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Mixed crystals of 2-carbamoylguanidinium with hydrogen fluorophosphonate and hydrogen phosphite in the ratios 1:0, 0.76 (2):0.24 (2) and 0.115 (7):0.885 (7)

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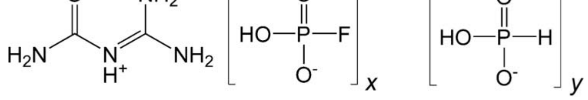
The title compounds, 2-carbamoylguanidinium hydrogen fluorophosphonate, $C_2H_7N_4O^+\cdot HFO_3P^-$, (I), 2-carbamoylguanidinium–hydrogen fluorophosphonate–hydrogen phosphite (1/0.76/0.24), $C_2H_7N_4O^+\cdot 0.76HFO_3P^-\cdot 0.24H_2O_3P^-$, (II), and 2-carbamoylguanidinium–hydrogen fluorophosphonate–hydrogen phosphite (1/0.115/0.885), $C_2H_7N_4O^+\cdot 0.115HFO_3P^-\cdot 0.885H_2O_3P^-$, (III), are isostructural with guanylurea hydrogen phosphite, $C_2H_7N_4O^+\cdot H_2O_3P^-$ [Fridrichová, Němec, Císařová & Němec (2010). *CrystEngComm*, **12**, 2054–2056]. They constitute structures where the hydrogen phosphite anion has been fully or partially replaced by hydrogen fluorophosphonate. The title structures are the fourth example of isostructural compounds which differ by the presence of hydrogen fluorophosphonate and hydrogen phosphite or fluorophosphonate and phosphite anions. Moreover, the present study reports structures with these mixed anions for the first time. In the reported mixed salts, the P and O atoms of either anion overlap almost exactly, as can be judged by comparison of their equivalent isotropic displacement parameters, while the P—F and P—H directions are almost parallel. There are strong O—H···O hydrogen bonds between the anions, as well as strong N—H···O hydrogen bonds between the 2-carbamoylguanidinium cations in the title structures. Altogether they form a three-dimensional hydrogen-bond pattern. Interestingly, rare N—H···F interactions are also present in the title structures. Another exceptional feature concerns the P—O(H) distances, which are about as long as the P—F distance. The dependence of P—F distances on the longest P—O distances in FO_3P^{2-} or HFO_3P^- is presented. The greater content of hydrogen phosphite in the mixed crystals causes a larger deformation of the cations from planarity.

Comment

Recently, an interesting structure of guanylurea hydrogen phosphite has been reported [$C_2H_7N_4O^+\cdot H_2O_3P^-$, GUHP; Fridrichová, Němec, Císařová & Němec, 2010; the structure is stored under the refcode CUYZEC in the Cambridge Structural Database (CSD; Version 5.32, April 2011 update; Allen, 2002)]. The compound is a promising phase-matchable material for the second harmonic generation of light. It has an excellent resistance to optical damage and high nonlinear optical coefficients (Fridrichová, Němec, Císařová & Chvostová, 2010). The latter property enabled observations of spontaneous noncollinear second harmonic generation (Kroupa & Fridrichová, 2011) due to scattering on crystal inhomogeneities which are presumably related to the presence of inversion twins in the structure of GUHP (Fridrichová, Němec, Císařová & Němec, 2010; Flack, 1983).



(I) $x = 1$, $y = 0$
(II) $x = 0.76$, $y = 0.24$
(III) $x = 0.115$, $y = 0.885$

Scheme 1

Since the constitution of the hydrogen phosphite anion is similar to that of hydrogen fluorophosphonate, it has been suggested that an analogous structure could be prepared by substitution of the hydrogen phosphite anion by hydrogen fluorophosphonate. The suggestion for the preparation of 2-carbamoylguanidinium hydrogen fluorophosphonate is even more intriguing because of the differences in the electronegativities between F and H atoms (Gilli & Gilli, 2009) which would affect the polar properties of the constituent ions with an effect on their optical properties. Indeed, it turned out that the structure of 2-carbamoylguanidinium hydrogen fluorophosphonate, (I) (Fig. 1), is isostructural with 2-carbamoylguanidinium hydrogen phosphite.

There are only three other examples of isostructurality between the structures containing (hydrogen) fluorophosphonate and (hydrogen) phosphite anions. Two of them refer to those with organic cations: the pair of ethylenediammonium fluorophosphonate (CSD refcode JEHFUY01; Fábry, Dušek, Krupková *et al.*, 2006) and ethylenediammonium hydridotrioxophosphate (KEWZAN; Honle *et al.*, 1990), and the pair of anilinium hydrogen monofluorophosphate (YUYKUY; Khaoulani Idrissi *et al.*, 1995) and anilinium hydrogen phosphite (WOCSAI; Paixão *et al.*, 2000). Among inorganic compounds, the only known isostructural structures are $Zn_2(H_2O)_4(PO_3F)_2\cdot H_2O$ (Durand *et al.*, 1983) and $Zn_2(H_2O)_4(HPO_3)_2\cdot H_2O$ (Ortiz-Avila *et al.*, 1989). Both structures were found in the Inorganic Crystal Structure Database (2011) (collection codes 35644 and 65825, respectively).

