O3 ^{xii} —Co1—O2	114.7 (2)
O2—Rb1—O2 ^{iv}	94.4 (2)	O2 ^{vi} —Co1—O2	103.7 (3)
O2 ⁱ —Rb1—O2 ^v	94.4 (2)	O2 ^v —Co1—O2	103.7 (3)
O2 ⁱⁱ —Rb1—O2 ^v	115.6 (3)	O3 ^{xii} —Co1—Rb1	128.51 (5)
O2 ⁱⁱⁱ —Rb1—O2 ^v	94.4 (2)	O2 ^{vi} —Co1—Rb1	116.8 (2)
O2—Rb1—O2 ^v	55.1 (2)	O2 ^v —Co1—Rb1	51.99 (12)
O2 ^{iv} —Rb1—O2 ^v	45.10 (12)	O2—Co1—Rb1	51.99 (12)
O2 ⁱ —Rb1—O4 ^{vi}	125.48 (7)	O3 ^{xii} —Co1—Rb1 ^{xv}	128.51 (5)
O2 ⁱⁱ —Rb1—O4 ^{vi}	179.2 (3)	O2 ^{vi} —Co1—Rb1 ^{xv}	51.99 (12)
O2 ⁱⁱⁱ —Rb1—O4 ^{vi}	134.74 (4)	O2 ^v —Co1—Rb1 ^{xv}	51.99 (12)
O2—Rb1—O4 ^{vi}	86.37 (11)	O2—Co1—Rb1 ^{xv}	116.8 (2)
O2 ^{iv} —Rb1—O4 ^{vi}	85.85 (12)	Rb1—Co1—Rb1 ^{xv}	85.33 (7)
O2 ^v —Rb1—O4 ^{vi}	65.15 (8)	O3 ^{xii} —Co1—Rb1 ^{xiv}	128.51 (5)
O2 ⁱ —Rb1—O4 ^v	85.85 (12)	O2 ^{vi} —Co1—Rb1 ^{xiv}	51.99 (12)
O2 ⁱⁱ —Rb1—O4 ^v	134.74 (4)	O2 ^v —Co1—Rb1 ^{xiv}	116.8 (2)
O2 ⁱⁱⁱ —Rb1—O4 ^v	179.2 (3)	O2—Co1—Rb1 ^{xiv}	51.99 (12)
O2—Rb1—O4 ^v	65.15 (8)	Rb1—Co1—Rb1 ^{xiv}	85.33 (7)
O2 ^{iv} —Rb1—O4 ^v	125.48 (7)	Rb1 ^{xv} —Co1—Rb1 ^{xiv}	85.33 (7)
O2 ^v —Rb1—O4 ^v	86.37 (11)	O2—P1—O2 ^{xiii}	106.9 (5)
O4 ^{vi} —Rb1—O4 ^v	45.39 (10)	O2—P1—O2 ⁱ	106.9 (5)
O2 ⁱ —Rb1—O4 ⁱⁱⁱ	179.2 (3)	O2 ^{xiii} —P1—O2 ⁱ	106.9 (5)
O2 ⁱⁱ —Rb1—O4 ⁱⁱⁱ	125.48 (7)	O2—P1—O1	111.9 (4)
O2 ⁱⁱⁱ —Rb1—O4 ⁱⁱⁱ	86.37 (11)	O2 ^{xiii} —P1—O1	111.9 (4)
O2—Rb1—O4 ⁱⁱⁱ	134.74 (4)	O2 ⁱ —P1—O1	111.9 (4)
O2 ^{iv} —Rb1—O4 ⁱⁱⁱ	65.15 (8)	O2—P1—Rb1	53.5 (2)
O2 ^v —Rb1—O4 ⁱⁱⁱ	85.85 (12)	O2 ^{xiii} —P1—Rb1	122.1 (5)
O4 ^{vi} —Rb1—O4 ⁱⁱⁱ	53.9 (2)	O2 ⁱ —P1—Rb1	53.5 (2)
O4 ^v —Rb1—O4 ⁱⁱⁱ	93.4 (2)	O1—P1—Rb1	126.00 (11)
O2 ⁱ —Rb1—O4 ^{vii}	65.15 (8)	O2—P1—Rb1 ^{xvii}	122.1 (5)
O2 ⁱⁱ —Rb1—O4 ^{vii}	86.37 (11)	O2 ^{xiii} —P1—Rb1 ^{xvii}	53.5 (2)
O2 ⁱⁱⁱ —Rb1—O4 ^{vii}	125.48 (7)	O2 ⁱ —P1—Rb1 ^{xvii}	53.5 (2)
O2—Rb1—O4 ^{vii}	85.85 (12)	O1—P1—Rb1 ^{xvii}	126.00 (11)
O2 ^{iv} —Rb1—O4 ^{vii}	179.2 (3)	Rb1—P1—Rb1 ^{xvii}	88.95 (15)
O2 ^v —Rb1—O4 ^{vii}	134.74 (4)	O2—P1—Rb1 ^{xiv}	53.5 (2)
O4 ^{vi} —Rb1—O4 ^{vii}	93.4 (2)	O2 ^{xiii} —P1—Rb1 ^{xiv}	53.5 (2)
O4 ^v —Rb1—O4 ^{vii}	53.9 (2)	O2 ⁱ —P1—Rb1 ^{xiv}	122.1 (5)
O4 ⁱⁱⁱ —Rb1—O4 ^{vii}	114.1 (3)	O1—P1—Rb1 ^{xiv}	126.00 (11)
O2 ⁱ —Rb1—O4 ^{viii}	134.74 (4)	Rb1—P1—Rb1 ^{xiv}	88.95 (15)
