Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two polymorphs of bis(2-carbamoylguanidinium) fluorophosphonate dihydrate

Jan Fábry,[a]* Michaela Fridrichová,[b] Michal Dušek,[a] Karla Fejfarová[a] and Radmila Krupková[a]

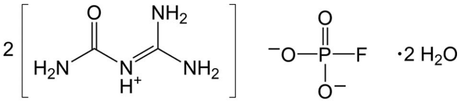
[a]Institute of Physics of the Czech Academy of Sciences, v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic, and [b]Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 43 Prague 2, Czech Republic
Correspondence e-mail: fabry@fzu.cz

Received 14 November 2011
Accepted 9 December 2011
Online 6 January 2012

Two polymorphs of bis(2-carbamoylguanidinium) fluorophosphonate dihydrate, $2C_2H_7N_4O^+\cdot FO_3P^{2-}\cdot 2H_2O$, are presented. Polymorph (I), crystallizing in the space group *Pnma*, is slightly less densely packed than polymorph (II), which crystallizes in *Pbca*. In (I), the fluorophosphonate anion is situated on a crystallographic mirror plane and the O atom of the water molecule is disordered over two positions, in contrast with its H atoms. The hydrogen-bond patterns in both polymorphs share similar features. There are O—H···O and N—H···O hydrogen bonds in both structures. The water molecules donate their H atoms to the O atoms of the fluorophosphonates exclusively. The water molecules and the fluorophosphonates participate in the formation of $R_4^4(10)$ graph-set motifs. These motifs extend along the *a* axis in each structure. The water molecules are also acceptors of either one [in (I) and (II)] or two [in (II)] N—H···O hydrogen bonds. The water molecules are significant building elements in the formation of a three-dimensional hydrogen-bond network in both structures. Despite these similarities, there are substantial differences between the hydrogen-bond networks of (I) and (II). The N—H···O and O—H···O hydrogen bonds in (I) are stronger and weaker, respectively, than those in (II). Moreover, in (I), the shortest N—H···O hydrogen bonds are shorter than the shortest O—H···O hydrogen bonds, which is an unusual feature. The properties of the hydrogen-bond network in (II) can be related to an unusually long P—O bond length for an unhydrogenated fluorophosphonate anion that is present in this structure. In both structures, the N—H···F interactions are far weaker than the N—H···O hydrogen bonds. It follows from the structure analysis that (II) seems to be thermodynamically more stable than (I).

Comment

Interest in the synthesis of the title structures was aroused by the preparation and structure determination of a series of mixed crystals of 2-carbamoylguanidinium hydrogen fluorophosphonate and 2-carbamoylguanidinium hydrogen phosphite (Fábry *et al.*, 2012*a*). Pure 2-carbamoylguanidinium hydrogen phosphite (Fridrichová, Němec, Císařová & Němec, 2010) shows interesting physical properties (Fridrichová, Němec, Císařová & Chvostová, 2010; Kroupa & Fridrichová, 2011), namely spontaneous noncollinear second-harmonic generation of light. This property of second-harmonic generation is related to the constitutent cation, which shows significant hyperpolarizability (Fridrichová, Němec, Císařová & Němec, 2010). Therefore, we were interested in the preparation of crystals with different cation–anion molar ratios of 2-carbamoylguanidinium and fluorophosphonate than in the above-mentioned structures (Fábry *et al.*, 2012*a*). The suggested ratios included a 2:1 cation–anion molar ratio, which was expected to yield a structure with a nonhydrogenated fluorophosphonate. Two such compounds have now been prepared and their structures are reported below.



(I)/(II)

Bis(2-carbamoylguanidinium) fluorophosphonate dihydrate crystallizes in the space group *Pnma* to give polymorph (I). It also crystallizes in the space group *Pbca* to give polymorph (II), which has a doubled unit-cell volume and is slightly more densely packed; the volume ratio per formula unit is 0.9917 compared with (I). In (I), the fluorophosphonate anion is situated on a crystallographic mirror plane and the O atom of the water molecule is disordered, in contrast with its H atoms. This means that two slightly different hydrogen-bond patterns co-exist in the same structure.

