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Ammonium dipotassium hydrogen difluorophosphate at room temperature

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$(NH_4)_{0.926}K_{2.074}[H(PO_3F)_2]$ crystallized from aqueous solution after mixing stoichiometric amounts of $(NH_4)_2PO_3F$ and K_2PO_3F in a 1:1 ratio. The structure contains two sites that are occupied by symmetry-independent cations; one site is occupied by potassium and ammonium in an approximate 1:1 ratio, while the other cation site is occupied exclusively by K. The anions are connected by a very short symmetry-restricted $O\cdots H\cdots O$ hydrogen bond (~2.47 Å) into pairs $[H(PO_3F)_2]^{3-}$. Ammonium is connected to anion O atoms by two- and three-centred $N-H\cdots O$ hydrogen bonds. Fluorines do not take part in the hydrogen-bond pattern.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.001 Å
Disorder in solvent or counterion
R factor = 0.021
wR factor = 0.054
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Though the structures of K_2PO_3F (Robinson, 1958; Harrison *et al.*, 1966; Payen *et al.*, 1979) and $(NH_4)_2PO_3F$ (Krupková *et al.*, 2002) are known, no structure determination of a trioxofluorophosphate with mixed potassium and ammonium cations has been reported. The structure of $(NH_4)_{2-x}K_xPO_3F$ can be inferred by analogy to existing series of $(NH_4)_{2-x}K_xSO_4$. On the other hand, the space groups of potassium and ammonium dihydrogensulphates at room temperature are the same (*Pnam*), while the space group of K_2PO_3F (*Pnam*) at room temperature differs from that of $(NH_4)_2PO_3F$ (*Pna*2_1). The original aim of this study was the preparation and structural characterization of $(NH_4)_{2-x}K_xPO_3F$. However, the compound that we isolated and studied had a different composition than we expected.

The main features of the title structure are described in the *Abstract*. All the H atoms could be distinguished in a differ-

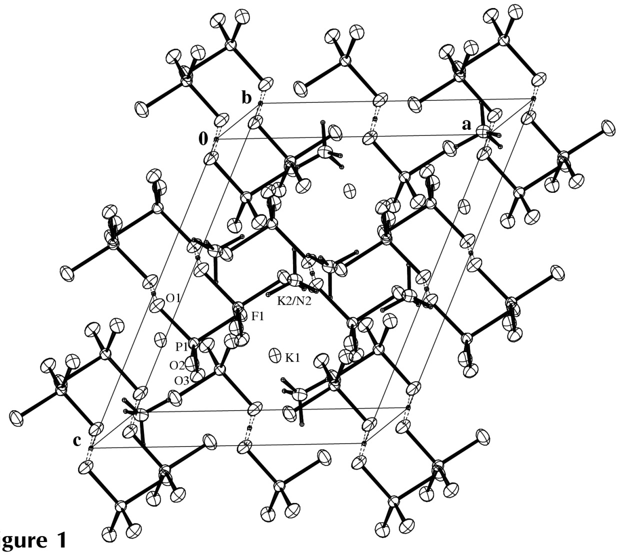

Figure 1
View of the title structure. Displacement ellipsoids are shown at the 30% probability level.

ence Fourier map. Atom H1 of the symmetry-restricted O1$\cdots$H1$\cdots$O1^{ix} hydrogen bond was found to reside on a centre of symmetry. The hydrogen bonds are listed in Table 2. A view of the unit-cell content is given in Fig. 1.

An interesting point concerns the fact that ammonium shares the same site with K2. On the other hand, the refinement showed that ammonium does not enter into the site occupied by K1. (The occupancies of K2 and ammonium are given in the CIF.) The qualitative reason is expressed by the bond-valence sums (Brese & O'Keeffe, 1991; García-Rodríguez *et al.*, 2000). The K1 site would be too overbonded [1.453 (2)] if ammonium entered into this site exclusively; for the bond-valence sum of K1 see Table 3. On the other hand, if the site K2/N2 is assumed to be occupied by potassium only, then this site would be underbonded [0.8813 (9)], in contrast to the overbonding [1.142 (1)] that is pertinent to the full occupancy of this site by ammonium. In other words, the K1 site is too small to permit ammonium to enter into this site in contrast to the site K2/N2, where optimal bonding is achieved by appropriate mixing of ammonium and potassium cations (see Table 3). The bond-valence sums were calculated using *JANA*2000 (Petříček & Dušek, 2000).

We are still trying to synthesize crystals of $(NH_4)_{2-x}K_xPO_3F$.