O2 ⁱⁱ —Rb1—O4 ^{viii}	85.85 (12)	Rb1 ^{xvii} —P1—Rb1 ^{xiv}	88.95 (15)
O2 ⁱⁱⁱ —Rb1—O4 ^{viii}	65.15 (8)	O3—P2—O4	109.9 (4)
O2—Rb1—O4 ^{viii}	179.2 (3)	O3—P2—O4 ^v	109.9 (4)
O2 ^{iv} —Rb1—O4 ^{viii}	86.37 (11)	O4—P2—O4 ^v	109.1 (4)
O2 ^v —Rb1—O4 ^{viii}	125.48 (7)	O3—P2—O4 ^{vi}	109.9 (4)
O4 ^{vi} —Rb1—O4 ^{viii}	93.4 (2)	O4—P2—O4 ^{vi}	109.1 (4)
O4 ^v —Rb1—O4 ^{viii}	114.1 (3)	O4 ^v —P2—O4 ^{vi}	109.1 (4)

O4 ⁱⁱⁱ —Rb1—O4 ^{viii}	45.39 (10)	O3—P2—Rb1 ^{xiv}	125.96 (9)
O4 ^{vii} —Rb1—O4 ^{viii}	93.4 (2)	O4—P2—Rb1 ^{xiv}	54.5 (2)
O2 ⁱ —Rb1—O4 ⁱ	86.37 (11)	O4 ^v —P2—Rb1 ^{xiv}	54.5 (2)
O2 ⁱⁱ —Rb1—O4 ⁱ	65.15 (8)	O4 ^{vi} —P2—Rb1 ^{xiv}	124.2 (4)
O2 ⁱⁱⁱ —Rb1—O4 ⁱ	85.85 (12)	O3—P2—Rb1 ^{xv}	125.96 (9)
O2—Rb1—O4 ⁱ	125.48 (7)	O4—P2—Rb1 ^{xv}	54.5 (2)
O2 ^{iv} —Rb1—O4 ⁱ	134.74 (4)	O4 ^v —P2—Rb1 ^{xv}	124.2 (4)
O2 ^v —Rb1—O4 ⁱ	179.2 (3)	O4 ^{vi} —P2—Rb1 ^{xv}	54.5 (2)
O4 ^{vi} —Rb1—O4 ⁱ	114.1 (3)	Rb1 ^{xiv} —P2—Rb1 ^{xv}	89.01 (13)
O4 ^v —Rb1—O4 ⁱ	93.4 (2)	O3—P2—Rb1	125.96 (9)
O4 ⁱⁱⁱ —Rb1—O4 ⁱ	93.4 (2)	O4—P2—Rb1	124.2 (4)
O4 ^{vii} —Rb1—O4 ⁱ	45.39 (10)	O4 ^v —P2—Rb1	54.5 (2)
O4 ^{viii} —Rb1—O4 ⁱ	53.9 (2)	O4 ^{vi} —P2—Rb1	54.5 (2)
O1 ^{ix} —Fe1—O4 ^x	113.1 (2)	Rb1 ^{xiv} —P2—Rb1	89.01 (13)
O1 ^{ix} —Fe1—O4 ^{xi}	113.1 (2)	Rb1 ^{xv} —P2—Rb1	89.01 (13)
O4 ^x —Fe1—O4 ^{xi}	105.6 (3)	P1—O1—Fe1 ^{xviii}	180.0
O1 ^{ix} —Fe1—O4	113.1 (2)	P1—O2—Co1	133.3 (6)
O4 ^x —Fe1—O4	105.6 (3)	P1—O2—Rb1	103.9 (3)
O4 ^{xi} —Fe1—O4	105.6 (3)	Co1—O2—Rb1	100.42 (9)
O1 ^{ix} —Fe1—Rb1 ^{xiv}	128.32 (5)	P1—O2—Rb1 ^{xiv}	103.9 (3)
O4 ^x —Fe1—Rb1 ^{xiv}	52.81 (12)	Co1—O2—Rb1 ^{xiv}	100.42 (9)
O4 ^{xi} —Fe1—Rb1 ^{xiv}	118.5 (2)	Rb1—O2—Rb1 ^{xiv}	115.6 (3)
O4—Fe1—Rb1 ^{xiv}	52.81 (12)	P2—O3—Co1 ^{xix}	180.0
O1 ^{ix} —Fe1—Rb1 ^{xv}	128.32 (5)	P2—O4—Fe1	137.0 (6)
O4 ^x —Fe1—Rb1 ^{xv}	118.5 (2)	P2—O4—Rb1 ^{xiv}	102.8 (2)
O4 ^{xi} —Fe1—Rb1 ^{xv}	52.81 (12)	Fe1—O4—Rb1 ^{xiv}	100.21 (8)
O4—Fe1—Rb1 ^{xv}	52.81 (12)	P2—O4—Rb1 ^{xv}	102.8 (2)
Rb1 ^{xiv} —Fe1—Rb1 ^{xv}	85.60 (7)	Fe1—O4—Rb1 ^{xv}	100.21 (8)
O1 ^{ix} —Fe1—Rb1 ^{xvi}	128.32 (5)	Rb1 ^{xiv} —O4—Rb1 ^{xv}	114.1 (3)

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