The molecules (Figs. 1 and 2) are linked together by water–fluorophosphonate O—H···O hydrogen bonds and N—H···O hydrogen bonds (Tables 2 and 4) in both structures. Fluorine – as is usual (Dunitz & Taylor, 1997) – avoids participation in strong hydrogen bonds, although there is, for example, a relatively short N41—H1N41···F1^{iii} interaction in (II) [symmetry code: (iii) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$; Table 4]. The oxo groups [atoms O3 in (I), and O41 and O42 in (II)] participate in intra- and intermolecular N—H···O hydrogen bonds with quite acute angles (Tables 2 and 4).

The water–fluorophosphonate O—H···O hydrogen bonds result in the same $R_4^4(10)$ graph-set motif (Etter *et al.*, 1990) in both structures (Figs. 3 and 4). These interactions contribute significantly to the formation of a three-dimensional hydrogen-bond network in each structure. However, there is an important difference between the two polymorphs in this respect. In (I), the 2-carbamoylguanidinium cations and fluorophosphonate anions form ribbons parallel to the *a* axis (Fig. 5), while the water molecules are indispensable for the construction of a three-dimensional hydrogen-bond network by linking these ribbons together. On the other hand, in (II), only the 2-carbamoylguanidinium cations and fluorophos-

doi:10.1107/S0108270111053133

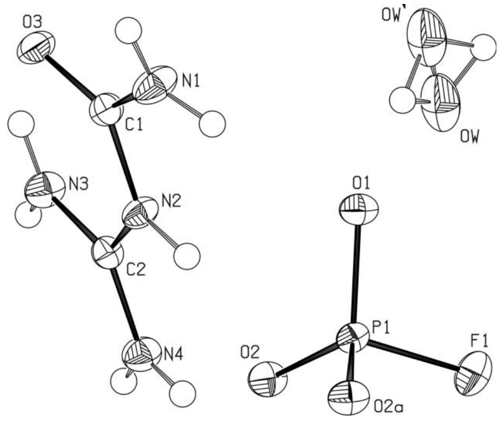


Figure 1
A view of the components and atoms of (I), showing the atom-numbering scheme. Displacement ellipsoids are depicted at the 50% probability level. Atom O2a is related to atom O2 by the transformation $(x, -y + \frac{1}{2}, z)$.

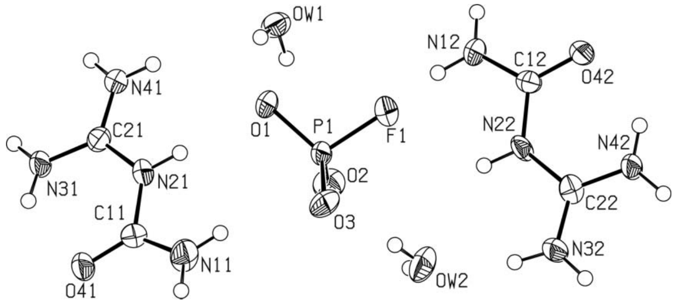


Figure 2
A view of the components and atoms of (II), showing the atom-numbering scheme. Displacement ellipsoids are depicted at the 50% probability level.

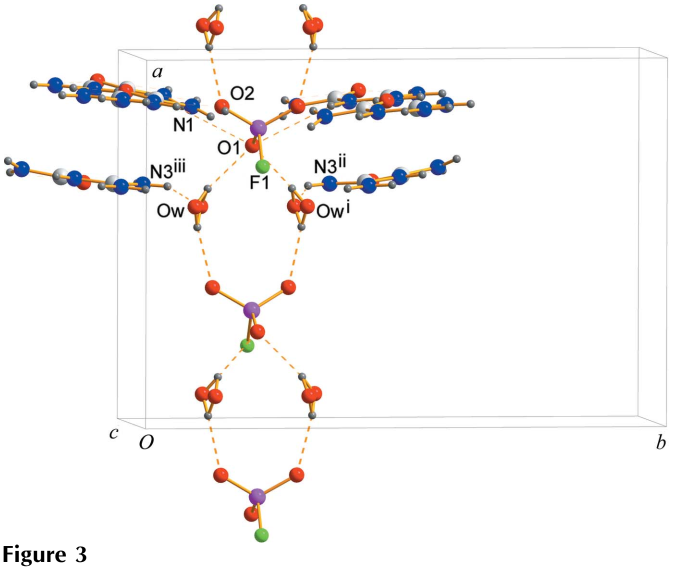


Figure 3
A section of the structure of (I), showing the $R^4_4(10)$ graph-set motifs extending along the a axis. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$.]

