Mixed-metal phosphates $K_{1.64}Na_{0.36}TiFe(PO_4)_3$ and $K_{0.97}Na_{1.03}Ti_{1.26}Fe_{0.74}(PO_4)_3$ with a langbeinite framework

Igor V. Zatovsky, a* Nataliia Yu. Strutynska, b Ivan V. Ogorodnyk, c Vyacheslav N. Baumer, d Nickolai S. Slobodyanik, b and Denis S. Butenko, f

a F.D. Ovcharenko Institute of Biocolloidal Chemistry, NAS Ukraine, 42 Acad. Vernadskoho blv., 03142 Kyiv, Ukraine,
b Department of Inorganic Chemistry, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., 01601 Kyiv, Ukraine,
c ShimUkraine LLC 18, Chigirina Str., office 429, 01042 Kyiv, Ukraine,
d STC “Institute for Single Crystals”, NAS of Ukraine, 60 Lenin ave., 61001 Kharkiv, Ukraine,
e Shenzhen Key Laboratory of Solid State Batteries, Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen 518055, People’s Republic of China,
f Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen 518055, People’s Republic of China. *Correspondence e-mail: zvigo@ukr.net

Single crystals of the langbeinite-type phosphates $K_{1.65}Na_{0.35}TiFe(PO_4)_3$ and $K_{0.97}Na_{1.03}Ti_{1.26}Fe_{0.74}(PO_4)_3$ were grown by crystallization from high-temperature self-fluxes in the system Na$_2$O–K$_2$O–P$_2$O$_5$–TiO$_2$–Fe$_2$O$_3$ using fixed molar ratios of (Na+K):P = 1.0, Ti:P = 0.20 and Na:K = 1.0 or 2.0 over the temperature range 1273–953 K. The three-dimensional framework of the two isotypic phosphates are built up from [(Ti/Fe)2(PO$_4$)$_3$] structure units containing two mixed [(Ti/Fe)O$_6$] octahedra (site symmetry 3) connected via three bridging PO$_4$ tetrahedra. The potassium and sodium cations share two different sites in the structure that are located in the cavities of the framework. One of these sites has nine and the other twelve surrounding O atoms.

1. Chemical context

Over the last decade, numerous research efforts have been directed towards the creation of new phosphate materials for Li- or Na-ion batteries (Nose et al., 2013; Zhang et al., 2021). In particular, significant progress has been made for complex phosphates with general formula $M^{I+}X_2(PO_4)_3$ ($M^{I} = Li, Na$; $X = polyvalent metals; x$ values can range from 0 to 3; Zatovsky et al., 2016) adopting NASICON-type structures. The composition of phosphates with a langbeinite-type structure is very similar to the composition of NASICON-type ones, and langbeinite-type phosphates are also considered to be potential hosts for new electrode materials (Luo et al., 2019). However, langbeinite-type phosphates with a composition $M^{I+}X_2(PO_4)_3$ (x = 0–1) can only be prepared with large monovalent cations (e.g., K, Rb, Cs, NH$_4$; Norberg, 2002; Ogorodnyk et al., 2007a). The langbeinite-type structure has only been reported for Na$_2Z^{III}$(PO$_4$)$_3$ ($Z^{III} = Cr, Fe$; Isasi & Daidouh, 2000). More recently, a good prospect for using such kinds of materials as anodes for Na-ion batteries has been predicted because of the recently reported migration mechanisms in langbeinite-type Na$_2$CrTi(PO$_4$)$_3$, determined by atomic simulation (Luo et al., 2019). However, according to Wang et al. (2019), the phosphate Na$_2$CrTi(PO$_4$)$_3$ belongs to the family of compounds with a NASICON-type structure. Therefore, the issue of preparing Na-containing langbeinite-type phosphates requires further research and development.
In recent years, the synthesis of K/Na-containing complex phosphates has been realized using the self-flux method and resulted in the compounds $K_{1.75}Na_{0.25}Ti_2(PO_4)_3$ (Zatovskiy et al., 2018) and $K_{0.877}Na_{0.48}Ti_2(PO_4)_3$ (Strutynska et al., 2016). Here, we report the preparation, structure analysis and characterization of two new mixed-metal phosphates $K_{1.65}Na_{0.35}TiFe(PO_4)_3$ and $K_{0.97}Na_{1.03}Ti_{1.26}Fe_{0.74}(PO_4)_3$ (II), which are isotypic with the mineral langbeinite, $K_2Mg_2(SO_4)_3$ (Zemann & Zemann, 1957; Mereiter, 1979).

2. Structural commentary

As it is illustrated in Fig. 1, two pairs of mixed sites occupied by alkali metals (K/Na) and transition metals (Ti/Fe) are located on threefold rotation axes (Wyckoff position 4 $a$), whereas the P and all O atoms occupy general sites (12 $b$). In the structures, the main structural element for building of the three-dimensional framework is a $[(Ti/Fe)_{2}(PO_4)_3]$ fragment consisting of two mixed-metal $[(Ti/Fe)O_9]$ octahedra and three PO$_4$ tetrahedra (Fig. 2a). Such building units run in three orthogonal directions along the cubic space diagonals (Fig. 2b), which is typical for the langbeinite-related family of compounds (sulfates, phosphates, vanadates etc, Ogorodnyk et al., 2007a).

Two octahedrally coordinated sites (Ti1/Fe1) and (Ti2/Fe2) show mixed occupancy with an Fe:Ti ratio close to 1:1. For (I), the Ti occupancy is 0.48 (3) for the M1 site, while for the M2 site it is 0.52 (3); for (II), the Ti occupancy is 0.61 (2) for the M1 site and 0.65 (2) for the M2 site. In the case of (I), this corresponds to Fe$^{3+}$ and Ti$^{4+}$ cations, while for (II), the simultaneous presence of Fe$^{3+}$, Ti$^{3+}$ and Ti$^{4+}$ is suggested. The prepared crystals of (II) are violet in color and the Ti$^{3+}$:Ti$^{4+}$ ratio is about 1:4 taking into account the total charge of the cationic part of the compound. Partial self-reduction of Ti$^{4+}$ to Ti$^{3+}$ often accompanies the synthesis of langbeinite-type complex phosphates in fluxes of multicomponent systems when various trivalent or divalent metals are present (Gustafsson et al., 2005; Zatovskii et al., 2006). For structures (I) and (II), the [Ti/FeO$_6$] octahedra are slightly distorted (Tables 1 and 2). The range of M—O bond lengths [1.938 (2) – 1.976 (3) Å] is close to those in other langbeinite-related phosphates containing Ti and transition metals, such as $K_2FeO_3Ti_{1.5}(PO_4)_3$ [1.940 (2)–1.992 (2) Å]; $K_2NiO_3Ti_{1.5}(PO_4)_3$ [1.938 (5)–1.962 (5) Å]; $K_2CoO_3Ti_{1.5}(PO_4)_3$ [1.945 (2)–1.974 (2) Å]; $K_2MnO_3Ti_{1.5}(PO_4)_3$ [1.961 (2)–2.002 (2) Å] (Ogorodnyk et al., 2008, 2007b, 2006). The P—O distances for both structures are in the narrow ranges of 1.516 (4)–1.523 (3) Å for (I) and 1.517 (3)–1.523 (2) Å for (II).

There are two sites where the alkali metal cations reside (Fig. 1). The first one, (K/Na)1 is occupied by K$^+$ and Na$^+$ cations at ratios of 0.85 (2):0.15 (2) and 0.676 (18):0.324 (18) for (I) and (II), respectively. The [(K/Na)$_1$(PO$_4$)$_3$] polyhedra show three sets of (K/Na)—O distances assuming a cut-off value for the contact lengths of 3.129 (4) Å; the bond lengths are similar for both structures (Tables 1 and 2). The coordination environment of the alkali cations related to the (K/Na)2 site consists of twelve O-atom neighbours with (K/Na)$_2$—O distances ranging from 2.843 (3) to 3.237 (3) Å, which includes four sets of distances (Tables 1 and 2). For this site, the K/Na ratios are 0.80 (3):0.20 (3) for (I) and 0.294 (19):0.706 (19) for (II). An interesting fact is that the substitution of potassium by sodium in the position (K/Na)2 is greater for (II) than for (I), but the (K/Na)$_2$—O distances change insignificantly.

