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Bis(ammonium) fluorophosphate at room temperature

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The title room-temperature phase of $(NH_4)_2(PO_3F)$ is orthorhombic ($Pna2_1$) and is related to the β-K_2SO_4 structure family. The title structure consists of ammonium cations, NH_4^+, and fluorophosphate anions, $(PO_3F)^{2-}$. These ions are connected by N—H···O hydrogen bonds. Two-centre N—H···F hydrogen bonds are not present in the structure. Phase transitions were detected at 251±2 and 274±2 K during cooling and heating, respectively.

Comment

The present structure determination had several objectives. First, although the preparation of the title structure has been described previously (*e.g.* Schülke & Kayser, 1991), and its powder patterns have even been recorded in the Powder Diffraction File (ICDD, 2001) as unindexed entries Nos. 18-0097 and 21-0022, its structure has not been reported, although the hydrate, $(NH_4)_2(PO_3F)\cdot H_2O$, was determined by Berndt & Sylvester (1972), Perloff (1972) and Durand *et al.* (1978).

Secondly, since the fluorophosphate anion is closely related to the sulfate anion, it is of interest to compare the structure of the title compound with that of $(NH_4)_2SO_4$. In particular, it is of great interest to find out whether or how the fluorine is involved in the hydrogen bonding. There are examples, such as NH_4SO_3F (O'Sullivan *et al.*, 1970), the α and β modifications of NH_4HPO_3F (Prescott *et al.*, 2002), $NH_4PO_2F_2$ (Harrison & Trotter, 1969) and $(NH_4)_2(PO_3F)\cdot H_2O$ (Perloff, 1972), where fluorine does not participate in the hydrogen bonding at all.

Thirdly, a phase transition can be expected in the title compound since, in the related compound $(NH_4)_2SO_4$, a ferroelectric phase transition ($Pnam \rightarrow Pna2_1$) was observed at about 223 K (*e.g.* Mattias & Remeika, 1956).

$(NH_4)_2SO_4$ belongs to the β-K_2SO_4 structure type. Okaya *et al.* (1958) mentioned the formation of a superstructure at room temperature in some cases. Hoshino *et al.* (1958) sometimes observed the doubling of the *b* and *c* axes with respect to the basic unit cell. The structure of $(NH_4)_2SO_4$ has been determined several times by single-crystal diffraction methods, both below and above the phase transition. Schlemper & Hamilton (1966) carried out a neutron diffraction study of the ferroelectric and paraelectric phases, Hasebe (1981) studied the structure by X-ray diffraction at several temperatures, both below and above the phase transition, and González-Silgo *et al.* (1997) redetermined the structure of the paraelectric phase. All these determinations coincided in finding that the sulfate is fairly regular. Jain & Bist (1974), however, inferred from Raman spectra that the sulfate anion should be distorted during the phase transition.

In contrast with the sulfate molecules, all these studies showed that the ammonium cations are quite irregular. For example, Schlemper & Hamilton (1966) stated that the H—N—H angles ranged from 100.2 (8) to 116 (1)° and from 104.7 (9) to 118.5 (2)° for the two independent ammonium cations in the paraelectric phase. Moreover, Hasebe (1981) found that both ammonium ions are disordered, both below and above the phase transition temperature, in contrast with the results published by Schlemper & Hamilton (1966) and González-Silgo *et al.* (1997).

The present structure determination of the title compound shows that it is closely related to the β-K_2SO_4 prototypic phase. Furthermore, no constituent groups of the title compound are disordered at room temperature. The ammonium groups are distorted in a similar way to those in $(NH_4)_2SO_4$, and the F atom, indeed, is not involved in two-centred hydrogen bonds (Table 2), in contrast with the O atoms. The terminology used herein for the characterization of the hydrogen bonds is based on Jeffrey (1995).

Table 2 shows that each of the atoms O1 and O3 accepts three H atoms, while atom O2 accepts two H atoms *via* two-centred hydrogen bonds. However, the small value of the N2—H8···$O2^{ii}$ angle and the presence of a short N2···$O2^{vi}$