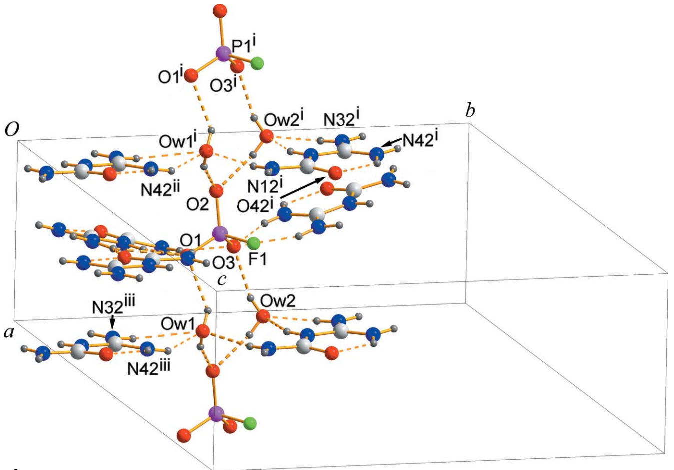


Figure 4
A section of the structure of (II), showing the $R^4_4(10)$ graph-set motifs extending along the a axis. [Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$.]

phonate anions are needed to form a three-dimensional hydrogen-bond network (Fig. 6), although the water molecules reinforce the three-dimensional hydrogen-bond network (Table 4) significantly in this structure.

There is another important difference between the hydrogen-bond networks in (I) and (II), related to the strengths of the water–fluorophosphonate O—H···O hydrogen bonds in (I) and (II) (Tables 2 and 4). These hydrogen bonds are weaker in (I); the H···O distances are about 0.2 Å longer in (I) than those in (II). On the other hand, the N—H···O hydrogen bonds in (I) are shorter than the water–fluorophosphonate O—H···O hydrogen bonds in (I). The latter feature is quite unusual; a search of the Cambridge Structural Database (CSD, Version 5.32 with updates including October 2011; Allen, 2002) for 4101 organic structures in which both O—H···O and N—H···O hydrogen bonds were simultaneously present yielded for O—H···O mean O—H and H···O values of 0.876 (3) and 1.996 (3) Å, respectively, while for N—H···O the retrieved values were 0.897 (1) Å for N—H and 2.140 (3) Å for H···O. The search was carried out on organic structures only, with $R < 0.05$, without any error or disorder, and excluding polymeric and ionic structures, as well as powder determinations.

In addition, the water–fluorophosphonate O—H···O angles in (I) are more acute than in (II). This is a manifestation of weaker hydrogen bonds (Jeffrey, 1995) of this type in (I) than in (II). This also seems to be related to the fact that the anion is situated in a special position in (I). Hence, only two symmetry-independent fluorophosphonate O atoms can be involved in the water–fluorophosphonate O—H···O hydrogen bonds, in contrast with (II), where there are three independent fluorophosphonate O atoms participating in this interaction. Moreover, since there is only one independent water molecule in (I), but two on general positions in (II), the molecules in the latter structure can better adjust in order to optimize their interactions.

The ability of the water molecules to interact with neighbouring molecules is also manifested by the number of N—H···O(water) hydrogen bonds. While the disordered water O atoms in (I) are acceptors of just one amine H atom, in (II) one of the water O atoms (O*W*2) accepts one H atom and the second (O*W*1) accepts two.

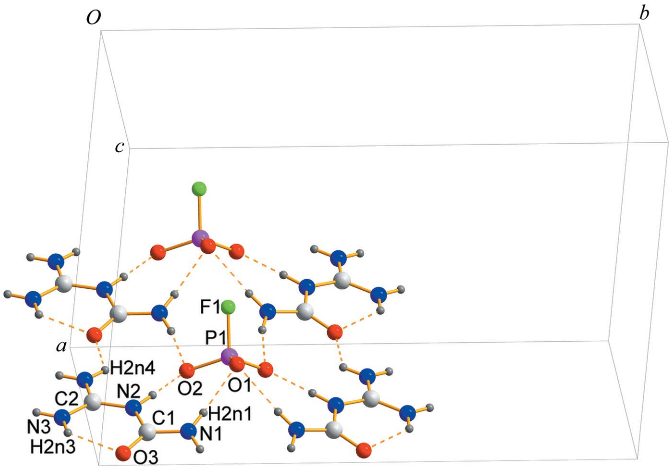


Figure 5
A section of the structure of (I), showing the hydrogen-bond network without water molecules. The fluorophosphonate anions and 2-carbamoylguanidinium cations form ribbons extending along the *c* axis.

