

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# Ammonium iron(III) phosphate(V) fluoride, $(\text{NH}_4)_{0.5}[(\text{NH}_4)_{0.375}\text{K}_{0.125}]\text{FePO}_4\text{F}$ , with ammonium partially substituted by potassium

Lei Wang, Yan Zhou, Ya-Xi Huang and Jin-Xiao Mi\*

Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of China  
Correspondence e-mail: jxmi@xmu.edu.cn

Received 28 October 2008; accepted 13 December 2008

Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{P}-\text{O}) = 0.004$  Å; H-atom completeness 58%; disorder in main residue;  $R$  factor = 0.031;  $wR$  factor = 0.054; data-to-parameter ratio = 13.9.

The title compound, ammonium potassium iron(III) phosphate fluoride,  $(\text{NH}_4)_{0.875}\text{K}_{0.125}\text{FePO}_4\text{F}$ , is built from zigzag chains  $\infty^1\{[\text{FeO}_4\text{F}_2]^{7-}\}$ , with  $\text{Fe}^{3+}$  in a distorted octahedral coordination, extending along both the [011] and  $[0\bar{1}1]$  directions. These chains are made up of alternating *trans*- $[\text{FeO}_4\text{F}_2]$  and *cis*- $[\text{FeO}_4\text{F}_2]$  octahedra *via* shared F-atom corners, and are linked by  $\text{PO}_4$  tetrahedra, resulting in an open-framework structure with channels along the [010] and [100] directions. There are two crystallographically independent ammonium sites: one in the [010] channels and the other, partially substituted by  $\text{K}^+$  ions, in the [100] channels. The ammonium in the [010] channels is fixed to the framework *via* eight hydrogen bonds (six  $\text{N}-\text{H}\cdots\text{O}$  and two  $\text{N}-\text{H}\cdots\text{F}$ ).

## Related literature

For general background, see: Hagerman & Poepfelmeier (1995). For related structures, see: Loiseau *et al.* (1994) for  $(\text{NH}_4)\text{Fe}(\text{PO}_4)\text{F}$ ; Loiseau *et al.* (2000) for  $(\text{NH}_4)\text{Ga}(\text{PO}_4)\text{F}$ ; Alda *et al.* (2003) for  $(\text{NH}_4)\text{V}(\text{PO}_4)\text{F}$ ; Slovokhotova *et al.* (1991) for  $\text{KAl}(\text{PO}_4)\text{F}$ ; Harrison *et al.* (1995) for  $\text{KGa}(\text{PO}_4)\text{F}$ ; Matvienko *et al.* (1979) for  $\text{KFe}(\text{PO}_4)\text{F}$ ; Slobodyanik *et al.* (1991) for  $\text{KCr}(\text{PO}_4)\text{F}$ ; Tordjman *et al.* (1974) for  $\text{K}(\text{TiO})(\text{PO}_4)$ .

## Experimental

### Crystal data

$(\text{NH}_4)_{0.5}[(\text{NH}_4)_{0.375}\text{K}_{0.125}]\text{FePO}_4\text{F}$   $b = 6.4382$  (2) Å  
 $M_r = 190.49$   $c = 10.6428$  (3) Å  
 Orthorhombic,  $Pna2_1$   $V = 886.67$  (5) Å<sup>3</sup>  
 $a = 12.9402$  (4) Å  $Z = 8$

Mo  $K\alpha$  radiation  
 $\mu = 3.82$  mm<sup>-1</sup>

$T = 173$  (2) K  
 $0.12 \times 0.09 \times 0.09$  mm

### Data collection

Oxford Diffraction CCD area-detector diffractometer  
 Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2005)  
 $T_{\text{min}} = 0.657$ ,  $T_{\text{max}} = 0.725$

5371 measured reflections  
 2162 independent reflections  
 1636 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.054$   
 $S = 0.88$   
 2162 reflections  
 155 parameters