Table 1

| Bond | Length (Å) |
|------|------------|
| Fe1—O2 | 1.954 (3) |
| Fe1—O1 | 1.976 (3) |
| Fe2—O2$^a$ | 1.938 (3) |
| Fe2—O4$^a$ | 1.970 (3) |
| K1—O1$^a$ | 2.830 (4) |
| K1—O2$^a$ | 3.129 (4) |
| K2—O3$^a$ | 2.854 (4) |

Symmetry codes: (i) $-z, x-\frac{1}{2}, -y+\frac{1}{2}$; (ii) $y+\frac{1}{2}, -z+\frac{1}{2}, x+\frac{1}{2}$; (iii) $z, x, y$; (iv) $-z, z-\frac{1}{2}, y+\frac{1}{2}$; (v) $z+\frac{1}{2}, -x+\frac{1}{2}, y-\frac{1}{2}$; (vi) $x, -y+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $y+\frac{1}{2}, z-\frac{1}{2}, -x+\frac{1}{2}$; (viii) $-z-\frac{1}{2}, x-\frac{1}{2}, y-\frac{1}{2}$.

Table 2

| Bond | Length (Å) |
|------|------------|
| Fe1—O2 | 1.940 (2) |
| Fe1—O1 | 1.974 (2) |
| Fe2—O3$^a$ | 1.938 (2) |
| Fe2—O4 | 1.954 (2) |
| K1—O1$^a$ | 2.820 (3) |
| K1—O4$^a$ | 3.122 (4) |
| K2—O3$^a$ | 2.843 (4) |

Symmetry codes: (i) $-z, x-\frac{1}{2}, -y+\frac{1}{2}$; (ii) $-z+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $z+z+\frac{1}{2}, -x+y+\frac{1}{2}$; (iv) $y+\frac{1}{2}, -z+\frac{1}{2}, -y+\frac{1}{2}$; (v) $z+\frac{1}{2}, -x+\frac{1}{2}, y+\frac{1}{2}$; (vi) $-z+\frac{1}{2}, x-\frac{1}{2}, y-\frac{1}{2}$; (vii) $-z+\frac{1}{2}, x-\frac{1}{2}, y-\frac{1}{2}$.
3. Synthesis and crystallization

Phosphates (I) and (II) were obtained from the melts of the system Na₂O–K₂O–P₂O₅–TiO₂–Fe₂O₃ at fixed molar ratios of (Na+K)/P = 1.0, Ti/P = 0.20 and different values of Na/K = 1.0 or 2.0 over the temperature range 1273–953 K. All initial components \( M'H₂PO₄ \) (\( M' = \text{Na, K} \)), Fe₂O₃ and TiO₂ were of an analytical grade.

A mixture of KH₂PO₄ (10 g), NaH₂PO₄ (8.82 g), Fe₂O₃ (2.35 g) and TiO₂ (2.35 g) was used for the preparation of (I), while a mixture of KH₂PO₄ (10 g), NaH₂PO₄ (17.64 g), Fe₂O₃ (3.53 g) and TiO₂ (3.53 g) was used for the preparation of (II). In both cases, the mixtures of calculated amounts of starting components were ground in an agate mortar and melted in a platinum crucible at 1273 K. The obtained melts were kept under isothermal conditions for 2 h for dissolving of the corresponding TiO₂ + Fe₂O₃ mixture in the phosphate melt. Then the temperature was decreased with a rate of 25 K h⁻¹ to 953 K and kept at this temperature for 2 h before cooling down to room temperature by turning off the furnace power. The obtained crystalline phases were separated from soluble salts by leaching with hot water and dried at 373 K.

The molar ratio Na/K in the initial melts had an influence on the composition of the obtained crystals. Light-yellow crystals formed in the melt with a ratio of Na:K = 1.0 while violet crystals were obtained for a ratio Na:K = 2.0 (Fig. 3). It should be noted that increasing the amount of sodium in the initial melts to a ratio Na/K = 2.0 caused the growth of crystals with sizes of 2–3 mm (Fig. 3b) in length.

The chemical compositions of the prepared samples (quantitative determination of K, Na, Ti, Fe and P) were confirmed by ICP–AES with a Shimadzu ICPE-9820 spectrometer. The analyses showed that the molar ratios of K:Na:Ti:Fe:P were close to 1.65:0.35:1:1:3 for (I) and 1:1:1.25:0.75:3 for (II).

The phosphates (I) and (II) were further characterized using Fourier transform infrared (FTIR) spectroscopy. The spectra were obtained using a PerkinElmer Spectrum BX spectrometer in the range 4000–400 cm⁻¹ (at 4 cm⁻¹ resolution) with sample material pressed into KBr pellets. The FTIR spectra for both compounds are similar in band positions of vibration modes (Fig. 4). The broad and intense bands in the frequency region 1150–900 cm⁻¹ are characteristic for P=O stretching vibrations [\( \nu_{as}(PO₄) \) – region 1150–1090 cm⁻¹ and \( \nu_{s}(PO₄) \) – region 1020–900 cm⁻¹] of the PO₄ tetrahedron. The band group at 650–550 cm⁻¹ is caused by bending δ(P=O) vibrations of P=O bonds. Some differences in the spectra were observed in the range 500–400 cm⁻¹, which are due to X–O (X = Ti, Fe) vibrations and correlate with insignificant differences in the composition of the prepared compounds (I) and (II).

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. According to the results of the chemical analysis, large quantities of Na and Ti are present in the structures. Taking into account possible coordination spheres of Na and Ti and previously reported langbeinite-type phosphates with a mixed-metal framework, we supposed that Ti occupies the same sites as Fe, and Na the same positions as K. Hence, the corresponding positions of Fe1 and Fe2, K1 and K2 were occupied with Ti and Na, respectively. As the Fe(Ti) positions are part of the rigid framework, we assumed that these sites show full occupancy, while the sites related with the alkali metal can be fully or partially occupied. At a first approach, the occupancies were refined using linear combinations of free variables (SUMP restraint). Two SUMP restraints were applied to occupancies of Fe1(Ti1) and Fe2(Ti2) sites. One more SUMP restraint was then applied to the sum of valence units of all metal-atom positions. This refinement resulted in satisfactory reliability factors. It was found that the occupancies of K1(Na1) and K2(Na2) are close to 1. Thus, to simplify the refinement we tried to refine the occupancies with free variable constraints instead of SUMP restraints while keeping the alkali metal site occupancies equal to 1. To each refined position, a unique free variable constraint was applied, plus constrained identical coordinates and ADPs for each site. The resulting reliability factors were lower.
found to be almost equal to those where the SUMP restraints were used. For the final refinement cycles, the second approach was applied to both structures.