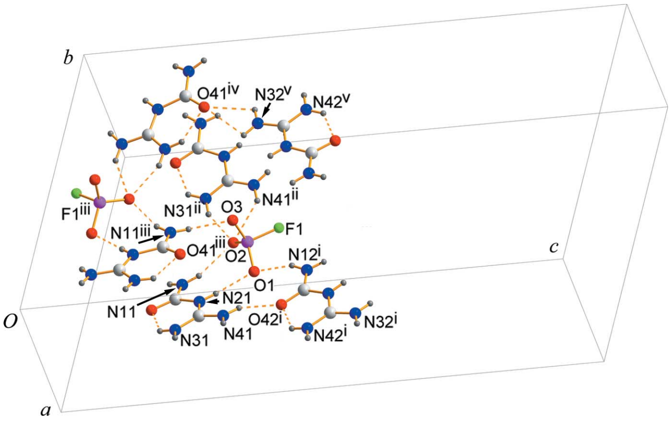


Figure 6
A section of the structure of (II), showing the formation of a three-dimensional hydrogen-bond network without water molecules. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - 1, y, z$.]

A plot of P—F *versus* longest P—O distance in the fluorophosphonate anion is given in the article by Fábry *et al.* (2012*a*), showing that the P—F distance is inversely proportional to the longest P—O distance in the anion. Therefore, this distance is quite sensitive to the hydrogenation of the fluorophosphonate because the P—O bond of the hydroxy group is longer than those of the remaining O atoms. Therefore, the fluorophosphonates and hydrogen fluorophosphonates can be readily distinguished. The distances within the anions for (I) and (II) are given in Tables 1 and 3, respectively.

In (II), the P—O and P—F distances are unusual because P1—O2 is quite long for a structure where the fluorophosphonate is not hydrogenated. The P1—F1 distance is correspondingly shortened. Hence, (II) is situated on the boundary between hydrogenated and nonhydrogenated fluorophosphonates. This peculiarity of (II) seems to be related to the hydrogen-bond network in which the fluorophosphonate is involved. Atom O3 is hydrogen bonded more strongly to neighbouring molecules than atoms O1 and O2. Atom O3 is also an acceptor of the strongest hydrogen bonds stemming from two water molecules [O*W*2—H2*W*2···O3^{viii} and O*W*1—H1*W*1···O3^{viii}; symmetry code: (viii) $x + 1, y, z$] and of another strong N—H···O hydrogen bond [Desiraju & Steiner, 1999; N11—H2N11···O3^{i}; symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$]. These O—H···O and N—H···O angles lie in the range 156–172°, which is typical for rather strong hydrogen bonds. A similar influence of the hydrogen bonds on P—O(acceptor) distances, and concomitantly on P—F distances, has recently been found in tris(2-carbamoylguanidinium) hydrogen fluorophosphonate fluorophosphonate monohydrate (Fábry *et al.*, 2012*b*). On the other hand, the P—O distances are quite short and the P—F distance quite long in (I).

Comparison of the hydrogen-bond distances pertinent to the bonding of the fluorophosphonates in (I) and (II) shows that the fluorophosphonate is less firmly bound in (I).

The χ^2 indices for the best planes through the non-H atoms of the cations are 19477.0, 36.29 and 84.29 for (I), the first cation in (II) and the second cation in (II), respectively. [The first and second cations in (II) contain atoms O41 and O42, respectively.] This is an enormous contrast, indicating that the cation in (I) is quite strained. The largest deviation from the best plane through the cationic non-H atoms in (I) is for atom N3, which is situated 0.12 (3) Å from this plane. In the case of the cations in (II), the atoms with the largest deviations from the best planes through the non-H atoms are N31 and N42, with deviations of 0.031 (9) and 0.055 (10) Å from their respective best planes. The χ^2 indices in the related structures of 2-carbamoylguanidinium hydrogen fluorophosphonate and 2-carbamoylguanidinium hydrogen phosphite are 1139.577 (Fábry *et al.*, 2012*a*) and 6515.041 (Fridrichová, Němec, Císařová & Němec, 2010; Fábry *et al.*, 2012*a*), respectively. It is also of interest that the equivalent isotropic displacement parameters of the non-H atoms in (I) are lower than those in (II) (Table 5).