5 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.52$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.56$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Fe1—O5 <sup>i</sup>	1.893 (4)	Fe2—O2	2.003 (4)
Fe1—O6	1.955 (4)	Fe2—O4	2.055 (3)
Fe1—O8 <sup>ii</sup>	1.963 (4)	P1—O1 <sup>i</sup>	1.531 (5)
Fe1—F1 <sup>i</sup>	1.988 (4)	P1—O7	1.532 (4)
Fe1—F2	2.010 (4)	P1—O6 <sup>iii</sup>	1.538 (4)
Fe1—O7	2.088 (4)	P1—O3 <sup>iii</sup>	1.551 (5)
Fe2—F2	1.936 (4)	P2—O2	1.530 (4)
Fe2—O3	1.944 (5)	P2—O8	1.533 (5)
Fe2—O1	1.986 (5)	P2—O4 <sup>iv</sup>	1.539 (4)
Fe2—F1	2.001 (4)	P2—O5	1.547 (5)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N2—H1 <sup>i</sup> ⋯F1 <sup>i</sup>	0.86 (4)	2.37 (5)	3.079 (6)	140 (4)
N2—H1 <sup>i</sup> ⋯O4 <sup>i</sup>	0.86 (4)	2.39 (3)	3.124 (6)	144 (4)
N2—H1 <sup>i</sup> ⋯O1 <sup>i</sup>	0.86 (4)	2.54 (5)	3.159 (7)	130 (4)
N2—H2 <sup>i</sup> ⋯O2	0.87 (4)	2.13 (4)	2.956 (6)	159 (4)
N2—H2 <sup>i</sup> ⋯F2	0.87 (4)	2.22 (5)	2.744 (6)	118 (4)
N2—H3 <sup>i</sup> ⋯O8 <sup>iii</sup>	0.85 (4)	2.29 (5)	2.775 (6)	117 (4)
N2—H3 <sup>i</sup> ⋯O3 <sup>iii</sup>	0.85 (4)	2.39 (5)	3.088 (7)	139 (4)
N2—H4 <sup>i</sup> ⋯O7 <sup>vii</sup>	0.84 (3)	2.06 (3)	2.823 (5)	151 (4)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

This project was supported by the Fund of the National Natural Science Foundation of China (No. 40472027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2066).

## References

- Alda, E., Bazab, B., Mesa, J. L., Pizarro, J. L., Arriortua, M. I. & Rojo, T. (2003). *J. Solid State Chem.* **173**, 101–108.
- Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Dowty, E. (2004). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
- Hagerman, M. E. & Poepfelmeier, K. R. (1995). *Chem. Mater.* **7**, 602–621.
- Harrison, W. T. A., Phillips, M. L. F. & Stucky, G. D. (1995). *Chem. Mater.* **7**, 1849–1856.
- Loiseau, T., Calage, Y., Lacorre, P. & Ferey, G. (1994). *J. Solid State Chem.* **111**, 390–396.
- Loiseau, T., Paulet, C., Simon, N., Munch, V., Taulelle, F. & Ferey, G. (2000). *Chem. Mater.* **12**, 1393–1399.
- Matvienko, E. N., Yakubovich, O. V., Simonov, M. A. & Belov, N. V. (1979). *Dokl. Akad. Nauk SSSR*, **246**, 875–878.
- Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction, Abingdon, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Slobodyanik, N. S., Nagornyi, P. G., Kornienko, Z. I. & Kapshuk, A. A. (1991). *Zh. Neorg. Khim.* **36**, 1390–1392.
- Slovokhotova, O. L., Ilyushin, G. D., Triodina, N. S., Mel'nikov, O. K., Dem'yanets, L. N., Gerr, R. G. & Tsirel'son, V. G. (1991). *Zh. Strukt. Khim.* **32**, 103–109.
- Tordjman, I., Masse, R. & Guitel, J. C. (1974). *Z. Kristallogr.* **139**, 103–115.

**supplementary materials**

*Acta Cryst.* (2009). E65, i4-i5 [ doi:10.1107/S1600536808042499 ]

## Ammonium iron(III) phosphate(V) fluoride, $(\text{NH}_4)_{0.5}[(\text{NH}_4)_{0.375}\text{K}_{0.125}]\text{FePO}_4\text{F}$ , with ammonium partially substituted by potassium

L. Wang, Y. Zhou, Y.-X. Huang and J.-X. Mi

### Comment

Compounds of the  $\text{KTiOPO}_4$  (KTP) group have attracted great attention in the past decades owing to their non-linear optical properties, and became a large family of compositions with formula  $\text{MM}'\text{OXO}_4$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$  or  $\text{Tl}$ ;  $\text{M}' = \text{Ti}, \text{Ge}, \text{Sn}$  and  $\text{X} = \text{P}$  or  $\text{As}$ ), where  $\text{M}$  and  $\text{M}'$  can be partially replaced by two or more different cations (Hagerman *et al.*, 1995). Tetravalent  $\text{M}'$  ions can be replaced by trivalent ions such as  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  with oxygen being substituted simultaneously by fluorine for charge balance. Many examples of fluorophosphates with the KTP-type structure are known, such as  $(\text{NH}_4)\text{Fe}(\text{PO}_4)\text{F}$ ,  $(\text{NH}_4)\text{Ga}(\text{PO}_4)\text{F}$  (Loiseau *et al.*, 1994, 2000), and  $(\text{NH}_4)\text{V}(\text{PO}_4)\text{F}$  (Alda *et al.*, 2003) in the ammonium series, and  $\text{KAl}(\text{PO}_4)\text{F}$  (Slovokhotova *et al.*, 1991),  $\text{KGa}(\text{PO}_4)\text{F}$  (Harrison *et al.*, 1995),  $\text{KFe}(\text{PO}_4)\text{F}$  (Matvienko *et al.*, 1979), and  $\text{KCr}(\text{PO}_4)\text{F}$  (Slobodyanik *et al.*, 1991) in the potassium series. However, to the best of our knowledge, sodium fluorophosphate compounds with the KTP-type structure have not been reported to date. Our attempt to synthesize KTP-type sodium fluorophosphates failed as well, instead we obtained a solid-solution ammonium fluorophosphate,  $(\text{NH}_4)((\text{NH}_4)_{0.75}\text{K}_{0.25})[\text{Fe}_2(\text{PO}_4)_2\text{F}_2]$ , partially substituted by potassium.

