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Two modifications of a $KH_2PO_4 \cdot HF$ adduct

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The structures of two modifications, (I) and (II), of potassium dihydrogenphosphate–hydrofluoric acid (1/1), $KH_2PO_4 \cdot HF$, were determined at 250 and 150 K, and at 292 and 150 K, respectively. Modifications (I) and (II) crystallize from stoichiometric aqueous solutions at 295 (1) and 308 (3) K, respectively. The H atoms were located clearly from the difference Fourier maps in each modification. The two modifications differ mainly in the arrangement of the dihydrogenphosphate anions, *i.e.* (I) contains looped dimeric and tetrameric units of the dihydrogenphosphate ions, whereas (II) contains two types of looped tetrameric unit. In addition, both structures contain a very short F—H···O hydrogen bond (2.38–2.40 Å). The K^+ ions are coordinated by O and F atoms, with similar K···O and K···F distances in both modifications.

Comment

The title compounds were prepared as part of an investigation of trioxofluorophosphates (PO_3F^{2-}) and trioxohydrogenfluorophosphates (HPO_3F^-). These anions decompose as a result of the hydrolysis reactions $H_2O + PO_3F^{2-} \rightarrow HF + HPO_4^{2-}$ and $H_2O + HPO_3F^- \rightarrow HF + H_2PO_4^-$. Therefore, it was of interest to investigate the formation of products that arise from the decomposition of the fluorophosphate anions, for example, in the reaction between dissolved KH_2PO_4 and HF.

The structures of (I) and (II) contain sheets of dihydrogenphosphate anions with attached HF molecules, and the anions in each sheet are connected to one another and to the HF molecules by hydrogen bonds. Each sheet can be viewed as being composed of two types of condensed closed loops of hydrogen-bonded dihydrogenphosphate anions (Figs. 1 and 2), dimers and tetramers in (I), and two types of tetramer in (II). The two modifications differ in the number of hydrogenphosphate ions forming these loops, the number of O atoms in the respective loops being four and ten in (I), and six and eight in (II). The loops are centrosymmetric.

The most interesting feature of each modification is a very short F—H···O hydrogen bond (Tables 2, 4, 6 and 8). The fact that fluorine is a hydrogen-bond donor is in accordance with the acid strengths of HF (pK_a = 3.20) and H_3PO_4 [pK_a = 2.16;

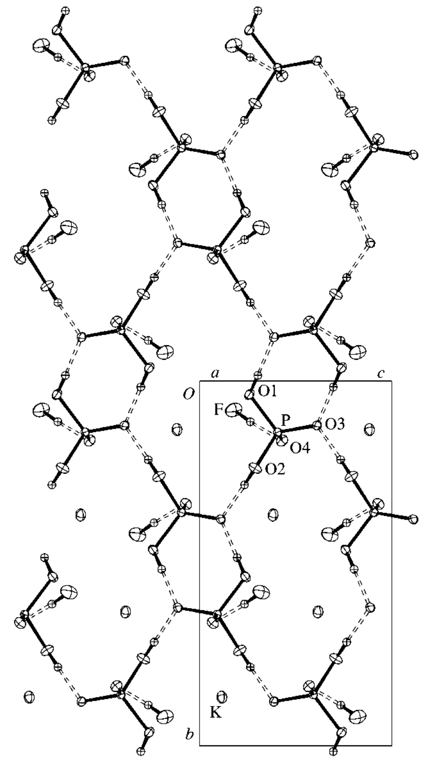

Figure 1
A view of modification (I) (250 K), projected along the *a* axis. Displacement ellipsoids are shown at the 30% probability level.

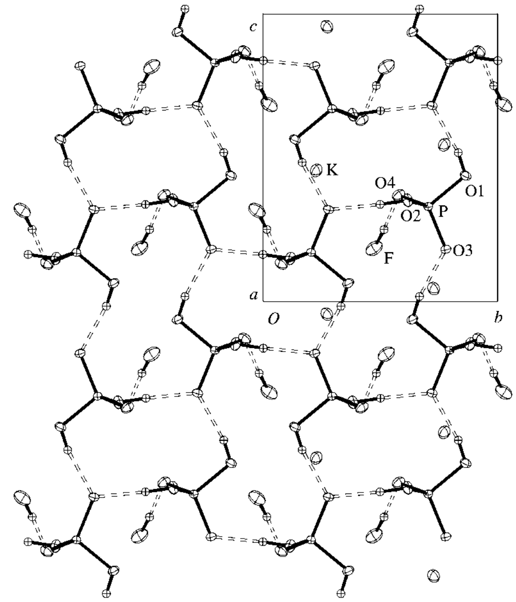

Figure 2
A view of modification (II) (292 K), projected along the *a* axis. Displacement ellipsoids are shown at the 30% probability level.