The above-mentioned facts [the disorder of the water O atoms, the features of the O—H···O and N—H···O hydrogen bonds, the position of the anions on special and general positions in (I) and (II), respectively] indicate that (II) seems to be thermodynamically more stable than (I), even though the molecules in (II) are only slightly more densely packed than those in (I).

The existence of two polymorphs indicates that complexity is present in solutions of 2-carbamoylguanidinium and fluorophosphonate in a 2:1 molar ratio. On the other hand, preparations of 2-carbamoylguanidinium hydrogen fluorophosphonate (Fábry *et al.*, 2012*a*) were easily reproducible. Another prepared compound was tris(2-carbamoylguanidinium) hydrogen fluorophosphonate fluorophosphonate monohydrate (Fábry *et al.*, 2012*b*).

Experimental

The title compounds were prepared by neutralization of stoichiometric amounts of solutions of guanylurea hydroxide and H_2PO_3F.

Guanylurea hydroxide was prepared from hydrochloride hemihydrate (1.18 g) by an exchange reaction on Anex. This solution was then concentrated using a vacuum rotatory evaporator.

Guanylurea chloride hemihydrate was prepared by acid hydrolysis of cyanoguanidine. A dilute aqueous solution (100 ml of water to every 0.1 mol of cyanoguanidine) of equimolar ratios of cyanoguanidine (99%, Sigma–Aldrich) and hydrochloric acid (p.a., Lachema) was gradually heated. After about 45 min, when the reaction mixture started boiling, the colourless mixture suddenly became grey and cloudy for a while and then an exothermic process occurred. This reaction was accompanied by very intense boiling of the reaction mixture. The heating was immediately interrupted and the reaction mixture placed on a cold magnetic stirrer while it was still boiling due to the exothermic reaction, and the mixture was stirred for another 15 min.

The liquid, which in the meantime had turned colourless again, was heated at boiling point for 2 h. The excess water was then evaporated under vacuum and a white crystalline product was filtered off. This was purified by recrystallization from water and characterized by powder X-ray diffraction. The powder diffraction pattern was found to be identical to the structure with CSD refcode JODZOR (Scoponi *et al.*, 1991). The IR spectrum was also recorded in order to exclude the possibility of contamination of the product by cyanoguanidine. The IR spectrum was in accordance with that obtained by Scoponi *et al.* (1991), whereas the intense doublet of the CN^- group typical for cyanoguanidine was absent.

A solution of H_2PO_3F was prepared from a solution of $(NH_4)_2PO_3F\cdot H_2O$ passed through a column of Catex. $(NH_4)_2PO_3F\cdot H_2O$ was prepared according to the method described by Schülke & Kayser (1991) and recrystallized in order to remove $(NH_4)H_2PO_4$ contamination. The volume of the eluted solution of H_2PO_3F was about 50 ml in the cases of (I) and (II). The solutions were placed in an evacuated desiccator over P_4O_{10}. Crystals appeared within about 10 d. The crystals of (I) and (II) were placed in special glass capillaries because they seemed to be hygroscopic.

The syntheses used 0.59 g $(NH_4)_2PO_3F\cdot H_2O$ and 0.936 g of guanylurea hydroxide. Each polymorph was prepared in a different batch.

Polymorph (I)

Crystal data

$2C_2H_7N_4O^+\cdot FO_3P^{2-}\cdot 2H_2O$
$M_r = 340.2$
Orthorhombic, *Pnma*
$a = 12.2788\ (1)$ Å
$b = 17.4866\ (2)$ Å
$c = 6.6851\ (1)$ Å

$V = 1435.39\ (3)$ Å^3
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 2.30$ mm^{-1}
$T = 120$ K
0.51 × 0.34 × 0.24 mm

Data collection

Oxford Xcalibur Gemini Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min} = 0.444$, $T_{\max} = 0.580$

20298 measured reflections
1326 independent reflections
1219 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.086$
$S = 2.93$
1326 reflections
110 parameters
5 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

P1—F1	1.5931 (15)	P1—O2	1.5092 (10)
P1—O1	1.5112 (17)	P1—O2$^{\rm i}$	1.5092 (10)