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References
Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). J. Appl. Cryst. 37, 335–338.
Blessing, R. H. (1995). Acta Cryst. A51, 33–38.
Brandenburg, K. (2006). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.
Gustafsson, J. C. M., Norberg, S. T., Svensson, G. & Albertsson, J. (2005). Acta Cryst. C61, i9–i13.
Isasi, J. & Daidouh, A. (2000). Solid State Ionics, 133, 303–313.
Luo, Y., Sun, T., Shui, M. & Shu, J. (2019). Mater. Chem. Phys. 233, 339–345.
Mereiter, K. (1979). N. Jb. Mineral. Monatsh. pp. 182–188.
Norberg, S. T. (2002). Acta Cryst. B58, 743–749.
Nose, M., Nakayama, H., Nobuhara, K., Yamaguchi, H., Nakashima, S. & Iba, H. (2013). J. Power Sources, 234, 175–179.
Ogorodnyk, I. V., Baumer, V. N., Zatovsky, I. V., Slobodyanik, N. S., Shishkin, O. V. & Domasevitch, K. V. (2007a). Acta Cryst. B63, 819–827.
Ogorodnyk, I. V., Zatovsky, I. V., Baumer, V. N., Slobodyanik, N. S., Shishkin, O. V. & Vorona, I. P. (2008). Z. Naturforsch. Teil B, 63, 261–266.
Ogorodnyk, I. V., Zatovsky, I. V. & Slobodyanik, N. S. (2007b). Russ. J. Inorg. Chem. 52, 121–125.
Ogorodnyk, I. V., Zatovsky, I. V., Slobodyanik, N. S., Baumer, V. N. & Shishkin, O. V. (2006). J. Solid State Chem. 179, 3461–3466.
Oxford Diffraction (2006). CrysAlis CCD and CrysAlis RED. Oxford Diffraction Ltd, Abingdon, England.
Parsons, S., Flack, H. D. & Wagner, T. (2013). Acta Cryst. B69, 249–259.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.
Strutynska, N., Bondarenko, M., Slobodyanik, N., Baumer, V., Zatovsky, I., Bychkov, K. & Puzan, A. (2016). Cryst. Res. Technol. 51, 627–633.
Wang, D., Wei, Z., Lin, Y., Chen, N., Gao, Y., Chen, G., Song, L. & Fu, J. (2019). J. Mater. Chem. A, 7, 20604–20613.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920–925.
Zatovskii, I. V., Slobodyanik, N. S., Ushchapivskaya, T. I., Ogorodnik, I. V. & Babarik, A. A. (2006). Russ. J. Appl. Chem. 79, 10–15.
Zatovsky, I. V., Strutynska, N. Yu., Hizhnyi, Y. A., Nedilko, S. G., Slobodyanik, N. S. & Klyui, N. I. (2018). ChemistryOpen, 7, 504–512.
Zatovsky, I. V., Strutynska, N. Yu., Ogorodnik, I. V., Baumer, V. N., Slobodyanik, N. S., Yatskin, M. M. & Odynets, I. V. (2016). Struct. Chem. 27, 323–330.
Zemann, A. & Zemann, J. (1957). Acta Cryst. 10, 409–413.
Zhang, B., Ma, K., Lv, X., Shi, K., Wang, Y., Nian, Z., Li, Y., Wang, L., Dai, L. & He, Z. (2021). J. Alloys Compd. 867, 159060.
Mixed-metal phosphates $K_{1.64}Na_{0.36}TiFe(PO_4)_3$ and $K_{0.97}Na_{1.03}Ti_{1.26}Fe_{0.74}(PO_4)_3$ with a langbeinite framework

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Computing details

For both structures, 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: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: WinGX (Farrugia, 2012), enCIFer (Allen et al., 2004) and publCIF (Westrip, 2010).

Potassium sodium titanium iron tris(phosphate) (I)

Crystal data

$D_x = 3.235$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1897 reflections

$\theta = 2.9$–29.0°
$\mu = 3.69$ mm$^{-1}$
$T = 293$ K
Tetrahedron, light yellow
0.13 × 0.10 × 0.07 mm

Data collection

Oxford Diffraction Xcalibur-3
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
(Blessing, 1995)

$T_{\text{min}} = 0.675$, $T_{\text{max}} = 0.782$
1897 measured reflections

Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.14$
847 reflections
63 parameters
0 restraints

$\omega = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.5767P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta \rho_{\text{max}} = 0.48$ e Å$^{-3}$
$\Delta \rho_{\text{min}} = -0.37$ e Å$^{-3}$

Extinction correction: SHELXL-2018/3 (Sheldrick 2015)
Extinction coefficient: 0.0042 (16)
Absolute structure: Flack $x$ determined using 339 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.02

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 (Å²)

|       | $x$     | $y$     | $z$     | $U_{iso}$/*$U_{eq}$ | Occ. (<1) |
|-------|---------|---------|---------|---------------------|-----------|
| Fe1   | 0.14303 (6) | 0.14303 (6) | 0.14303 (6) | 0.0085 (3)          | 0.52 (3)  |
| Ti1   | 0.14303 (6) | 0.14303 (6) | 0.14303 (6) | 0.0085 (3)          | 0.48 (3)  |
| Fe2   | 0.41389 (6) | 0.41389 (6) | 0.41389 (6) | 0.0087 (3)          | 0.48 (3)  |
| Ti2   | 0.41389 (6) | 0.41389 (6) | 0.41389 (6) | 0.0087 (3)          | 0.52 (3)  |
| K1    | 0.70712 (13) | 0.70712 (13) | 0.70712 (13) | 0.0254 (7)          | 0.85 (2)  |
| Na1   | 0.70712 (13) | 0.70712 (13) | 0.70712 (13) | 0.0254 (7)          | 0.15 (2)  |
| K2    | 0.93216 (12) | 0.93216 (12) | 0.93216 (12) | 0.0228 (8)          | 0.80 (3)  |
| Na2   | 0.93216 (12) | 0.93216 (12) | 0.93216 (12) | 0.0228 (8)          | 0.20 (3)  |
| P3    | 0.45810 (10) | 0.22783 (10) | 0.12639 (11) | 0.0089 (3)          |           |
| O1    | 0.3106 (3)   | 0.2345 (3)   | 0.0792 (3)   | 0.0181 (7)          |           |
| O2    | 0.5477 (4)   | 0.2988 (4)   | 0.0217 (3)   | 0.0214 (8)          |           |
| O3    | 0.5021 (3)   | 0.0809 (3)   | 0.1494 (4)   | 0.0207 (7)          |           |
| O4    | 0.4787 (4)   | 0.3041 (4)   | 0.2590 (4)   | 0.0254 (9)          |           |

Atomic displacement parameters (Å²)

|       | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| Fe1   | 0.0085 (3) | 0.0085 (3) | 0.0085 (3) | −0.0002 (2) | −0.0002 (2) | −0.0002 (2) |
| Ti1   | 0.0085 (3) | 0.0085 (3) | 0.0085 (3) | −0.0002 (2) | −0.0002 (2) | −0.0002 (2) |
| Fe2   | 0.0087 (3) | 0.0087 (3) | 0.0087 (3) | −0.0005 (2) | −0.0005 (2) | −0.0005 (2) |
| Ti2   | 0.0087 (3) | 0.0087 (3) | 0.0087 (3) | −0.0005 (2) | −0.0005 (2) | −0.0005 (2) |
| K1    | 0.0254 (7) | 0.0254 (7) | 0.0254 (7) | 0.0004 (5)  | 0.0004 (5)  | 0.0004 (5)  |
| Na1   | 0.0254 (7) | 0.0254 (7) | 0.0254 (7) | 0.0004 (5)  | 0.0004 (5)  | 0.0004 (5)  |
| K2    | 0.0228 (8) | 0.0228 (8) | 0.0228 (8) | −0.0021 (4) | −0.0021 (4) | −0.0021 (4) |
| Na2   | 0.0228 (8) | 0.0228 (8) | 0.0228 (8) | −0.0021 (4) | −0.0021 (4) | −0.0021 (4) |
| P3    | 0.0078 (5) | 0.0098 (5) | 0.0090 (5) | −0.0003 (3) | 0.0014 (4)  | 0.0001 (4)  |
| O1    | 0.0103 (14) | 0.0218 (16) | 0.0222 (17) | −0.0032 (12) | −0.0019 (12) | 0.0080 (14) |
| O2    | 0.0190 (17) | 0.0273 (17) | 0.0178 (16) | 0.0001 (14)  | 0.0060 (14)  | 0.0096 (14)  |
| O3    | 0.0225 (16) | 0.0123 (14) | 0.0273 (17) | 0.0070 (13)  | 0.0027 (14)  | 0.0027 (14)  |
| O4    | 0.0278 (19) | 0.029 (2)   | 0.0190 (17) | −0.0027 (15) | 0.0019 (15)  | −0.0148 (15) |