The crystal structure of the title compound is built from one-dimensional zigzag ferric octahedral chains  $\infty^1\{[\text{FeO}_4\text{F}_2]^{7-}\}$  (see Fig. 1) linked by  $\text{PO}_4$  tetrahedra via common O-corners, resulting in a three dimensional open framework structure (see Fig.2). The zigzag ferric octahedral chains are made up of alternating *trans*- $[\text{FeO}_4\text{F}_2]$  and *cis*- $[\text{FeO}_4\text{F}_2]$  octahedra via common fluorine-corners, and are along both  $[011]$  and  $[0-11]$  directions. Each  $\text{PO}_4$  tetrahedron shares all oxygen corners with four neighboring  $[\text{FeO}_4\text{F}_2]$  octahedra, and each  $[\text{FeO}_4\text{F}_2]$  octahedron shares its four oxygen atoms with four  $\text{PO}_4$  tetrahedra. The negative charge of the framework is compensated by ammonium ions and potassium cations. Two crystallographically independent ammonium sites are found. One resides in the channels along  $[010]$ , linking to the framework via hydrogen bonds ( $\text{N-H}\cdots\text{O}(\text{F})$ ). If this ammonium ion is considered as a normal cation, its coordination number is 8 with an average bond distance of 2.969 Å (i.e., to neighboring oxygen and fluorine atoms). The other ammonium site, partially occupied by  $\text{K}^+$  ions, resides in the channels along  $[100]$ . The potassium (ammonium) has a coordination number of 8 with a mean bond distance of 2.882 Å. Therefore, the ammonium site in the  $[010]$  channels is slightly larger in size than its counterpart in the  $[100]$  channels. Consequently, potassium ions preferentially substitute for the ammonium ions in the  $[100]$  channels. We suggest that the potassium-to-ammonium ratio in the title compound is controlled by the size effect. It is possible that the size effect in hydrothermally synthesized crystals at lower temperatures is more pronounced than those from a solid state reaction route.

### Experimental

Transparent, colorless single crystals of the title compound were synthesized hydrothermally. A mixture of 0.055 g  $\text{NaBF}_4$ , 1.035 g  $\text{NH}_4\text{H}_2\text{PO}_4$ , 0.342 g  $\text{NH}_4\text{HF}_2$  and 0.048 g  $\text{Fe}_2\text{O}_3$  in an approximate molar ratio of  $\text{Na}:\text{NH}_4:\text{P}:\text{Fe} = 0.5:15:9:$

## supplementary materials

6, was dissolved in 9 ml distilled water while stirring. The prepared solution was transferred to a Teflon-lined stainless steel autoclave (internal volume 30 ml, degree of filling 33%) and held at 453 K for three days under autogenous pressure. Then the autoclave was cooled to room temperature by turning off the power. Products were filtered off, washed with distilled water and dried at room temperature. The presence of potassium in the crystal that was used for single crystal X-ray data collection, was determined by semi-quantitative chemical analysis on an Oxford Instruments Energy Dispersive Spectrometer(EDS)(calcd K: 2.56 %, Obsd K: ~3%). Sodium was not detectable in the crystal by EDS. It is supposed that potassium should be introduced into the sample as impurities in the reagents.

### Refinement

There are two possible space groups  $Pna2_1(abc)$  and  $Pnna(acb)$  for the KTP-type compounds. Initially, the centrosymmetric  $Pnna$  (No.52) space group was selected according to the observed systematic absences. All the framework atoms fit to the centrosymmetric model, except that the ammonium ions resided in the channel are in disordered manner and have abnormally short (1.46 Å) N–N distances. Furthermore, the structural refinement converged to only  $R1(gt)=0.0783$  and  $wR(all)=0.1813$ , which are much higher than those from the noncentrosymmetric model (i.e., all anisotropic atoms resulting in  $R1(gt)=0.031$ , and  $wR(all)=0.054$  using 155 parameters). Therefore, the noncentrosymmetric space group  $Pna2_1$ (No.33) was chosen to solve and refine the crystal structure as an inversion twin with twin components 0.48 (3)/0.52 (3). During the structure refinement, five constrained parameters were set, one for the constraint of N1 and K1 atoms (i.e., EXYZ and EADP) sharing the same site, the other four for geometrical constraints (i.e., HFIX: fixed bond distance 0.89 Å) of N2–H1, N2–H2, N2–H3, and N2–H4, respectively. Hydrogen coordinate parameters linked to N2 were obtained from difference electron density synthesis and refined by constrained N–H bond distances, their displacement parameters refined via setting to a common variable. Hydrogen atoms linked to N1 were not determined in the present paper.