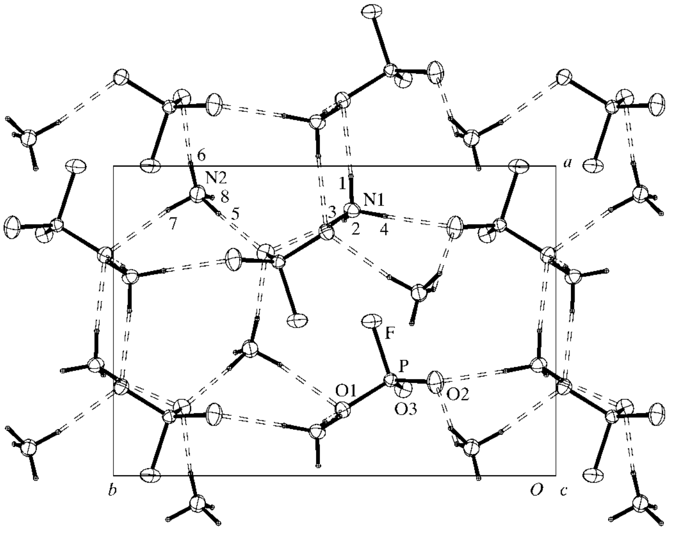

Figure 1
A view of the unit cell of $(NH_4)_2(PO_3F)$ along the *c* axis. Symmetry-independent atoms are labelled and N—H···O hydrogen bonds are shown as dashed bonds. Displacement ellipsoids are drawn at the 30% probability level and arabic numerals refer to H atoms.

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contact in N2—H8···O2^{vi} [symmetry codes: (ii) $1-x, 1-y, z-\frac{1}{2}$; (vi) $\frac{3}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$] enable us to consider these latter two contacts as bifurcated N—H···O hydrogen bonds. The values of the H···O—P angles (see *Supplementary data*) indicate participation of O-atom orbitals in the hydrogen bonding.

The hydrogen bonding in the title compound differs from that of $(NH_4)_2SO_4$, where each anionic ligand (*i.e.* O in the sulfate anion), in contrast with F in the title structure, is an acceptor of a two-centered hydrogen bond (Schlemper & Hamilton, 1966). On the other hand, most of the hydrogen bonds in $(NH_4)_2SO_4$ are weaker than those in $(NH_4)_2(PO_3F)$.

During cooling of three samples, we observed cracking of the single crystals. More careful cooling in 2 K steps showed that this cracking takes place between 252 and 250 K, most probably due to a phase transition. A phase transition was confirmed by a differential scanning calorimetry (DSC) experiment (see *Experimental*). The DSC curves show a broad (20 K) peak with an extrapolated onset, *i.e.* the phase transition temperature is at 251 ± 2 K on cooling (exothermic effect) and 274 ± 2 K on heating (endothermic effect). The absolute value of the enthalpy change was 3 ± 0.5 J g^{-1}. The temperature hysteresis and cracking of the crystals suggest a first-order character for the transition.

The observed DSC peaks were sometimes corrugated. This, together with the width of the peaks, indicates that the transition does not start simultaneously in different parts of the sample. An additional peak was observed at ~145 K. The enthalpy change of this peak was dependent on the thermal history of the sample; previous heating above 310 K increased the enthalpy change. This peak was ascribed to the 5–10 mass% of $(NH_4)H_2PO_4$ present in the sample; *cf.* the phase transition temperature of 148 K quoted in the literature (*e.g.* Pérès *et al.*, 1997). This impurity obviously originated from the hydrolysis of $(NH_4)_2(PO_3F)$.

The stability of β-K_2SO_4 phases was discussed in Fábry & Pérez-Mato (1994). It was shown that the structural instability of members of this family can be related to the ratios of the pseudo-hexagonal unit-cell axis (for the setting of the title compound, this is the *a* axis) to the other two. In $(NH_4)_2(PO_3F)$, the *a*:*b* ratio of 0.700 is extremely small, while the *a*:*c* ratio of 1.315 is relatively high. These values indicate the possibility of a phase transition such as that described above. For comparison, the respective values for the *a*:*b* and *a*:*c* ratios in K_2SO_4 (McGinnety, 1972) are 0.742 and 1.297, respectively, while for the paraelectric phase of $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966), they are 0.732 and 1.299, respectively.

File No. 18-0097 of the Powder Diffraction File (ICDD, 2001) can be well indexed using the present structure determination, while file No. 21-0022 cannot.

Work on the investigation of the ferroic properties, especially the ferroelectricity, of the title compound, and the structure determination of a low-temperature phase, are being undertaken. Preparation of samples of the systems K_2PO_3F and $(NH_4)_{2-x}K_xPO_3F$, as well as of K_2PO_3F–K_2SO_4 and $(NH_4)_2SO_4$–$(NH_4)_2(PO_3F)$, is in progress.