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pK_a values from Lide (1995)]. The bond length of this F—H···O hydrogen bond is very similar to that observed in the KH_2PO_3·HF adduct (F···O = 2.383 Å; Altenburg & Mootz, 1971), although the F—H···O angle [144.5 (2)°] in the latter compound is not in accordance with those in the present structures and seems to be improbably small for such a short hydrogen bond (Desiraju & Steiner, 1999).

In both modifications, the displacement parameters of the F atoms are substantially larger than those of the O atoms, and therefore the occupancy parameters of atoms F and H3 were refined. The results showed that, within 2 s.u., the occupancy of HF in either modification at each temperature is close to 1.0. Therefore, these occupational parameters were not refined in the final model. The dependence of the equivalent isotropic displacement parameters of the F and the O atoms on temperature also indicates full occupancy of the F atoms in either modification.

The K^+ cation is coordinated irregularly in both modifications. Its coordination polyhedron is formed by seven O atoms and two F atoms in each modification, with the distances to the F atoms being the shortest (Tables 1, 3, 5 and 7). In (I), the coordination polyhedron is in the form of a distorted capped tetragonal antiprism with F atoms in *cis* positions. In (II), the closest atoms (five O atoms and two F atoms) form an irregular pentagonal bipyramid around the K atom, with the F atoms in equatorial positions.

Unexpectedly, although (II) grows at a higher temperature than (I), (II) has a higher density. Furthermore, the O1···O3 and O2···O3 hydrogen bonds are significantly shorter in (I). Differential scanning calorimetry (DSC) measurements showed no reproducible anomaly that would indicate the presence of a structural phase transition. Signs of decomposition were observed above 360 K for both modifications. The structures determined at low and high temperature are quite similar, thus confirming the results of the DSC measurements. The fractional parameters of the respective non-H atoms are affected by temperature only at the third decimal place.

Experimental

To KH_2PO_4 (3.58 g; Fluka) was added commercial HF (1.38 g of 38 wt%; Spolek pro hutní a chemickou výrobu, Czech Republic) and enough water to dissolve the crystals of KH_2PO_4. The initial volume of the mixture was 20 ml. The solution was placed in a desiccator over P_4O_{10}, and a few crystals of KH_2PO_4, several millimeters in size, grew after 30 d. These crystals were hand-picked from the solution, weighed (1.20 g) and checked on a diffractometer. A batch of crystals of modification (II) of the adduct grew from the remaining solution after 14 d. The shape of these crystals clearly differed from those of the first batch, and a crystal from the second batch was used for the structure determination of modification (II). The preparation was repeated several times with KH_2PO_4 (2.38 g) and the same quantities of the other reagents as given above, and it was found that the growth of a particular modification depended on the ambient temperature; at 295 (1) K, crystals of modification (I) were obtained, whereas crystallization at 308 (3) K yielded modification (II). The growth of the crystal of modification (II) that was used for the structure determination can be explained by a temporary increase of the temperature in the desiccator. The evolution of diffraction patterns recorded on a diffractometer equipped with a position-sensitive detector showed the gradual appearance of Debye rings, thus indicating that the crystals are unstable when kept in a glass capillary. For this reason, the data collection of modification (I) was carried out under a stream of nitrogen gas. If crystals of either modification are left in a desiccator over P_4O_{10} for several months, the crystals become opaque and covered with a white powder. DSC measurements were carried with a Perkin Elmer DSC7 instrument and *PYRIS* software (Perkin Elmer, 2001) over the temperature range 95–390 K at a scanning rate of 10 K min^{-1}.