### Figures

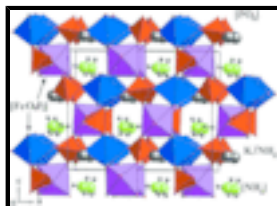


Fig. 1. Unit cell of  $(NH_4)((NH_4)_{0.75}K_{0.25}) [Fe_2(PO_4)_2F_2]$  in a view along  $b$ . *Trans*- $[FeO_4F_2]$ , in blue octahedra; *cis*- $[FeO_4F_2]$ , in pink octahedra;  $PO_4$ , in red tetrahedra; black spheres: disordered K/ $NH_4$ ; green spheres:  $NH_4$ .

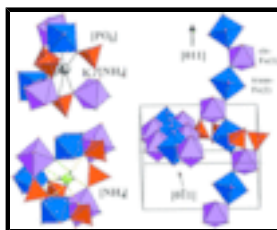


Fig. 2. Left: (1). Coordination environment of eight coordinated potassium/ammonium ions(upper); (2). Coordination environment of ammonium ions via hydrogen bonds(down).Right: chains built up of alternate *trans*- $[FeO_4F_2]$  and *cis*- $[FeO_4F_2]$  octahedra running along  $[011]$  and  $[0-11]$  respectively;

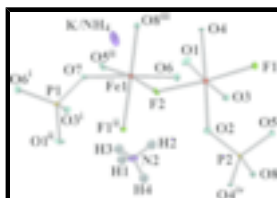


Fig. 3. Coordination environment of Fe and P atoms, with displacement ellipsoids drawn at the 50% probability level (symmetry codes: (i)  $x, 1+y, z$ ; (ii)  $1/2-x, 1/2+y, 1/2+z$ ; (iii)  $-1/2+x, 1/2-y, z$ ; (iv)  $1/2+x, 1/2-y, z$ ).

**Ammonium iron(III) phosphate(V) fluoride**

*Crystal data*

(NH<sub>4</sub>)<sub>0.875</sub>K<sub>0.125</sub>FePO<sub>4</sub>F

$M_r = 190.49$

Orthorhombic, *Pna*2<sub>1</sub>

Hall symbol: P 2c -2n

$a = 12.9402$  (4) Å

$b = 6.4382$  (2) Å

$c = 10.6428$  (3) Å

$V = 886.67$  (5) Å<sup>3</sup>

$Z = 8$

$F_{000} = 752$

$D_x = 2.854$  Mg m<sup>-3</sup>

Mo *K*α radiation

$\lambda = 0.71073$  Å

Cell parameters from 5001 reflections

$\theta = 3.0$ – $32.5^\circ$

$\mu = 3.82$  mm<sup>-1</sup>

$T = 173$  (2) K

Prism, colorless

$0.12 \times 0.09 \times 0.09$  mm

*Data collection*

Oxford Diffraction CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

326 images,  $\Delta\omega = 1^\circ$ , Exp time: 40 s. scans

Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2005)

$T_{\min} = 0.657$ ,  $T_{\max} = 0.725$

5371 measured reflections

2162 independent reflections

1636 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 32.5^\circ$

$\theta_{\min} = 2.5^\circ$

$h = -19 \rightarrow 16$

$k = -4 \rightarrow 9$

$l = -10 \rightarrow 16$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.054$