Experimental

The title compound was prepared using a slight modification of the method of Schülke & Kayser (1991). Instead of NH_4HF_2, we used the product formed immediately after the neutralization of $(NH_4)_2CO_3$ with HF in a 1:2 molar ratio, and the mixture (calculated for 20 g of the product) was then heated to 438 (5) K for 2 h. The product was dissolved in water and acetone and left to crystallize at room temperature over P_4O_{10}. The precipitated product was a mixture of crystals of $(NH_4)_2(PO_3F)$ and $(NH_4)H_2PO_4$, which differed in their crystal habit; $(NH_4)_2(PO_3F)$ crystallized as tiny tetrahedra, while $(NH_4)H_2PO_4$ crystallized as tiny plates. $(NH_4)_2(PO_3F)$ is slightly hygroscopic; at higher relative humidity, it is deliquescent, changing to the monohydrate. Further preparations with $(NH_4)HF_2$ showed that a longer heating time resulted in the subsequent precipitation of $(NH_4)_2(PO_3F)\cdot H_2O$ or $(NH_4)_2(PO_3F)$. Samples from other batches, which were prepared by the unmodified method of Schülke & Kayser (1991), were used for the differential scanning calorimetry (DSC) experiment [PerkinElmer Pyris Diamond DSC, using *Pyris Software* (PerkinElmer Instruments, 2001), m = 7–20 mg, scanning rate 10 K min^{-1}, temperature calibration on extrapolated onsets of phase transition peaks in cyclopentane and cyclohexane, aluminium pans]. The $(NH_4)_2(PO_3F)$ crystals from these further batches grew as needles.

Crystal data

$(NH_4)_2(PO_3F)$
M_r = 134.05
Orthorhombic, $Pna2_1$
a = 7.9481 (2) Å
b = 11.3472 (3) Å
c = 6.0425 (3) Å
V = 544.97 (3) Å^3
Z = 4
D_x = 1.633 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4119 reflections
θ = 1.0–27.5°
μ = 0.44 mm^{-1}
T = 292 (1) K
Pyramid, colourless
0.43 × 0.34 × 0.30 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.834, T_{max} = 0.879
6096 measured reflections

1211 independent reflections
1173 reflections with $I > 3\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -7 \rightarrow 7$

Refinement

Refinement on F
R = 0.022
wR = 0.031
S = 1.76
1211 reflections
96 parameters
All H-atom parameters refined
$w = 1/(\sigma^2F + 0.0001F^2)$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: Becker & Coppens (1974) type 1 Lorentzian isotropic
Extinction coefficient: 1.38 (19) × 10^{-4}
Absolute structure: Flack (1983)
Flack parameter = −0.01 (9)

Table 1
Selected geometric parameters (Å, °).

P—F	1.5875 (8)	P—O2	1.489 (1)
P—O1	1.512 (1)	P—O3	1.503 (1)
F—P—O1	102.79 (5)	O1—P—O2	115.41 (7)
F—P—O2	104.55 (6)	O1—P—O3	112.12 (7)
F—P—O3	103.73 (7)	O2—P—O3	116.17 (7)

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

Table 2

Geometric details of the N—H···O hydrogen bonds and the closest N—H···F contacts; N···O and N···F distances up to 3.3 Å are included (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···F	0.88 (2)	2.80 (2)	2.898 (1)	87 (1)
N1—H3···F	0.91 (2)	2.76 (2)	2.898 (1)	89 (1)
N1—H4···F	0.89 (2)	2.73 (2)	2.898 (1)	92 (1)
N1—H1···O1^{i}	0.87 (1)	1.98 (1)	2.851 (2)	173 (2)
N1—H2···O1^{ii}	0.88 (2)	1.95 (2)	2.829 (2)	172 (4)
N1—H3···O3^{iii}	0.91 (2)	1.99 (2)	2.879 (2)	164 (2)
N1—H4···O2^{iv}	0.89 (2)	1.92 (2)	2.812 (2)	176 (2)
N2—H6···F^{v}	0.89 (2)	2.96 (2)	3.197 (1)	97 (1)
N2—H7···F^{v}	0.86 (2)	2.61 (2)	3.197 (1)	126 (2)
N2—H7···O1^{v}	0.86 (2)	2.01 (2)	2.864 (2)	171 (2)
N2—H8···O2^{ii}	0.88 (2)	2.16 (2)	2.877 (2)	139 (2)
N2—H8···O2^{vi}	0.88 (2)	2.74 (2)	3.160 (2)	111 (2)
N2—H5···O3^{iii}	0.92 (2)	1.85 (2)	2.761 (2)	174 (2)
N2—H6···O3^{vii}	0.89 (2)	2.02 (2)	2.902 (2)	171 (2)

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

The H atoms were clearly visible in the difference Fourier map and were refined isotropically. The resulting N—H distances varied from 0.78 (2) to 0.91 (2) Å, while the angles varied from 101 (2) to 117 (2)°. Therefore, the bond lengths to the H atoms were restrained to 0.90 (5) Å. These restraints to the N—H distances had a negligible influence on the final *R* factor values. Applying restraints to the H—N—H angles resulted in higher *R* factors of 0.023 and 0.033 for observed and all reflections, respectively. Therefore, having regard to the known shape of ammonium ions in related compounds determined by neutron diffraction, no restraints were applied to the H—N—H angles.

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: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *JANA*2000 (Petříček & Dušek, 2000); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *JANA*2000.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1363). Services for accessing these data are described at the back of the journal.

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