Experimental

The title compound was prepared from the solution from which $(NH_4)_{2-x}K_xPO_3F$ was intended to be prepared. Stoichiometric amounts of $K_2CO_3\cdot1.5H_2O$ (2.13 g) and $(NH_4)_2CO_3$ (1.24 g) in a 1:1 ratio were neutralized with H_2PO_3F. The latter compound was prepared just before the neutralization, by elution of $(NH_4)_2PO_3F\cdot H_2O$ (3.92 g) through the ionex amberlite–IR-120 (35 ml of the wet form). The resulting volume of the solution before crystallization was ~ 120 ml. The solution in a polypropylene crucible was put into a desiccator over P_4O_{10} and within two months almost all water was removed. More phases were probably present than the phase that was studied. Plate-like crystals of the title structure were under the upper crust. The crystals were fragile and the chips had a typical triangular form. The composition determined by X-ray structure determination indicates that most probably a phase that was more rich in potassium had precipitated before the title crystals were formed.

Crystal data

$(H_4N)_{0.926}K_{2.074}(HF_2O_6P_2)$
$M_r = 294.75$
Monoclinic, $C2/c$
$a = 7.9470$ (3) Å
$b = 11.6800$ (4) Å
$c = 9.7290$ (3) Å
$\beta = 113.570$ (3)°
$V = 827.71$ (5) Å^3
$Z = 4$
$D_x = 2.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4538 reflections
$\theta = 1$–27.5°
$\mu = 1.60$ mm^{-1}
$T = 293$ (2) K
Triangular plate, colourless
0.50 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{min} = 0.715$, $T_{max} = 0.796$
5391 measured reflections
942 independent reflections
908 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.054$
$S = 1.11$
942 reflections
79 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.6144P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0124 (18)

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.4843 (10)	K2—O3^{i}	2.9532 (11)
P1—O2	1.4897 (10)	K2—F1^{v}	2.9557 (10)
P1—O1	1.5358 (10)	K2—O3^{vi}	2.9599 (12)
P1—F1	1.5947 (9)	K2—O2^{vi}	2.9622 (12)
K1—O3	2.7445 (10)	K2—O2^{vii}	3.0834 (12)
K1—O2^{i}	2.7921 (10)	K2—O1^{viii}	3.1366 (11)
K1—O1^{ii}	2.8990 (11)	K2—F1^{vii}	3.1999 (10)
K2—O3^{iii}	2.8573 (11)	K2—O1^{i}	3.2848 (11)
K2—O2^{iv}	2.9058 (11)		
O3—P1—O2	117.90 (6)	O3—P1—F1	104.87 (5)
O3—P1—O1	112.56 (6)	O2—P1—F1	105.23 (5)
O2—P1—O1	112.89 (6)	O1—P1—F1	101.28 (6)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O2^{vii}	0.911 (10)	2.36 (3)	3.0834 (12)	136 (3)
N2—H2$\cdots$O3^{iii}	0.911 (10)	2.29 (4)	2.8573 (11)	120 (3)
N2—H3$\cdots$O1^{i}	0.903 (10)	2.43 (2)	3.2848 (11)	159 (5)
N2—H3$\cdots$O3^{i}	0.903 (10)	2.24 (4)	2.9532 (11)	136 (5)
N2—H4$\cdots$O2^{vi}	0.908 (10)	2.092 (18)	2.9622 (12)	160 (4)
N2—H4$\cdots$O3^{vi}	0.908 (10)	2.30 (4)	2.9599 (12)	129 (4)
N2—H5$\cdots$O2^{iv}	0.920 (10)	1.999 (14)	2.9058 (11)	168 (4)
O1—H1$\cdots$O1^{ix}	1.24	1.24	2.471 (2)	180

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

Table 3
Bond-valence sums for non-H atoms (Brese & O'Keeffee, 1991; García-Rodríguez *et al.*, 2000) for the sites in the title structure.

P	K1	K2/N2	F1	O1	O2	O3
4.766 (7)	1.184 (1)	1.002 (1)	1.032 (3)	1.914 (3)	1.931 (5)	2.010 (5)

A search of the Cambridge Structural Database (Allen, 2002) yielded 348 hits of ammonium-containing structures with R factors $\leq$ 0.05. The average ammonium N—H bond length and its s.u. given in parentheses was thus established as 0.91 (1) Å. Assuming an ideal tetrahedral H—N—H angle, the corresponding H$\cdots$H distance is 1.486 Å in the ammonium molecule. These values were applied in the *SHELXL*97 restraints (Sheldrick, 1997) by the instructions *DFIX* 0.91 0.01 N2 H2 . . . for N—H bond lengths and DANG 1.486 0.04 H2 H3 . . . . (The value 0.04 corresponds to the estimated standard uncertainty of the pertinent distances.)

Acta Cryst. (2003). E**59**, i14–i16 Jan Fábry *et al.* • $(H_4N)_{0.926}K_{2.074}(HF_2O_6P_2)$ **i15**

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Cascarano *et al.*, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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i16 Jan Fábry *et al.* • $(H_4N)_{0.926}K_{2.074}(HF_2O_6P_2)$ *Acta Cryst.* (2003). E**59**, i14–i16