$S = 0.88$

2162 reflections

155 parameters

5 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0164P)^2]$

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

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

$\Delta\rho_{\max} = 0.52$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>

Extinction correction: none

# supplementary materials

---

## 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.** 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  $F^2 > 2\sigma(F^2)$  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. The crystal structure of the title compound was refined by a inversion twin matrix so the Flack parameter is equal to zero.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.11299 (4)	0.48776 (11)	0.41908 (14)	0.00427 (10)	
Fe2	0.25117 (7)	0.25076 (13)	0.16711 (14)	0.00434 (9)	
K1	0.1161 (2)	0.7780 (4)	0.1155 (3)	0.0243 (9)	0.249 (5)
N1	0.1161 (2)	0.7780 (4)	0.1155 (3)	0.0243 (9)	0.75
N2	0.4008 (3)	0.6749 (6)	0.3543 (4)	0.0094 (7)	
P1	0.18531 (6)	0.9964 (2)	0.4152 (2)	0.00453 (15)	
P2	0.49699 (14)	0.17105 (12)	0.1701 (2)	0.00426 (15)	
F1	0.2694 (3)	0.0303 (7)	0.0365 (3)	0.0067 (8)	
F2	0.2233 (3)	0.4707 (7)	0.2864 (3)	0.0070 (8)	
O1	0.2426 (3)	0.4522 (9)	0.0261 (4)	0.0082 (9)	
O2	0.4023 (3)	0.3113 (6)	0.1847 (4)	0.0075 (8)	
O3	0.2540 (3)	0.0417 (9)	0.2989 (4)	0.0076 (9)	
O4	0.0953 (3)	0.1996 (6)	0.1474 (4)	0.0056 (8)	
O5	0.4803 (4)	0.0316 (8)	0.0535 (3)	0.0095 (9)	
O6	0.1173 (3)	0.1868 (5)	0.4430 (4)	0.0069 (8)	
O7	0.1172 (3)	0.8075 (5)	0.3867 (4)	0.0061 (8)	
O8	0.5104 (3)	0.0264 (8)	0.2834 (3)	0.0057 (9)*	
H1	0.372 (3)	0.678 (8)	0.427 (3)	0.020 (7)*	
H2	0.386 (4)	0.580 (7)	0.299 (4)	0.020 (7)*	
H3	0.385 (4)	0.780 (6)	0.310 (4)	0.020 (7)*	
H4	0.462 (2)	0.634 (8)	0.365 (5)	0.020 (7)*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe1	0.0045 (2)	0.0046 (2)	0.00376 (18)	0.0002 (3)	-0.0004 (5)	0.0001 (2)
Fe2	0.00452 (18)	0.00472 (17)	0.00377 (17)	0.00037 (17)	0.00040 (18)	0.0003 (2)
K1	0.0311 (16)	0.0146 (14)	0.0271 (14)	-0.0069 (11)	0.0077 (11)	-0.0039 (10)
N1	0.0311 (16)	0.0146 (14)	0.0271 (14)	-0.0069 (11)	0.0077 (11)	-0.0039 (10)
N2	0.0038 (17)	0.0161 (18)	0.0083 (17)	-0.0023 (15)	0.0024 (14)	0.0011 (15)
P1	0.0048 (4)	0.0048 (3)	0.0039 (4)	-0.0008 (6)	-0.0017 (9)	0.0010 (3)

P2	0.0041 (4)	0.0046 (3)	0.0041 (3)	-0.0001 (6)	-0.0001 (3)	-0.0030 (7)
F1	0.0066 (18)	0.0067 (14)	0.0070 (16)	-0.0007 (14)	0.0021 (13)	-0.0002 (13)
F2	0.0077 (18)	0.0096 (15)	0.0037 (15)	-0.0016 (15)	0.0019 (13)	-0.0036 (13)
F1	0.0066 (18)	0.0067 (14)	0.0070 (16)	-0.0007 (14)	0.0021 (13)	-0.0002 (13)
F2	0.0077 (18)	0.0096 (15)	0.0037 (15)	-0.0016 (15)	0.0019 (13)	-0.0036 (13)
O1	0.008 (2)	0.0123 (18)	0.0045 (19)	0.0027 (19)	0.0029 (15)	0.0042 (17)
O2	0.005 (2)	0.0119 (15)	0.005 (2)	-0.0012 (15)	0.0027 (18)	0.0014 (15)
O3	0.007 (2)	0.0091 (18)	0.0067 (19)	0.0002 (18)	0.0000 (14)	0.0012 (17)
O4	0.0036 (19)	0.0049 (14)	0.008 (2)	0.0006 (13)	-0.0034 (17)	0.0000 (14)
O5	0.0102 (18)	0.0095 (15)	0.0089 (16)	0.0032 (14)	-0.0035 (12)	-0.0052 (11)
O6	0.0095 (18)	0.0063 (13)	0.005 (2)	0.0009 (17)	0.0009 (19)	0.0017 (13)
O7	0.0070 (17)	0.0053 (13)	0.006 (2)	0.0005 (16)	-0.0013 (19)	-0.0034 (12)