Geometric parameters (Å, º)

|       | $d$     | $\theta$ |
|-------|---------|----------|
| Fe1—O2$^i$ | 1.954 (3) | 3.019 (4) |
| Fe1—O2$^{ii}$ | 1.954 (3) | 3.129 (4) |

Acta Cryst. (2021). E77, 1299-1302
Fe1—O2\textsuperscript{iii} 1.954 (3) K1—O4\textsuperscript{viii} 3.129 (4)
Fe1—O1 1.976 (3) K1—O4\textsuperscript{vii} 3.129 (4)
Fe1—O1\textsuperscript{iv} 1.976 (3) K1—P3\textsuperscript{v} 3.4416 (16)
Fe1—O1\textsuperscript{v} 1.976 (3) K1—P3\textsuperscript{viii} 3.4416 (16)
Fe1—K2\textsuperscript{vi} 3.587 (2) K1—P3\textsuperscript{vii} 3.4416 (16)
Fe1—K1\textsuperscript{vii} 3.7927 (9) K2—O3\textsuperscript{xvi} 2.854 (4)
Fe1—K1\textsuperscript{viii} 3.7927 (9) K2—O3\textsuperscript{xvii} 2.854 (4)
Fe1—K1\textsuperscript{ix} 3.7927 (9) K2—O3\textsuperscript{xviii} 2.854 (4)
Fe2—O3\textsuperscript{x} 1.938 (3) K2—O2\textsuperscript{xx} 2.911 (4)
Fe2—O3\textsuperscript{xi} 1.938 (3) K2—O2\textsuperscript{xxi} 2.911 (4)
Fe2—O3\textsuperscript{xii} 1.938 (3) K2—O2\textsuperscript{xxii} 2.911 (4)
Fe2—O4\textsuperscript{v} 1.970 (3) K2—O4\textsuperscript{vii} 3.007 (4)
Fe2—O4\textsuperscript{iv} 1.970 (3) K2—O4\textsuperscript{viii} 3.007 (4)
Fe2—O4 1.970 (3) K2—O4\textsuperscript{ix} 3.007 (4)
Fe2—O4\textsuperscript{iv} 1.970 (3) K2—O4\textsuperscript{x} 3.007 (4)
Fe2—O4 1.970 (3) K2—O4\textsuperscript{xi} 3.007 (4)
Fe2—K2\textsuperscript{xiii} 3.7237 (7) K2—O2\textsuperscript{xiv} 2.911 (4)
Fe2—K2\textsuperscript{xiv} 3.7237 (7) K2—O2\textsuperscript{xv} 2.911 (4)
Fe2—K2\textsuperscript{xv} 3.7237 (7) K2—O2\textsuperscript{xvi} 2.911 (4)
K1—O1\textsuperscript{xii} 2.830 (4) P3—O4 1.516 (4)
K1—O1\textsuperscript{x} 2.830 (4) P3—O2 1.522 (3)
K1—O1\textsuperscript{xi} 2.830 (4) P3—O3 1.523 (3)
K1—O1\textsuperscript{x} 2.830 (4) P3—O1 1.523 (3)

O2—Fe1—O2\textsuperscript{ii} 89.19 (16) O4\textsuperscript{viii}—K1—P3\textsuperscript{viii} 69.72 (7)
O2—Fe1—O2\textsuperscript{iii} 89.19 (16) O4\textsuperscript{vii}—K1—P3\textsuperscript{viii} 103.33 (10)
O2—Fe1—O2\textsuperscript{iv} 89.19 (16) O4\textsuperscript{viii}—K1—P3\textsuperscript{viii} 26.12 (7)
O2—Fe1—O1 177.99 (16) P3\textsuperscript{v}—K1—P3\textsuperscript{viii} 94.91 (5)
O2—Fe1—O1 88.89 (15) O1\textsuperscript{x}—K1—P3\textsuperscript{vii} 94.57 (7)
O2—Fe1—O2 90.18 (14) O1\textsuperscript{x}—K1—P3\textsuperscript{vii} 79.17 (7)
O2—Fe1—O1\textsuperscript{v} 88.88 (15) O2\textsuperscript{xvi}—K1—P3\textsuperscript{viii} 169.22 (7)
O2—Fe1—O1\textsuperscript{iv} 90.18 (14) O2\textsuperscript{xvi}—K1—P3\textsuperscript{viii} 108.29 (8)
O2—Fe1—O1\textsuperscript{v} 177.99 (16) O2\textsuperscript{xvi}—K1—P3\textsuperscript{viii} 26.23 (6)
O1—Fe1—O1\textsuperscript{iv} 91.72 (14) O2\textsuperscript{xii}—K1—P3\textsuperscript{viii} 115.08 (8)
O2—Fe1—O1\textsuperscript{x} 90.18 (14) O4\textsuperscript{viii}—K1—P3\textsuperscript{viii} 103.33 (10)
O2—Fe1—O1\textsuperscript{v} 177.99 (16) O4\textsuperscript{viii}—K1—P3\textsuperscript{viii} 26.12 (7)
O1—Fe1—O1\textsuperscript{v} 88.88 (15) O4\textsuperscript{viii}—K1—P3\textsuperscript{viii} 69.72 (7)
O1—Fe1—O1\textsuperscript{iv} 91.71 (14) P3\textsuperscript{v}—K1—P3\textsuperscript{viii} 94.91 (5)
O1—Fe1—O1\textsuperscript{v} 91.72 (14) P3\textsuperscript{v}—K1—P3\textsuperscript{viii} 94.91 (5)
O2—Fe1—K2\textsuperscript{vi} 54.17 (11) O3\textsuperscript{v}—K2—O3\textsuperscript{viii} 100.76 (10)
O2—Fe1—K2\textsuperscript{vi} 54.17 (11) O3\textsuperscript{v}—K2—O3\textsuperscript{viii} 100.76 (10)
O2—Fe1—K2\textsuperscript{vi} 54.17 (11) O3\textsuperscript{v}—K2—O3\textsuperscript{viii} 100.76 (10)
O1—Fe1—K2\textsuperscript{vi} 124.04 (10) O3\textsuperscript{v}—K2—O2\textsuperscript{ix} 100.42 (10)
O1—Fe1—K2\textsuperscript{vi} 124.04 (10) O3\textsuperscript{v}—K2—O2\textsuperscript{ix} 100.42 (10)
O2—Fe1—K1\textsuperscript{viii} 52.19 (11) O3\textsuperscript{v}—K2—O2\textsuperscript{x} 95.97 (10)
O2—Fe1—K1\textsuperscript{viii} 131.75 (12) O3\textsuperscript{v}—K2—O2\textsuperscript{x} 95.97 (10)
O2—Fe1—K1\textsuperscript{viii} 65.77 (11) O3\textsuperscript{v}—K2—O2\textsuperscript{x} 100.42 (10)
O1—Fe1—K1\textsuperscript{viii} 129.13 (11) O2\textsuperscript{ix}—K2—O2\textsuperscript{x} 56.22 (11)
sup-4