Symmetry code: (i) $x, -y+\frac{1}{2}, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$O2$^{\rm ii}$	0.86	2.21	3.0491 (17)	164
N1—H2N1$\cdots$O1	0.86	2.06	2.9152 (18)	175
N2—H1N2$\cdots$O2	0.89	1.95	2.8286 (17)	167
N3—H1N3$\cdots$F1$^{\rm iii}$	0.86	2.69	3.2984 (10)	129
N3—H1N3$\cdots$O$W'^{\rm iv}$	0.86	2.50	3.164 (4)	134
N3—H2N3$\cdots$O3	0.86	2.01	2.6395 (17)	129
N3—H2N3$\cdots$O$W^{\rm iii}$	0.86	2.70	3.430 (4)	144
N4—H1N4$\cdots$O$W^{\rm iv}$	0.86	1.95	2.789 (3)	166
N4—H1N4$\cdots$O$W'^{\rm iv}$	0.86	1.92	2.735 (3)	158
N4—H2N4$\cdots$O2	0.86	2.62	3.3211 (14)	139
N4—H2N4$\cdots$O3$^{\rm v}$	0.86	2.15	2.7091 (17)	122
OW—H1O$W\cdots$O2$^{\rm vi}$	0.820 (6)	2.078 (5)	2.771 (3)	142.1 (8)
OW'—H1O$W\cdots$O2$^{\rm vi}$	0.821 (7)	2.078 (5)	2.783 (3)	143.9 (15)
OW—H2O$W\cdots$O1	0.820 (13)	2.130 (14)	2.798 (3)	138.6 (9)
OW'—H2O$W\cdots$O1	0.821 (10)	2.130 (14)	2.848 (3)	146.1 (15)

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

Polymorph (II)

Crystal data

$2C_2H_7N_4O^+\cdot FO_3P^{2-}\cdot 2H_2O$
$M_r = 340.2$
Orthorhombic, *Pbca*
$a = 6.5362\ (3)$ Å
$b = 16.6485\ (6)$ Å
$c = 26.1629\ (15)$ Å

$V = 2847.0\ (2)$ Å^3
$Z = 8$
Cu $K\alpha$ radiation
$\mu = 2.32$ mm^{-1}
$T = 120$ K
0.43 × 0.14 × 0.04 mm

Data collection

Oxford Xcalibur Gemini Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min} = 0.718$, $T_{\max} = 0.908$

7251 measured reflections
2210 independent reflections
968 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.110$
$\theta_{\max} = 62.3°$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.193$
$S = 1.43$
2210 reflections
202 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.84$ e Å^{-3}
$\Delta\rho_{\min} = -0.60$ e Å^{-3}

All H atoms were discernible in difference electron-density maps for both structures. The applied constraints and restraints were as similar as possible for the refinement of each structure. The N—H distances for primary and secondary amine H atoms were constrained to 0.86 and 0.89 Å, respectively, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$. The water O—H distances were restrained to 0.820 (1) Å, and the interatomic angles in the water molecules were restrained to 107.90 (1)° (this value was retrieved from the CSD), with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. Additionally, in the case of (I), the displacement parameters of

Table 3
Selected bond lengths (Å) for (II).

P1—F1	1.584 (4)	P1—O2	1.499 (6)
P1—O1	1.497 (5)	P1—O3	1.531 (6)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H1N11···O2	0.86	2.20	3.036 (8)	164
N11—H2N11···O3^{i}	0.86	2.05	2.904 (8)	172
N21—H1N21···O1	0.89	1.99	2.873 (8)	170
N31—H1N31···O41	0.86	2.04	2.668 (7)	129
N31—H1N31···C11	0.86	2.58	2.882 (8)	102
N31—H1N31···O*W*2^{ii}	0.86	2.55	3.164 (9)	129
N31—H2N31···O2^{iii}	0.86	2.06	2.862 (7)	154
N41—H1N41···O42^{iv}	0.86	2.13	2.751 (7)	129
N41—H2N41···F1^{iii}	0.86	2.55	3.337 (6)	152
N41—H2N41···O2^{iii}	0.86	2.37	3.091 (7)	142
N12—H1N12···O*W*1	0.86	2.06	2.908 (7)	168
N12—H2N12···O1^{v}	0.86	2.19	3.004 (7)	157
N22—H1N22···O*W*2	0.89	2.35	3.109 (9)	143
N32—H1N32···O*W*2	0.86	1.94	2.766 (7)	161
N32—H2N32···O*W*1^{vi}	0.86	2.54	3.205 (7)	135
N42—H1N42···F1^{vii}	0.86	2.41	3.000 (7)	126
N42—H1N42···O42	0.86	1.99	2.629 (7)	130
N42—H2N42···O*W*1^{vi}	0.86	2.08	2.852 (7)	150
O*W*1—H1*W*1···O3^{viii}	0.82 (5)	1.89 (6)	2.665 (8)	156 (8)
O*W*1—H2*W*1···O1	0.82 (5)	2.09 (5)	2.778 (8)	141 (7)
O*W*2—H2*W*2···O3^{viii}	0.82 (5)	1.89 (6)	2.692 (8)	164 (8)
O*W*2—H1*W*2···O2	0.82 (5)	1.94 (5)	2.727 (9)	162 (6)