*Geometric parameters (Å, °)*

Fe1—O5 <sup>i</sup>	1.893 (4)	N2—O7 <sup>iv</sup>	2.823 (5)
Fe1—O6	1.955 (4)	N2—O2	2.956 (6)
Fe1—O8 <sup>ii</sup>	1.963 (4)	N2—F1 <sup>i</sup>	3.079 (6)
Fe1—F1 <sup>i</sup>	1.988 (4)	N2—O3 <sup>iii</sup>	3.088 (7)
Fe1—F2	2.010 (4)	N2—O4 <sup>i</sup>	3.124 (6)
Fe1—O7	2.088 (4)	N2—O1 <sup>i</sup>	3.159 (7)
Fe2—F2	1.936 (4)	P1—O1 <sup>i</sup>	1.531 (5)
Fe2—O3	1.944 (5)	P1—O7	1.532 (4)
Fe2—O1	1.986 (5)	P1—O6 <sup>iii</sup>	1.538 (4)
Fe2—F1	2.001 (4)	P1—O3 <sup>iii</sup>	1.551 (5)
Fe2—O2	2.003 (4)	P2—O2	1.530 (4)
Fe2—O4	2.055 (3)	P2—O8	1.533 (5)
K1—F1 <sup>iii</sup>	2.697 (5)	P2—O4 <sup>v</sup>	1.539 (4)
K1—O5 <sup>ii</sup>	2.739 (6)	P2—O5	1.547 (5)
K1—O4 <sup>iii</sup>	2.749 (4)	F1—Fe1 <sup>vi</sup>	1.988 (4)
K1—O1	2.825 (6)	F1—K1 <sup>vii</sup>	2.697 (5)
K1—O7	2.893 (5)	O1—P1 <sup>vi</sup>	1.531 (5)
K1—O8 <sup>ii</sup>	2.985 (5)	O3—P1 <sup>vii</sup>	1.551 (5)
K1—F2	3.025 (5)	O3—K1 <sup>vii</sup>	3.142 (6)
K1—O3 <sup>iii</sup>	3.142 (6)	O4—P2 <sup>ii</sup>	1.539 (4)
N2—H1	0.86 (2)	O4—K1 <sup>vii</sup>	2.749 (4)
N2—H2	0.87 (2)	O5—Fe1 <sup>vi</sup>	1.893 (4)
N2—H3	0.85 (2)	O5—K1 <sup>v</sup>	2.739 (6)
N2—H4	0.84 (2)	O6—P1 <sup>vii</sup>	1.538 (4)
N2—F2	2.744 (6)	O8—Fe1 <sup>v</sup>	1.963 (4)
N2—O8 <sup>iii</sup>	2.775 (6)	O8—K1 <sup>v</sup>	2.985 (5)
O5 <sup>i</sup> —Fe1—O6	93.9 (2)	F1 <sup>iii</sup> —K1—O3 <sup>iii</sup>	56.70 (12)
O5 <sup>i</sup> —Fe1—O8 <sup>ii</sup>	97.58 (10)	O5 <sup>ii</sup> —K1—O3 <sup>iii</sup>	155.13 (16)
O6—Fe1—O8 <sup>ii</sup>	94.0 (2)	O4 <sup>iii</sup> —K1—O3 <sup>iii</sup>	56.31 (13)