O1v—Fe1—K1viii 113.38 (10)  O3xvi—Fe1—K1viii 129.13 (11)
O1—Fe1—K1viii 46.69 (10)  O3xviii—K2—O2xvi 149.92 (11)
K2—Fe1—K1viii 78.252 (17)  O3xviii—K2—O2xvii 95.97 (10)
O2—Fe1—K1viii 65.77 (11)  O2x—K2—O2xvii 100.42 (10)
O2vi—Fe1—K1viii 52.19 (11)  O2xx—K2—O2xvii 56.22 (11)
O2v—Fe1—K1viii 131.75 (12)  O2xxi—K2—O2xvii 56.22 (11)
O1—Fe1—K1viii 113.38 (10)  O3xiv—K2—O2xvii 52.44 (10)
O1v—Fe1—K1viii 46.69 (10)  O3xvi—K2—O2xvii 49.39 (9)
O1—Fe1—K1viii 129.13 (11)  O3xviii—K2—O2xvii 115.63 (12)
K2v—Fe1—K1viii 78.252 (17)  O3xiv—K2—O2xviii 94.39 (10)
K1vii—Fe1—K1viii 115.965 (12)  O2x—K2—O2xviii 132.45 (10)
O2—Fe1—K1ix 131.75 (12)  O3xiv—K2—O2xviii 49.39 (9)
O2v—Fe1—K1ix 65.77 (11)  O3xviii—K2—O2xviii 115.63 (12)
O2—Fe1—K1ix 52.19 (11)  O3xvi—K2—O2xviii 52.44 (10)
O1—Fe1—K1ix 46.69 (10)  O2x—K2—O2xviii 94.39 (10)
O1v—Fe1—K1ix 129.13 (11)  O2xx—K2—O2xviii 132.45 (10)
O1—Fe1—K1ix 113.38 (10)  O2xxi—K2—O2xviii 140.25 (11)
K2—Fe1—K1ix 78.252 (17)  O3xiv—K2—O2xviii 87.30 (11)
K1vii—Fe1—K1ix 115.965 (12)  O3xvi—K2—O4xxxii 115.63 (12)
K1viii—Fe1—K1ix 115.965 (12)  O3xiv—K2—O4xxxii 52.44 (10)
O3—Fe2—O3xi 92.72 (15)  O3xviii—K2—O4xxxii 49.39 (9)
O3—Fe2—O3xii 92.72 (15)  O2x—K2—O4xxxii 132.45 (10)
O3—Fe2—O3iii 92.72 (15)  O2xx—K2—O4xxxii 140.25 (11)
O3—Fe2—O4v 171.85 (17)  O2xxi—K2—O4xxxii 94.39 (10)
O3—Fe2—O4v 94.47 (15)  O2xiv—K2—O4xxxii 87.30 (11)
O3—Fe2—O4v 94.47 (15)  O3xiii—K2—O4xxxii 87.30 (11)
O3—Fe2—O4v 83.11 (16)  O3x—K2—O4xxiv 85.99 (9)
O3—Fe2—O4v 171.85 (17)  O3xviii—K2—O4xxiv 156.61 (10)
O3—Fe2—O4v 83.11 (16)  O3xix—K2—O4xxiv 88.46 (10)
O3—Fe2—O4v 94.47 (15)  O2xx—K2—O4xxiv 132.45 (10)
O3—Fe2—O4v 94.47 (15)  O2xv—K2—O4xxiv 46.20 (9)
O3—Fe2—O4v 83.11 (16)  O2xiv—K2—O4xxiv 101.11 (10)
O3—Fe2—O4v 90.22 (16)  O3xv—K2—O4xxiv 53.02 (13)
O3—Fe2—O4v 90.22 (16)  O3xiii—K2—O4xxiv 156.61 (10)
O3—Fe2—O4v 94.47 (15)  O3xiv—K2—O4xxiv 55.86 (9)
O3—Fe2—O4v 171.85 (17)  O2x—K2—O4xxiv 85.99 (9)
O3—Fe2—O4v 94.47 (15)  O2xx—K2—O4xxiv 101.11 (10)
O4—Fe2—O4v 83.11 (16)  O2xv—K2—O4xxiv 88.46 (10)
O4—Fe2—O4v 90.22 (16)  O3xiii—K2—O4xxiv 132.45 (10)
O4—Fe2—O4v 90.22 (16)  O3xiv—K2—O4xxiv 46.20 (9)
O4—Fe2—O4v 83.11 (16)  O3xv—K2—O4xxiv 101.11 (10)
O4—Fe2—O4v 94.47 (15)  O3xiii—K2—O4xxvi 137.03 (8)
O4—Fe2—O4v 94.47 (15)  O3xiv—K2—O4xxvi 53.02 (13)
O3—Fe2—O4 118.56 (11)  O3xvi—K2—O4xxvi 115.75 (5)
O3—Fe2—O4 118.56 (11)  O3xvii—K2—O4xxvi 85.99 (9)
O3—Fe2—O4 83.11 (16)  O3xviii—K2—O4xxvi 156.61 (10)
O3—Fe2—O4 90.22 (16)  O3xvi—K2—O4xxvi 55.86 (9)
O3—Fe2—O4 90.22 (16)  O2x—K2—O4xxvi 85.99 (9)
O3—Fe2—O4 127.93 (11)  O2—K2—O4xxvi 101.11 (10)
O3—Fe2—K2viii 118.56 (11)  O2—K2—O4xxvi 88.46 (10)
O3—Fe2—K2viii 84.96 (11)  O2xx—K2—O4xxvi 46.20 (9)
O3—Fe2—K2viii 53.60 (12)  O2x—K2—O4xxv 104.40 (2)
O3—Fe2—K2viii 129.40 (12)  O4xiv—K2—O4xxv 137.03 (8)
O3—Fe2—K2viii 60.13 (13)  O4xiv—K2—O4xxv 53.02 (13)
O3—Fe2—K2viii 60.13 (13)  O4xii—K2—O4xxv 115.75 (5)
O4—Fe2—K2viii 53.60 (12)  O3xvii—K2—O4xxv 85.99 (9)
O4—Fe2—K2viii 129.40 (12)  O3xviii—K2—O4xxv 156.61 (10)
O4—Fe2—K2viii 60.13 (13)  O3xviii—K2—O4xxv 55.86 (9)
O4—Fe2—K2viii 113.261 (15)  O3xix—K2—O4xxv 156.61 (10)
K2viii—Fe2—K2viii 113.261 (15)  O3xviii—K2—O4xxv 55.86 (9)

Acta Cryst. (2021). E77, 1299-1302
| Bond                  | Value (°) (ESD) |
|-----------------------|-----------------|
| O3x—Fe2—K2xv         | 48.96 (11)      |
| O3vi—Fe2—K2xv        | 127.93 (11)     |
| O3vii—Fe2—K2xv       | 118.56 (11)     |
| O4—Fe2—K2xv          | 129.40 (12)     |
| K2xiii—Fe2—K2xv      | 113.261 (15)    |
| O1xii—K1—O1x         | 92.24 (11)      |
| O1xii—K1—O1xi        | 92.24 (12)      |
| O1x—K1—O1xi          | 92.24 (11)      |
| O1xii—K1—O2xvi       | 56.73 (9)       |
| O1x—K1—O2xvi         | 148.02 (12)     |
| O1xii—K1—O2xvii      | 82.44 (10)      |
| O1x–K1—O2xvii        | 82.44 (10)      |
| O1x–K1—O2xvii        | 56.73 (9)       |
| O1xii–K1—O2xvii      | 148.02 (12)     |
| O2xvi—K1—O2xviii     | 118.99 (3)      |
| O1xii—K1—O2xviii     | 148.02 (12)     |
| O1x–K1—O2xviii       | 82.44 (10)      |
| O1x–K1—O2xviii       | 56.73 (9)       |
| O2xvi—K1—O2xviii     | 118.99 (3)      |
| O1xii—K1—O2xviii     | 118.99 (3)      |
| O1xii—K1—O4xvi       | 103.04 (9)      |
| O1x–K1—O4xvi         | 164.18 (10)     |
| O1x–K1—O4xvi         | 83.19 (10)      |
| O2xvi—K1—O4xvi       | 46.48 (9)       |
| O2xvii—K1—O4xvii     | 128.76 (12)     |
| O2xiii–K1—O4xvii     | 83.10 (12)      |
| O1xii–K1—O4xvii      | 164.18 (10)     |
| O1x–K1—O4xvii        | 83.19 (10)      |
| O1x–K1—O4xvii        | 103.04 (9)      |
| O1xii–K1—O4xvii      | 164.18 (10)     |
| O2xvi–K1—O4xviii     | 82.41 (10)      |
| O2xiii–K1—O4xviii    | 46.48 (9)       |
| O2x–K1–O4xvii        | 128.76 (12)     |
| O4xi–K1–O4xviii      | 83.10 (12)      |
| O1xii–K1–O4xviii     | 164.18 (10)     |
| O1x–K1–O4xviii       | 83.19 (10)      |
| O1x–K1–O4xviii       | 103.04 (9)      |
| O2xvi–K1–O4xviii     | 82.41 (10)      |
| O2xiii–K1–O4xviii    | 46.48 (9)       |
| O4xvi–K1–O4xviii     | 83.10 (12)      |
| O4xvii–K1–O4xviii    | 83.10 (12)      |
| O1xii–K1–P3xvi       | 79.17 (7)       |
| O1–K1–P3xvi          | 169.22 (7)      |
| O1–K1–P3xvi          | 94.57 (7)       |
| O2xvi–K1–P3xvi       | 26.23 (6)       |
| O2xiii–K1–P3xvi      | 118.99 (3)      |
| O2x–K1–P3xvi         | 82.41 (10)      |
| O2xiii–K1–P3xvi      | 46.48 (9)       |
| O4xvi–K1–P3xvi       | 83.10 (12)      |
| O4xvii–K1–P3xvi      | 83.10 (12)      |
| O1xii–K1–P3xvi       | 79.17 (7)       |
| O1–K1–P3xvi          | 169.22 (7)      |
| O1–K1–P3xvi          | 94.57 (7)       |
| O2xvi–K1–P3xvi       | 26.23 (6)       |
Potassium sodium titanium iron tris(phosphate) (II)

