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Ethylenediammonium fluorotrioxophosphate at 150 K

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The structure of the title compound, $H_3NCH_2CH_2NH_3^{2+}\cdot FPO_3^{2-}$, has been determined at 150 K. Ions are connected by N—H···O hydrogen bonds, with the F atom involved in a weak C—H···F hydrogen bond (F···H = 2.48 Å). The ethylenediammonium dication is present in its less common conformation, with an N—C—C—N torsion angle of −65.92 (14)°. A reversible glass-like phase transition is observed at 197±2 K; however, the crystal structures determined at 292 and 150 K are similar.

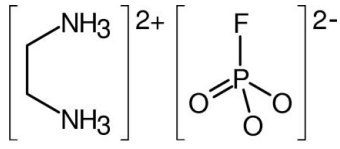
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.076
Data-to-parameter ratio = 15.7

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

Comment

The title compound, (I), was synthesized during our studies of fluorophosphates (Fábry *et al.*, 2006) and its structure determined at 292 K [deposited with Cambridge Structural Database (CSD) (Version 5.27, update of May 2006; Allen, 2002; CCDC 606529)] and 150 K (reported here). All bond lengths, including P—F, are normal (Table 1). Ions are connected by N—H···O and C—H···O hydrogen bonds (Fig. 1 and Table 2). Each of the constituent ions, *viz.* ethylenediammonium and fluorotrioxophosphate, is attached to five different ions through N—H···O contacts (Fig. 2 and Table 2). The F atom is not involved in two-centred N—H···F hydrogen bonds (Jeffrey, 1995) in the presence of the O-atom acceptors. This is in accordance with previous observations in fluorotrioxophosphates or fluorotrioxosulfates (Dunitz & Taylor, 1997; Prescott *et al.*, 2000). However, the F atom in (I) is involved in a weak C—H···F hydrogen bond (Desiraju & Steiner, 1999; Table 2).



(I)

A search of the CSD for structures containing ethylenediammonium shows that the distribution of N—C—C—N absolute torsion angles is confined to two intervals for almost all structures: 161–180°, with 275 hits, and 62–90°, with 101 hits. Compound (I) belongs to the less populated conformer, with an N1—C1—C2—N2 torsion angle of −65.92 (14)°.

Differential scanning calorimetry (DSC) experiments showed a glass-like phase transition for (I) at 197±2 K (see archived CIF for experimental details on DSC). Therefore the structure was determined above and below this temperature. A comparison of the two structure determinations, at 292 and 150 K, revealed differences of the corresponding fractional

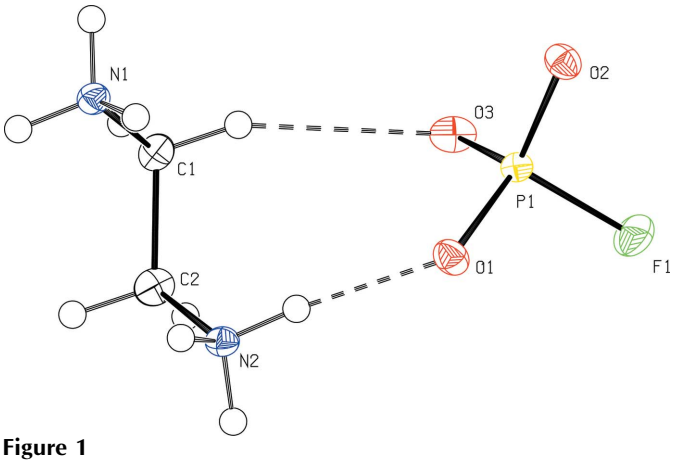


Figure 1
View of (I) at 150 K, with displacement ellipsoids drawn at the 50% probability level. The dashed lines represent hydrogen bonds.

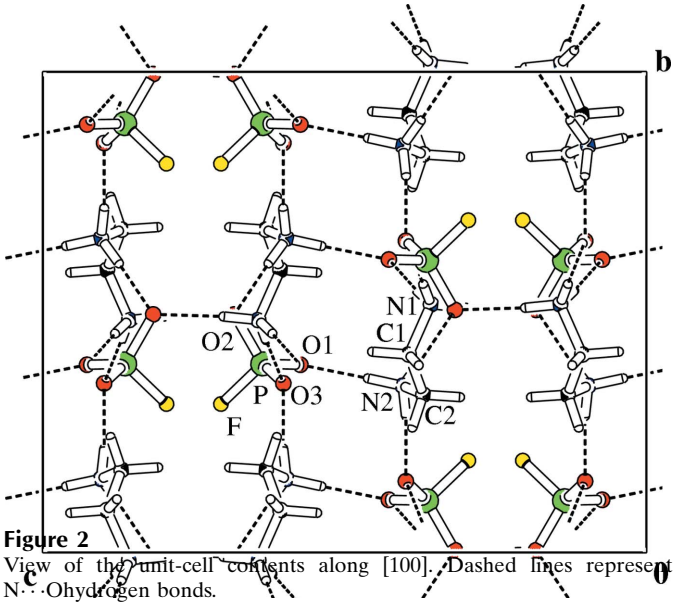


Figure 2
View of the unit-cell contents along [100]. Dashed lines represent N···O hydrogen bonds.