## supplementary materials

---

O5 <sup>i</sup> —Fe1—F1 <sup>i</sup>	89.56 (19)	O1—K1—O3 <sup>iii</sup>	106.34 (16)
O6—Fe1—F1 <sup>i</sup>	91.87 (18)	O7—K1—O3 <sup>iii</sup>	48.85 (13)
O8 <sup>ii</sup> —Fe1—F1 <sup>i</sup>	170.45 (17)	O8 <sup>ii</sup> —K1—O3 <sup>iii</sup>	104.06 (15)
O5 <sup>i</sup> —Fe1—F2	172.51 (19)	F2—K1—O3 <sup>iii</sup>	73.71 (16)
O6—Fe1—F2	90.97 (18)	H1—N2—H2	122 (5)
O8 <sup>ii</sup> —Fe1—F2	87.76 (17)	H1—N2—H3	112 (5)
F1 <sup>i</sup> —Fe1—F2	84.57 (10)	H2—N2—H3	98 (5)
O5 <sup>i</sup> —Fe1—O7	89.7 (2)	H1—N2—H4	107 (5)
O6—Fe1—O7	176.27 (15)	H2—N2—H4	95 (5)
O8 <sup>ii</sup> —Fe1—O7	86.68 (19)	H3—N2—H4	124 (5)
F1 <sup>i</sup> —Fe1—O7	87.03 (17)	O1 <sup>i</sup> —P1—O7	110.8 (3)
F2—Fe1—O7	85.37 (17)	O1 <sup>i</sup> —P1—O6 <sup>iii</sup>	110.4 (3)
F2—Fe2—O3	92.1 (2)	O7—P1—O6 <sup>iii</sup>	109.98 (13)
F2—Fe2—O1	90.43 (16)	O1 <sup>i</sup> —P1—O3 <sup>iii</sup>	107.56 (14)
O3—Fe2—O1	176.3 (3)	O7—P1—O3 <sup>iii</sup>	108.7 (3)
F2—Fe2—F1	175.3 (2)	O6 <sup>iii</sup> —P1—O3 <sup>iii</sup>	109.4 (3)
O3—Fe2—F1	90.44 (16)	O2—P2—O8	111.7 (3)
O1—Fe2—F1	86.9 (2)	O2—P2—O4 <sup>v</sup>	111.00 (12)
F2—Fe2—O2	88.75 (18)	O8—P2—O4 <sup>v</sup>	111.0 (2)
O3—Fe2—O2	92.82 (18)	O2—P2—O5	108.2 (3)
O1—Fe2—O2	89.87 (19)	O8—P2—O5	107.11 (13)
F1—Fe2—O2	95.06 (17)	O4 <sup>v</sup> —P2—O5	107.7 (3)
F2—Fe2—O4	90.05 (17)	Fe1 <sup>vi</sup> —F1—Fe2	128.6 (2)
O3—Fe2—O4	88.90 (18)	Fe1 <sup>vi</sup> —F1—K1 <sup>vii</sup>	132.5 (2)
O1—Fe2—O4	88.46 (18)	Fe2—F1—K1 <sup>vii</sup>	97.14 (16)
F1—Fe2—O4	86.05 (18)	Fe2—F2—Fe1	129.3 (2)
O2—Fe2—O4	177.9 (2)	Fe2—F2—K1	99.74 (15)
F1 <sup>iii</sup> —K1—O5 <sup>ii</sup>	146.65 (16)	Fe1—F2—K1	93.52 (16)
F1 <sup>iii</sup> —K1—O4 <sup>iii</sup>	61.07 (13)	P1 <sup>vi</sup> —O1—Fe2	132.1 (3)
O5 <sup>ii</sup> —K1—O4 <sup>iii</sup>	133.26 (16)	P1 <sup>vi</sup> —O1—K1	118.3 (3)
F1 <sup>iii</sup> —K1—O1	85.20 (17)	Fe2—O1—K1	105.24 (19)
O5 <sup>ii</sup> —K1—O1	75.57 (15)	P2—O2—Fe2	131.1 (2)
O4 <sup>iii</sup> —K1—O1	146.27 (16)	P1 <sup>vii</sup> —O3—Fe2	134.0 (3)
F1 <sup>iii</sup> —K1—O7	105.53 (14)	P1 <sup>vii</sup> —O3—K1 <sup>vii</sup>	94.0 (2)
O5 <sup>ii</sup> —K1—O7	106.92 (14)	Fe2—O3—K1 <sup>vii</sup>	85.15 (16)
O4 <sup>iii</sup> —K1—O7	79.17 (13)	P2 <sup>ii</sup> —O4—Fe2	135.1 (2)
O1—K1—O7	112.44 (15)	P2 <sup>ii</sup> —O4—K1 <sup>vii</sup>	129.4 (2)
F1 <sup>iii</sup> —K1—O8 <sup>ii</sup>	156.77 (16)	Fe2—O4—K1 <sup>vii</sup>	94.26 (14)
O5 <sup>ii</sup> —K1—O8 <sup>ii</sup>	51.09 (8)	P2—O5—Fe1 <sup>vi</sup>	141.5 (3)
O4 <sup>iii</sup> —K1—O8 <sup>ii</sup>	121.95 (15)	P2—O5—K1 <sup>v</sup>	98.0 (2)
O1—K1—O8 <sup>ii</sup>	88.83 (16)	Fe1 <sup>vi</sup> —O5—K1 <sup>v</sup>	118.9 (2)
O7—K1—O8 <sup>ii</sup>	56.47 (12)	P1 <sup>vii</sup> —O6—Fe1	141.4 (3)

F1 <sup>iii</sup> —K1—F2	104.14 (16)	P1—O7—Fe1	139.9 (2)
O5 <sup>ii</sup> —K1—F2	87.88 (16)	P1—O7—K1	104.6 (2)
O4 <sup>iii</sup> —K1—F2	128.06 (15)	Fe1—O7—K1	95.74 (14)
O1—K1—F2	56.72 (12)	P2—O8—Fe1 <sup>v</sup>	133.1 (3)
O7—K1—F2	55.97 (11)	P2—O8—K1 <sup>v</sup>	88.85 (19)
O8 <sup>ii</sup> —K1—F2	54.57 (13)	Fe1 <sup>v</sup> —O8—K1 <sup>v</sup>	95.74 (18)

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H1 $\cdots$ F1 <sup>i</sup>	0.86 (4)	2.37 (5)	3.079 (6)	140 (4)
N2—H1 $\cdots$ O4 <sup>i</sup>	0.86 (4)	2.39 (3)	3.124 (6)	144 (4)
N2—H1 $\cdots$ O1 <sup>i</sup>	0.86 (4)	2.54 (5)	3.159 (7)	130 (4)
N2—H2 $\cdots$ O2	0.87 (4)	2.13 (4)	2.956 (6)	159 (4)
N2—H2 $\cdots$ F2	0.87 (4)	2.22 (5)	2.744 (6)	118 (4)
N2—H3 $\cdots$ O8 <sup>iii</sup>	0.85 (4)	2.29 (5)	2.775 (6)	117 (4)
N2—H3 $\cdots$ O3 <sup>iii</sup>	0.85 (4)	2.39 (5)	3.088 (7)	139 (4)
N2—H4 $\cdots$ O7 <sup>iv</sup>	0.84 (3)	2.06 (3)	2.823 (5)	151 (4)

Symmetry codes: (i)  $-x+1/2, y+1/2, z+1/2$ ; (iii)  $x, y+1, z$ ; (iv)  $x+1/2, -y+3/2, z$ .