Crystal data

\[
\text{K}_{0.97}\text{Na}_{1.03}\text{Ti}_{1.26}\text{Fe}_{0.74}(\text{PO}_4)_3
\]

\(M_r = 448.16\)

Cubic, \(\text{P}2_13\)

Hall symbol: \(\text{P 2ac 2ab 3}\)

\(a = 9.7945\) (1) Å

\(V = 939.61\) (3) Å\(^3\)

\(Z = 4\)

\(F(000) = 870.9\)

\(D_\text{x} = 3.168\) Mg m\(^{-3}\)

Mo \(\text{K}α\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 10546 reflections

\(\theta = 2.9–29.0^\circ\)

\(\mu = 3.27\) mm\(^{-1}\)

\(T = 293\) K

Tetrahedron, violet

\(0.15 \times 0.11 \times 0.08\) mm

Data collection

Oxford Diffraction Xcalibur-3

diffractometer

Graphite monochromator

\(\varphi \text{ and } \omega\) scans

Absorption correction: multi-scan

(Blessing, 1995)

\(T_{\text{min}} = 0.622, T_{\text{max}} = 0.835\)

837 independent reflections

833 reflections with \(I > 2\sigma(I)\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.016\)

\(wR(F^2) = 0.043\)

\(S = 1.12\)

837 reflections

63 parameters

0 restraints

\(\omega = 1/[\sigma(F_o^2) + (0.0186P)^2 + 1.1348P]\)

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

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

\(\Delta \rho_{\text{max}} = 0.28\) e Å\(^{-3}\)

\(\Delta \rho_{\text{min}} = -0.27\) e Å\(^{-3}\)

Extinction correction: SHELXL-2018/3

(Sheldrick 2015)

Extinction coefficient: 0.0015 (10)

Absolute structure: Flack \(x\) determined using

349 quotients \([I'(I)]/[I(0) + I]\) (Parsons \textit{et al.}, 2013)

Absolute structure parameter: 0.02
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 (Å²)**

|        | x             | y             | z             | U_{iso}/U_{eq} | Occ. (<1) |
|--------|---------------|---------------|---------------|----------------|-----------|
| Fe1    | 0.14198 (4)   | 0.14198 (4)   | 0.14198 (4)   | 0.0079 (2)     | 0.39 (2)  |
| Ti1    | 0.14198 (4)   | 0.14198 (4)   | 0.14198 (4)   | 0.0079 (2)     | 0.61 (2)  |
| Fe2    | 0.41334 (4)   | 0.41334 (4)   | 0.41334 (4)   | 0.0079 (2)     | 0.35 (2)  |
| Ti2    | 0.41334 (4)   | 0.41334 (4)   | 0.41334 (4)   | 0.0079 (2)     | 0.65 (2)  |
| K1     | 0.70732 (10)  | 0.70732 (10)  | 0.70732 (10)  | 0.0266 (6)     | 0.676 (18)|
| Na1    | 0.70732 (10)  | 0.70732 (10)  | 0.70732 (10)  | 0.0266 (6)     | 0.324 (18)|
| K2     | 0.93159 (11)  | 0.93159 (11)  | 0.93159 (11)  | 0.0254 (8)     | 0.294 (19)|
| Na2    | 0.93159 (11)  | 0.93159 (11)  | 0.93159 (11)  | 0.0254 (8)     | 0.706 (19)|
| P3     | 0.45787 (7)   | 0.22778 (7)   | 0.12657 (7)   | 0.00815 (19)   |           |
| O1     | 0.3100 (2)    | 0.2337 (3)    | 0.0789 (2)    | 0.0210 (5)     |           |
| O2     | 0.5478 (3)    | 0.2989 (3)    | 0.0220 (3)    | 0.0266 (6)     |           |
| O3     | 0.5024 (3)    | 0.0810 (2)    | 0.1492 (3)    | 0.0269 (5)     |           |
| O4     | 0.4786 (3)    | 0.3034 (3)    | 0.2602 (3)    | 0.0313 (6)     |           |

**Atomic displacement parameters (Å²)**

|        | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|--------|--------|--------|--------|--------|--------|--------|
| Fe1    | 0.0079 (2) | 0.0079 (2) | 0.0079 (2) | 0.00028 (15) | 0.00028 (15) | 0.00028 (15) |
| Ti1    | 0.0079 (2) | 0.0079 (2) | 0.0079 (2) | 0.00028 (15) | 0.00028 (15) | 0.00028 (15) |
| Fe2    | 0.0079 (2) | 0.0079 (2) | 0.0079 (2) | −0.00052 (15) | −0.00052 (15) | −0.00052 (15) |
| Ti2    | 0.0079 (2) | 0.0079 (2) | 0.0079 (2) | −0.00052 (15) | −0.00052 (15) | −0.00052 (15) |
| K1     | 0.0266 (6) | 0.0266 (6) | 0.0266 (6) | 0.0015 (4)    | 0.0015 (4)    | 0.0015 (4)    |
| Na1    | 0.0266 (6) | 0.0266 (6) | 0.0266 (6) | 0.0015 (4)    | 0.0015 (4)    | 0.0015 (4)    |
| K2     | 0.0254 (8) | 0.0254 (8) | 0.0254 (8) | −0.0021 (4)   | −0.0021 (4)   | −0.0021 (4)   |
| Na2    | 0.0254 (8) | 0.0254 (8) | 0.0254 (8) | −0.0021 (4)   | −0.0021 (4)   | −0.0021 (4)   |
| P3     | 0.0075 (3) | 0.0087 (3) | 0.0083 (3) | −0.0003 (2)   | 0.0015 (2)    | −0.0007 (2)   |
| O1     | 0.0088 (9) | 0.0299 (12) | 0.0242 (12) | −0.0033 (8)   | −0.0020 (8)   | 0.0089 (10)   |
| O2     | 0.0197 (11) | 0.0361 (14) | 0.0241 (12) | −0.0014 (10)  | 0.0088 (10)   | 0.0136 (11)   |
| O3     | 0.0263 (12) | 0.0128 (10) | 0.0415 (14) | 0.0088 (9)    | 0.0053 (11)   | 0.0032 (11)   |
| O4     | 0.0333 (14) | 0.0373 (15) | 0.0232 (12) | −0.0027 (12)  | 0.0014 (11)   | −0.0206 (11)  |