coordinates for non-H atoms in the interval 0.001–0.004 for the *x* coordinate, while differences for other coordinates are one order of magnitude smaller. Differences divided by the average of the pertinent s.u. values fall in the range 1–40 (*x* coordinates). These values are comparable to those regarding modifications of KH_2PO_4·HF (Krupková *et al.*, 2003), for which no phase transition has been detected, in contrast to (I).

The glass-like reversible phase transition observed in (I) does not contradict the moderate displacements of the atoms when varying the temperature. A repeated data collection at both temperatures on the same crystal showed good reproducibility of the measurement (coordinate/s.u. ratios are less than 3 for structure refinements based on data measured at the same temperature). X-ray data thus confirm the reversibility of the phase transition in (I).

Experimental

The title compound was prepared by neutralization of stoichiometric amounts (0.0312 mol) of ethylenediamine and H_2PO_3F. The starting material H_2PO_3F was obtained from an 8 ml aqueous solution of $(NH_4)_2PO_3F·H_2O$ (0.0312 mol) that was passed through a catex column (Schülke & Kayser, 1991), followed by recrystallization of the raw material in order to remove $NH_4H_2PO_4$. The volume of the eluted solution of H_2PO_3F was about 150 ml. The solution was placed in a desiccator over P_4O_{10}, at 292 K. The volume was reduced to ~5 ml over a fortnight and colourless 5–8 mm long crystals appeared. Owing to their hygroscopic nature, crystals were mounted in a capillary for data collection.

Crystal data

$C_2H_{10}N_2^{2+}·FO_3P^{2-}$
M_r = 160.1
Orthorhombic, *Pbca*
a = 6.7916 (10) Å
b = 12.694 (9) Å
c = 15.930 (7) Å
V = 1373.4 (12) Å^3
Z = 8
D_x = 1.548 Mg m^{-3}
Mo *K*α radiation
μ = 0.37 mm^{-1}
T = 150 K
Block, colourless
0.41 × 0.32 × 0.25 mm

Data collection

Oxford Diffraction XCalibur-2 CCD diffractometer
ω scans
Absorption correction: none
16882 measured reflections
1588 independent reflections
1259 reflections with $I > 3\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.076
S = 1.41
1588 reflections
101 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/(\sigma^2(I) + 0.0016I^2)$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.0029 (8)

Table 1
Selected bond lengths (Å).

P1—O1	1.5147 (9)	N1—C1	1.4871 (17)
P1—O2	1.5188 (9)	C1—C2	1.5129 (19)
P1—O3	1.5108 (9)	C2—N2	1.4952 (17)
P1—F1	1.5945 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1C1···O3	0.97	2.49	3.3915 (16)	155
C2—H1C2···F1^{i}	0.97	2.48	3.2478 (15)	136
N1—H1N1···O3^{ii}	0.91 (2)	1.86 (2)	2.7648 (14)	178 (2)
N1—H2N1···O2^{iii}	0.91 (2)	1.87 (2)	2.7786 (14)	174 (1)
N1—H3N1···O1^{iv}	0.96 (2)	1.83 (2)	2.7790 (14)	173 (2)
N2—H1N2···O3^{v}	0.93 (2)	1.84 (2)	2.7520 (14)	168 (2)
N2—H2N2···O1	0.91 (2)	1.86 (2)	2.7655 (15)	172 (1)
N2—H3N2···O2^{iv}	0.94 (2)	1.87 (2)	2.8104 (14)	178 (1)

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

Though all the H atoms were found in a difference Fourier map, the carbon-bound H atoms were positioned geometrically (C—H = 0.97 Å) and refined as riding , with $U_{iso} = 1.2U_{eq}$(C). H atoms of the ammonium groups were found in difference maps and their coordinates refined. The shortest and the longest N—H bond lengths are 0.907 (17) and 0.958 (17) Å [corresponding values are 0.92 (2) and

0.96 (2) Å for the determination at 292 K]. Displacement parameters for these H atoms were fixed at $U_{iso} = 1.2U_{eq}$(N).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *JANA2000* (Petříček *et al.*, 2005); program(s) used to refine structure: *JANA2000*; molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *JANA2000*.

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