Fig. 1

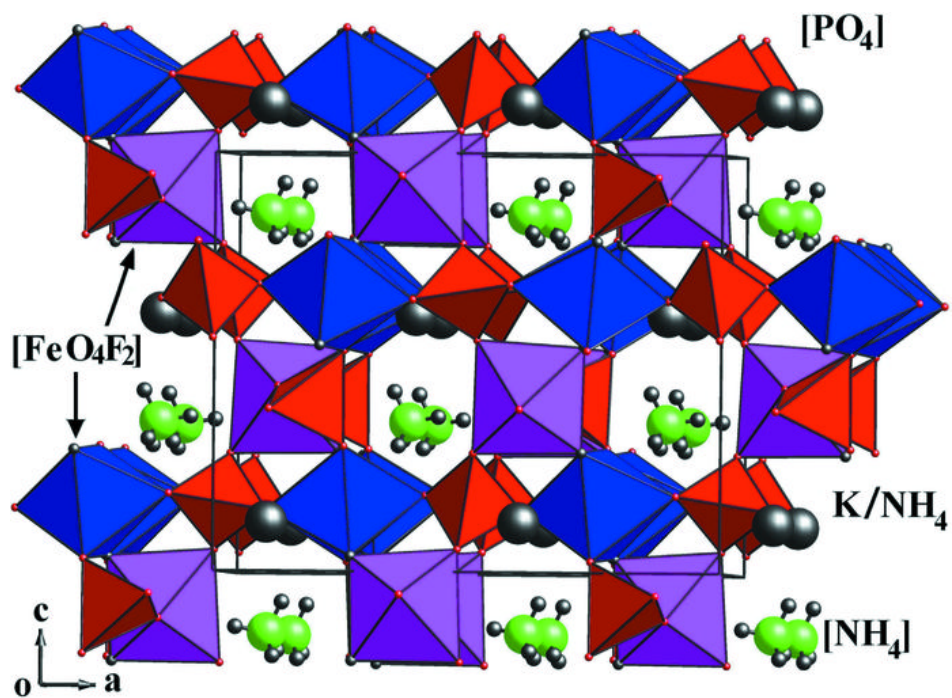


Fig. 2

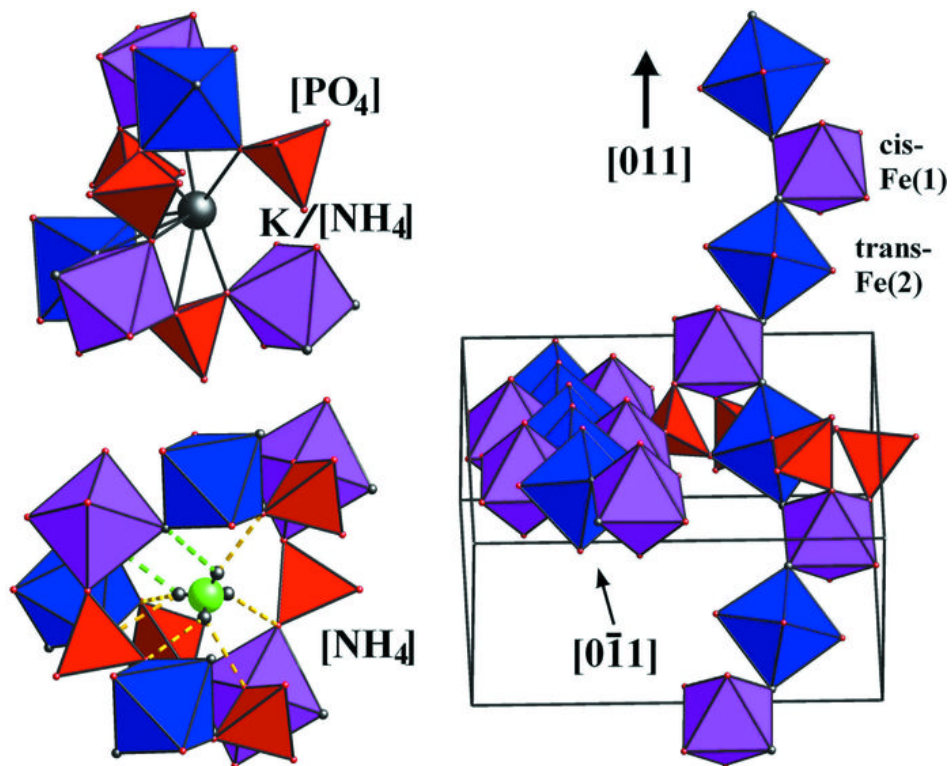


Fig. 3