**Geometric parameters (Å, °)**

|        | K1—O2^1vii | K1—O2^ii | K1—O4^vii | K1—O4^xi | K1—O1^iv | K1—O1^v |
|--------|------------|----------|-----------|----------|----------|---------|
| Fe1—O2  | 1.940 (2)  | 1.940 (2) | 1.940 (2) | 1.940 (2) | 1.974 (2) | 1.974 (2) |
| Fe1—O2^ii | 1.940 (2) | 1.940 (2) | 1.940 (2) | 1.940 (2) | 1.974 (2) | 1.974 (2) |
| Fe1—O2^iii | 1.940 (2) | 1.940 (2) | 1.940 (2) | 1.940 (2) | 1.974 (2) | 1.974 (2) |
| Fe1—O1   | 1.974 (2)  | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) |
| Fe1—O1^iv | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) |
| Fe1—O1^v  | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) | 1.974 (2) |
| Bond  | Length   |
|-------|----------|
| Fe1—K2vi | 3.569 (2)   |
| Fe1—K1vii | 3.7806 (7)   |
| Fe1—K1viii | 3.7806 (7)   |
| Fe1—K1ix | 3.7806 (7)   |
| Fe2—O3x  | 1.938 (2)   |
| Fe2—O3xi | 1.938 (2)   |
| Fe2—O3xii | 1.938 (2)   |
| Fe2—O4   | 1.954 (2)   |
| Fe2—O4iv | 1.954 (2)   |
| Fe2—K2xiii | 3.7084 (6) |
| Fe2—K2xiv | 3.7084 (6) |
| K1—O1xi | 2.820 (3)   |
| K1—O1xii | 2.820 (3)   |
| K1—O1x  | 2.820 (3)   |
| K1—O2xvi | 3.009 (3)   |
| K1—O2xvii | 3.009 (3) |
| O2—Fe1—O2ii | 89.72 (12) |
| O2—Fe1—O2iii | 89.72 (12) |
| O2—Fe1—O1   | 178.52 (12) |
| O2—Fe1—O1v | 91.38 (10)  |
| O2—Fe1—O1v  | 91.38 (10)  |
| O2—Fe1—O1v  | 91.38 (10)  |
| O2—Fe1—O1v  | 91.38 (10)  |
| O2—Fe1—O1v  | 91.38 (10)  |
| O2—Fe1—O1v  | 91.38 (10)  |
| O2—Fe1—K2vi | 54.54 (9)   |
| O2—Fe1—K2vi | 54.54 (9)   |
| O2—Fe1—K2vi | 54.54 (9)   |
| O2—Fe1—K2vi | 124.28 (7)  |
| O2—Fe1—K2vi | 124.28 (7)  |
| O2—Fe1—K2vi | 124.28 (7)  |
| O2—Fe1—K1vii | 132.34 (9) |
| O2—Fe1—K1vii | 66.00 (8)   |
| O2—Fe1—K1vii | 52.14 (8)   |
| O2—Fe1—K1vii | 46.70 (7)   |
| O2—Fe1—K1vii | 113.14 (8)  |
| O2—Fe1—K1vii | 129.02 (8)  |
| K2—Fe1—K1vii | 78.502 (13) |
| K2—Fe1—K1vii | 66.00 (8)   |
| K1—P3xvi | 3.4327 (11) |
| K2—O3xvii | 2.843 (3)   |
| K2—O3xviii | 2.843 (3)   |
| K2—O2xix | 2.910 (3)   |
| K2—O2xx | 2.910 (3)   |
| K2—O2xxi | 2.910 (3)   |
| K2—O2xxii | 2.982 (4)   |
| K2—O2xxiii | 2.982 (4)   |
| K2—O3xvi  | 2.843 (3)   |
| K2—O4xiv  | 3.237 (3)   |
| K2—O4xv   | 3.237 (3)   |
| K2—P3xvii | 1.517 (3)   |
| K2—O3xviii| 1.518 (2)   |
| K2—O2xx   | 1.520 (2)   |
| K2—O4xiv  | 1.523 (2)   |
| P3—O4   | 1.517 (3)   |
| P3—O3   | 1.518 (2)   |
| P3—O2   | 1.520 (2)   |
| P3—O1   | 1.523 (2)   |
| O4viii—K1—P3xvi | 26.22 (5) |
| O4viii—K1—P3xvii | 103.21 (8) |
| O4viii—K1—P3xvii | 69.59 (5) |
| P3xviii—K1—P3xvii | 94.92 (4) |
| O1x—K1—P3xvi | 94.74 (5) |
| O1xii—K1—P3xvii | 79.13 (5) |
| O1x—K1—P3xvi | 169.06 (5) |
| O2xvi—K1—P3xvi | 26.25 (5) |
| O2xvii—K1—P3xvi | 108.35 (6) |
| O2xvii—K1—P3xvii | 115.09 (6) |
| O2xviii—K1—P3xvi | 103.21 (8) |
| O2xviii—K1—P3xvii | 69.59 (5) |
| O2xvi—K1—P3xvi | 26.22 (5) |
| O2xviii—K1—P3xvi | 94.92 (4) |
| O2xviii—K1—P3xvi | 94.92 (4) |
| O2xviii—K2—O2xix | 100.89 (8) |
| O2xviii—K2—O2xix | 100.89 (8) |
| O2xviii—K2—O2xix | 149.75 (9) |
| O2xviii—K2—O2xix | 95.89 (7) |
| O2xviii—K2—O2xix | 95.89 (7) |
| O2xviii—K2—O2xix | 149.75 (9) |
| O2xviii—K2—O2xix | 95.89 (7) |
| O2xviii—K2—O2xix | 95.89 (7) |
| Bond                  | Distance (Å)          |
|----------------------|-----------------------|
| O2—Fe—K1             | 52.14 (8)             |
| O2—Fe—K1             | 132.34 (9)            |
| O1—Fe—K1             | 113.14 (8)            |
| O1—Fe—K1             | 129.02 (8)            |
| O1—Fe—K1             | 46.70 (7)             |
| O1—Fe—K1             | 78.502 (13)           |
| O1—Fe—K1             | 116.129 (8)           |
| O2—Fe—K1             | 52.14 (8)             |
| O2—Fe—K1             | 132.34 (9)            |
| O1—Fe—K1             | 66.00 (8)             |
| O1—Fe—K1             | 129.02 (8)            |
| O1—Fe—K1             | 46.70 (7)             |
| K2—Fe—K1             | 113.14 (8)            |
| K2—Fe—K1             | 78.502 (13)           |
| K2—Fe—K1             | 116.129 (8)           |
| O3—Fe—O3             | 92.37 (12)            |
| O3—Fe—O3             | 92.37 (12)            |
| O3—Fe—O3             | 92.37 (12)            |
| O3—Fe—O4             | 94.89 (12)            |
| O3—Fe—O4             | 171.47 (13)           |
| O3—Fe—O4             | 82.87 (13)            |
| O3—Fe—O4             | 82.87 (13)            |
| O3—Fe—O4             | 94.90 (12)            |
| O3—Fe—O4             | 171.46 (13)           |
| O3—Fe—O4             | 90.46 (12)            |
| O3—Fe—O4             | 171.46 (13)           |
| O3—Fe—O4             | 82.87 (13)            |
| O3—Fe—O4             | 94.90 (12)            |
| O3—Fe—O4             | 90.46 (12)            |
| O3—Fe—K2             | 118.47 (8)            |
| O3—Fe—K2             | 49.04 (9)             |
| O3—Fe—K2             | 127.81 (8)            |
| O4—Fe—K2             | 129.70 (9)            |
| O4—Fe—K2             | 60.69 (10)            |
| O4—Fe—K2             | 53.21 (10)            |
| O3—Fe—K2             | 127.81 (8)            |
| O3—Fe—K2             | 118.47 (8)            |
| O3—Fe—K2             | 49.04 (9)             |
| O3—Fe—K2             | 53.21 (10)            |
| O3—Fe—K2             | 127.81 (8)            |
| O3—Fe—K2             | 118.47 (8)            |
| O4—Fe—K2             | 60.69 (10)            |
| O4—Fe—K2             | 113.409 (11)          |
| O4—Fe—K2             | 49.04 (9)             |
| O4—Fe—K2             | 53.21 (10)            |
| O4—Fe—K2             | 127.81 (8)            |
| O3—Fe—K2             | 60.69 (10)            |
| O3—Fe—K2             | 113.409 (11)          |
| O3—Fe—K2             | 49.04 (9)             |
| O3—Fe—K2             | 127.81 (8)            |
| O4—Fe—K2             | 127.81 (8)            |
| O4—Fe—K2             | 118.47 (8)            |
| O4—Fe—K2             | 60.69 (10)            |
| O3—Fe—K2             | 127.81 (8)            |
| O3—Fe—K2             | 118.47 (8)            |
| O4—Fe—K2             | 60.69 (10)            |