Modification (I) at 250 K

Crystal data

KH_2PO_4·HF
M_r = 156.09
Monoclinic, $P2_1/c$
a = 6.1903 (1) Å
b = 12.0733 (2) Å
c = 7.0741 (1) Å
β = 115.6700 (8)°
V = 476.519 (13) $Å^3$
Z = 4
D_x = 2.176 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1419 reflections
θ = 1.0–30.0°
μ = 1.38 mm^{-1}
T = 250 (1) K
Irregular, colourless
0.50 × 0.47 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *PLATON* (Spek, 2003)
T_{min} = 0.669, T_{max} = 0.736
7968 measured reflections
1381 independent reflections
1318 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 30.1°
$h = -8 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.057
S = 1.11
1381 reflections
77 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.1671P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.28 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.50 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.398 (11)

Table 1
Selected geometric parameters (Å) for modification (I) at 250 K.

K—F^{i}	2.6371 (9)	K—$O2^{vi}$	3.0066 (10)
K—F^{ii}	2.7141 (10)	K—$O1^{ii}$	3.2045 (9)
K—$O2^{iii}$	2.8880 (9)	P—O1	1.5723 (8)
K—$O3^{iv}$	2.9007 (9)	P—O2	1.5718 (8)
K—$O4^{iv}$	2.9143 (9)	P—O3	1.5102 (8)
K—$O4^{v}$	2.9802 (9)	P—O4	1.5064 (8)
K—$O1^{vi}$	2.9934 (9)		

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

Table 2
Hydrogen-bonding geometry (Å, °) for modification (I) at 250 K.

D—H···A	D—H	H···A	D···A	D—H···A
F—H3···O4	0.88 (3)	1.52 (3)	2.3953 (12)	176 (3)
O1—H1···$O3^{vii}$	0.90 (2)	1.70 (2)	2.5999 (11)	175.5 (19)
O2—H2···$O3^{ix}$	0.87 (2)	1.67 (2)	2.5365 (11)	174 (2)

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

Modification (I) at 150 K

Crystal data

$KH_2PO_4 \cdot HF$
$M_r = 156.09$
Monoclinic, $P2_1/c$
$a = 6.1624$ (1) Å
$b = 12.0744$ (2) Å
$c = 7.0448$ (1) Å
$\beta = 115.7400$ (9)°
$V = 472.172$ (13) Å^3
$Z = 4$

$D_x = 2.196$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1412 reflections
$\theta = 1.0$–30.0°
$\mu = 1.39$ mm^{-1}
$T = 150$ (1) K
Irregular, colourless
0.50 × 0.47 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *PLATON* (Spek, 2003)
$T_{\min} = 0.662$, $T_{\max} = 0.733$
8085 measured reflections
1373 independent reflections

1322 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.038$
$\theta_{\max} = 30.0°$
$h = -8 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.059$
$S = 1.23$
1373 reflections
77 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 0.1281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.165 (7)

Table 3
Selected geometric parameters (Å) for modificatiion (I) at 150 K.

K—F$^{\text{i}}$	2.6286 (8)	K—O2$^{\text{vi}}$	2.9864 (9)
K—F$^{\text{ii}}$	2.7003 (8)	K—O1$^{\text{ii}}$	3.1959 (8)
K—O2$^{\text{iii}}$	2.8729 (8)	P—O1	1.5737 (8)
K—O3$^{\text{iv}}$	2.8864 (8)	P—O2	1.5737 (8)
K—O4$^{\text{iv}}$	2.9021 (8)	P—O3	1.5122 (8)
K—O4$^{\text{v}}$	2.9582 (8)	P—O4	1.5093 (8)
K—O1$^{\text{vi}}$	2.9764 (8)		

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

Table 4
Hydrogen-bonding geometry (Å, °) for modification (I) at 150 K.

D—H···A	D—H	H···A	D···A	D—H···A
F—H3···O4	0.92 (2)	1.48 (2)	2.3998 (10)	178.5 (9)
O1—H1···O3$^{\text{vii}}$	0.92 (2)	1.68 (2)	2.5955 (11)	175.5 (19)
O2—H2···O3$^{\text{ix}}$	0.86 (2)	1.67 (2)	2.5310 (11)	176 (2)

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

Modification (II) at 292 K

Crystal data

$KH_2PO_4 \cdot HF$
$M_r = 156.09$
Monoclinic, $P2_1/c$
$a = 6.5004$ (2) Å
$b = 7.6116$ (2) Å
$c = 9.5029$ (2) Å
$\beta = 101.1500$ (16)°
$V = 461.31$ (2) Å^3
$Z = 4$

$D_x = 2.247$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5501 reflections
$\theta = 1.0$–30.0°
$\mu = 1.43$ mm^{-1}
$T = 292$ (2) K
Plate, colourless
0.65 × 0.50 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.355$, $T_{\max} = 0.582$
8372 measured reflections
1344 independent reflections

1305 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.041$
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.071$
$S = 1.11$
1344 reflections
77 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0480P)^2 + 0.1751P]$ where $P = (F_o^2+2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.147 (9)

Table 5
Selected geometric parameters (Å) for modification (II) at 292 K.