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

disordered water atoms O*W* and O*W*′ were constrained to be equal; these water O atoms were refined anisotropically. A trial refinement which included refinement of the occupational parameters of O*W* and O*W*′ resulted in values of 0.499 (3) and 0.501 (3) and therefore the occupancy factors of the water O atoms in (I) were set at 0.5.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *JANA2006*.

Table 5
Comparison of the equivalent isotropic displacement parameters $U_{\rm eq}$ (Å^2) of the non-H atoms in polymorphs (I) and (II).

Atom	(I)	(II), cation 1	(II), cation 2
P1	0.01375 (18)	0.0273 (7)	
O1	0.0184 (5)	0.0355 (19)	
O2	0.0186 (3)	0.042 (2)	
O2/O3	0.0186 (3)	0.041 (2)	
F1	0.0242 (4)	0.0393 (16)	
O3/O41/O42	0.0203 (3)	0.037 (2)	0.0330 (19)
C1/C11/C12	0.0165 (5)	0.030 (3)	0.028 (3)
N1/N11/N12	0.0236 (4)	0.041 (3)	0.038 (2)
N2/N21/N22	0.0165 (4)	0.033 (2)	0.031 (2)
C2/C21/C22	0.0162 (5)	0.027 (3)	0.027 (3)
N3/N31/N32	0.0197 (4)	0.030 (2)	0.035 (2)
N4/N41/N42	0.0200 (4)	0.034 (2)	0.034 (2)
O*W*/O*W*1/O*W*2	0.0349 (8)	0.035 (2)	0.045 (2)

The authors gratefully acknowledge support of this work by the Praemium Academiae project of the Academy of Sciences of the Czech Republic, by grant No. 58608 of the Grant Agency of the Charles University in Prague, and by the Czech Science Foundation (grant No. 203/09/0878), as part of the long-term Research Plan of the Ministry of Education of the Czech Republic (grant No. MSM0021620857).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3423). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Brandenburg, K. (2010). *DIAMOND*. Version 3.2e. Crystal Impact GbR, Bonn, Germany.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, p. 13. New York: Oxford University Press Inc.

Dunitz, J. D. & Taylor, R. (1997). *Chem. Eur. J.* **3**, 89–98.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Fábry, J., Fridrichová, M., Dušek, M., Fejfarová, K. & Krupková, R. (2012*a*). *Acta Cryst.* C**68**, o76–o83.

Fábry, J., Fridrichová, M., Dušek, M., Fejfarová, K. & Krupková, R. (2012*b*). *Acta Cryst.* E**68**, o47–o48.

Fridrichová, M., Němec, I., Císařová, I. & Chvostová, D. (2010). *Phase Transitions*, **83**, 761–767.

Fridrichová, M., Němec, I., Císařová, I. & Němec, P. (2010). *CrystEngComm*, **12**, 2054–2056.

Jeffrey, G. A. (1995). *Crystallogr. Rev.* **4**, 213–259.

Kroupa, J. & Fridrichová, M. (2011). *J. Opt.* **13**, 035204.

Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic.

Schülke, U. & Kayser, R. (1991). *Z. Anorg. Allg. Chem.* **600**, 221–226.

Scoponi, M., Polo, E., Bertolasi, V., Carassiti, V. & Bertelli, G. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 1619–1624.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.