*Acta Cryst.* (2021). E77, 1299-1302
| Bond          | Angle         | Bond          | Angle         |
|---------------|---------------|---------------|---------------|
| O4v—Fe2—K2xv  | 53.21 (10)    | O4xvi—K2—O4xxi | 137.10 (6)    |
| O4v—Fe2—K2xv  | 129.70 (9)    | O4xvi—K2—O4xxi | 104.497 (19)  |
| K2xii—Fe2—K2xv | 113.409 (11)  | O4xv—K2—O4xv  | 115.71 (4)    |
| K2xiv—Fe2—K2xv | 113.409 (11)  | O4xv—K2—O4xv  | 115.71 (4)    |
| O1x—K1—O1xii | 92.11 (9)     | O4—P3—O3      | 107.34 (18)   |
| O1x—K1—O1x   | 92.11 (9)     | O4—P3—O2      | 106.27 (16)   |
| O1xii—K1—O1x | 92.11 (9)     | O3—P3—O2      | 111.46 (16)   |
| O1x—K1—O2xvi | 82.55 (7)     | O4—P3—O1      | 111.89 (15)   |
| O1xii—K1—O2xvi | 56.64 (6)    | O3—P3—O1      | 110.74 (14)   |
| O1—K1—O2xvi  | 147.84 (9)    | O2—P3—O1      | 109.06 (14)   |
| O1—K1—O2xvii | 56.64 (6)     | O4—P3—K2xv    | 71.04 (13)    |
| O1xii—K1—O2xvii | 147.84 (9)  | O3—P3—K2xv    | 167.62 (11)   |
| O1—K1—O2xvii | 82.55 (7)     | O2—P3—K2xv    | 58.68 (11)    |
| O2xvi—K1—O2xvii | 119.008 (19)| O1—P3—K2xv    | 80.72 (10)    |
| O1x—K1—O2xviii | 147.84 (9)   | O4—P3—K1xiv   | 65.37 (11)    |
| O1xii—K1—O2xviii | 82.55 (7)    | O3—P3—K1xiv   | 82.38 (11)    |
| O1—K1—O2xviii | 56.64 (6)     | O2—P3—K1xiv   | 61.12 (11)    |
| O2xvi—K1—O2xviii | 119.008 (19)| O1—P3—K1xiv   | 166.43 (11)   |
| O2xv—K1—O2xvii | 56.64 (6)    | O2—P3—K1xiv   | 126.42 (11)   |
| O2xvi—K1—O2xvii | 128.67 (9)   | O1—P3—K1xiv   | 124.51 (10)   |
| O2xv—K1—O2xvii | 128.67 (9)   | K2xv—P3—K1xiv | 85.93 (3)     |
| O1x—K1—O4xvii | 103.13 (7)    | O4—P3—K1xiv   | 126.74 (3)    |
| O1xii—K1—O4xvii | 164.24 (7)   | O3—P3—K1xiv   | 66.11 (4)     |
| O1—K1—O4xvii  | 83.46 (8)     | O2—P3—K1xiv   | 149.07 (13)   |
| O2xvi—K1—O4xvii | 103.13 (7)   | O3—P3—K1xiv   | 101.87 (12)   |
| O2xv—K1—O4xvii | 83.46 (8)    | O1—P3—K1xiv   | 71.24 (11)    |
| O2xv—K1—O4xvii | 164.24 (7)   | O1—P3—K1xiv   | 46.09 (9)     |
| O2xvi—K1—O4xvii | 128.67 (9)   | K2xv—P3—K1xiv | 82.54 (3)     |
| O2xv—K1—O4xvii | 128.67 (9)   | K1xiv—P3—K1xiv | 129.74 (3)   |
| O2xvii—K1—O4xvii | 46.65 (7)   | K2xiv—P3—K1xiv | 150.05 (3)   |
| O2xv—K1—O4xvii | 83.46 (8)    | P3—O1—Fe1     | 132.78 (15)   |
| O1xii—K1—O4xvii | 103.13 (7)   | O3—P1—K1xiv   | 111.02 (12)   |
| O1x—K1—O4xvi  | 164.24 (7)    | Fe1—O1—K1xiv  | 102.66 (9)    |
| O2xv—K1—O4xvi  | 46.65 (7)     | O3—Fe1—K1xiv  | 165.93 (19)   |
| O2xv—K1—O4xvi  | 82.39 (7)     | P3—O2—K1xiv   | 94.82 (12)    |
| O2xv—K1—O4xvi  | 128.67 (9)    | Fe2—O2—K1xiv  | 92.57 (10)    |
| O2xvii—K1—O4xvii | 128.67 (9)  | P3—O2—K1xiv   | 92.63 (12)    |
| O4xv—K1—O4xvii | 82.84 (10)    | Fe1—O1—K1xiv  | 97.25 (10)    |
| O4xv—K1—O4xvii | 82.84 (10)    | K2xv—O2—K1xiv | 103.64 (9)    |
| O1x—K1—P3xiv   | 169.06 (5)    | P3—O2—K1xiv   | 151.51 (19)   |
| O1x—K1—P3xiv   | 94.74 (5)     | O3—Fe2—K1xiv  | 104.38 (14)   |
| O1x—K1—P3xiv   | 79.13 (5)     | P3—O3—K2xiv   | 100.00 (10)   |
| O2xvi—K1—P3xiv  | 108.35 (6)    | O3—O4—Fe2    | 152.6 (2)     |
| O2xvii—K1—P3xiv | 115.09 (6)   | O3—O4—K2xiv   | 98.53 (14)    |
| O4xv—K1—P3xiv  | 26.25 (5)     | Fe2—O4—K2xiv  | 95.14 (11)    |
| O4xv—K1—P3xiv  | 26.22 (5)     | P3—O4—K1xiv   | 88.41 (12)    |
| Bond                  | Distance (Å)  | Bond                  | Distance (Å)  |
|----------------------|---------------|----------------------|---------------|
| O4xvi—K1—P3xviii     | 103.21 (8)    | Fe2—O4—K1xiv        | 117.90 (11)   |
| O1x—K1—P3xvii       | 79.13 (5)     | K2xv—O4—K1xv       | 77.09 (8)     |
| O1xii—K1—P3xvii     | 169.06 (5)    | P3—O4—K2xv         | 82.65 (13)    |
| O1xiv—K1—P3xvii     | 94.74 (5)     | Fe2—O4—K2xv        | 87.54 (11)    |
| O2xvi—K1—P3xvii     | 115.09 (6)    | K2xv—O4—K2xv       | 171.00 (11)   |
| O2xii—K1—P3xvii     | 26.25 (5)     | K1xv—O4—K2xv       | 94.06 (9)     |
| O2xviii—K1—P3xvii   | 108.35 (6)    |                      |               |

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