K—F$^{\text{viii}}$	2.6526 (11)	K—O2$^{\text{xi}}$	3.1673 (11)
K—F$^{\text{x}}$	2.7650 (13)	K—O1$^{\text{iv}}$	3.3668 (12)
K—O4	2.7933 (11)	K—F	3.4003 (12)
K—O3$^{\text{xi}}$	2.9026 (11)	P—O1	1.5696 (10)
K—O2$^{\text{xii}}$	2.9301 (10)	P—O2	1.5699 (10)
K—O4$^{\text{iv}}$	2.9800 (11)	P—O3	1.5038 (10)
K—O1$^{\text{xiii}}$	3.0550 (10)	P—O4	1.5089 (10)

Symmetry codes: (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $2-x, 1-y, 1-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (x) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xii) $1-x, 1-y, 1-z$; (xiii) $x, y-1, z$.

Table 6
Hydrogen-bonding geometry (Å, °) for modification (II) at 292 K.

D—H···A	D—H	H···A	D···A	D—H···A
F—H3···O4	0.90 (3)	1.48 (3)	2.3787 (14)	175 (3)
O1—H1···O3$^{\text{xv}}$	0.83 (3)	1.82 (3)	2.6386 (14)	168 (3)
O2—H2···O3$^{\text{xi}}$	0.86 (3)	1.73 (3)	2.5898 (14)	174 (3)

Symmetry codes: (xi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xv) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

Modification (II) at 150 K

Crystal data

$KH_2PO_4 \cdot HF$
$M_r = 156.09$
Monoclinic, $P2_1/c$
$a = 6.4480$ (2) Å
$b = 7.5660$ (2) Å
$c = 9.4760$ (3) Å
$\beta = 101.2370$ (18)°
$V = 453.43$ (2) Å^3
$Z = 4$

$D_x = 2.287$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4563 reflections
$\theta = 1.0$–30.0°
$\mu = 1.45$ mm^{-1}
$T = 150$ (2) K
Plate, colourless
0.65 × 0.50 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.423$, $T_{\max} = 0.571$
6815 measured reflections
1297 independent reflections

1265 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.038$
$\theta_{\max} = 30.1°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.18$
1297 reflections
77 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.2532P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.063 (9)

Table 7
Selected geometric parameters (Å) for modification (II) at 150 K.

K—F$^{\text{viii}}$	2.6416 (9)	K—O2$^{\text{xi}}$	3.1441 (10)
K—F$^{\text{x}}$	2.7382 (10)	K—O1$^{\text{iv}}$	3.3390 (11)
K—O4	2.7749 (10)	K—F	3.3821 (10)
K—O3$^{\text{xi}}$	2.8827 (10)	P—O1	1.5722 (10)
K—O2$^{\text{xii}}$	2.9096 (10)	P—O2	1.5714 (10)
K—O4$^{\text{iv}}$	2.9459 (10)	P—O3	1.5057 (10)
K—O1$^{\text{xiii}}$	3.0114 (10)	P—O4	1.5127 (9)

Symmetry codes: (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $2 - x, 1 - y, 1 - z$; (viii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (x) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xi) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xii) $1 - x, 1 - y, 1 - z$; (xiii) $x, y - 1, z$.

Table 8
Hydrogen-bonding geometry (Å, °) for modification (II) at 150 K.

D—H···A	D—H	H···A	D···A	D—H···A
F—H3···O4	0.90 (3)	1.48 (3)	2.3827 (13)	176 (3)
O1—H1···O3$^{\text{xv}}$	0.82 (3)	1.83 (3)	2.6342 (14)	169 (3)
O2—H2···O3$^{\text{xi}}$	0.83 (3)	1.76 (3)	2.5846 (13)	174 (3)

Symmetry codes: (xi) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xv) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

For both modifications at each temperature, data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* 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 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1019). Services for accessing these data are described at the back of the journal.

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