The experiments in the preparation of mixed crystals containing both hydrogen fluorophosphonate and hydrogen

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phosphite yielded crystals with the composition $C_2H_7N_4O^+\cdot x(HFO_3P)^-\cdot(1-x)(H_2O_3P)$, where x refined to $x = 0.76$ (2) for (II) (Fig. 2) and $x = 0.115$ (7) for (III) (Fig. 3). {We will also mention (IV), with a composition similar to (III), *i.e.* with $x = 0.184$ (7), although the aim was to prepare a structure with $x = 0.5$. The indicators of the refinement are comparable to those of the other title structures. The R factor on the observed diffractions only $[I > 3\sigma(I)]$ resulted in 0.0225 for (IV). Data for (IV) are in the *Supplementary materials.*}

The hydrogen-bond patterns are similar in all the title structures and correspond quite well to the pattern found in pure GUHP (Fridrichová, Němec, Císařová & Němec, 2010). In all these structures, a quite strong O—H···O hydrogen bond (Desiraju & Steiner, 1999) interconnects the anions into chains which propagate along the [$\bar{1}$10] and [110] directions (Fig. 4). The increasing proportion of hydrogen fluorophosphonate results in a shortening of the O1—H1···O2^{i} [symmetry code: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$] hydrogen bonds, with O1···O2^{i} distances of 2.554 (5), 2.560 (5), 2.5776 (19) and 2.590 (2) Å for (I), (II), (III) and GUHP, respectively. [Compound (IV) is in accordance with this tendency, the O1···O2^{i} distance being 2.579 (2) Å.] All remaining anion atoms are acceptors of another two N—H···O hydrogen bonds stemming from the amine groups.

In the title structures, all the amine H atoms are involved in hydrogen bonds. N—H···O hydrogen bonds interconnect the 2-carbamoylguanidinium cations into ribbons that are extended along the unit-cell a axis. The planes of the ribbons are parallel to (011) and (0$\bar{1}$1) (Fig. 5).

The title structures are rather exceptional because the F1 atoms are involved in interactions that can be considered as weak, bent hydrogen bonds as in the case of (I) (Table 1 and Fig. 6). Usually fluorine avoids involvement in hydrogen bonds in the fluorophosphonates (Krupková *et al.*, 2002; see also Dunitz & Taylor, 1997).

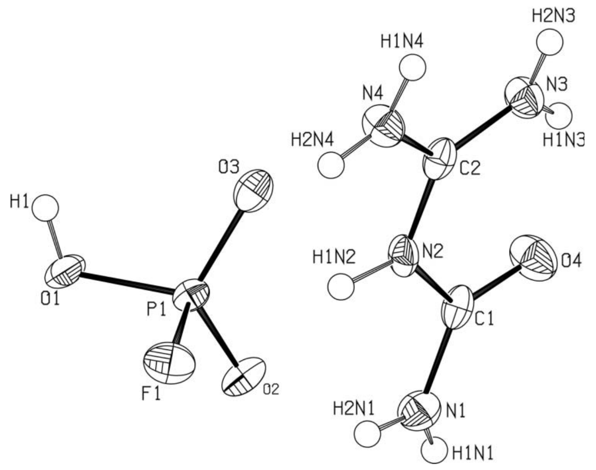


Figure 1
A view of (I), with displacement ellipsoids drawn at the 50% probability level.

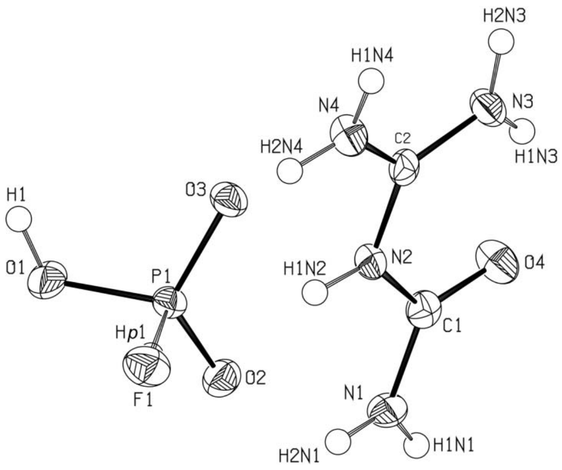


Figure 2
A view of (II), with displacement ellipsoids drawn at the 50% probability level.

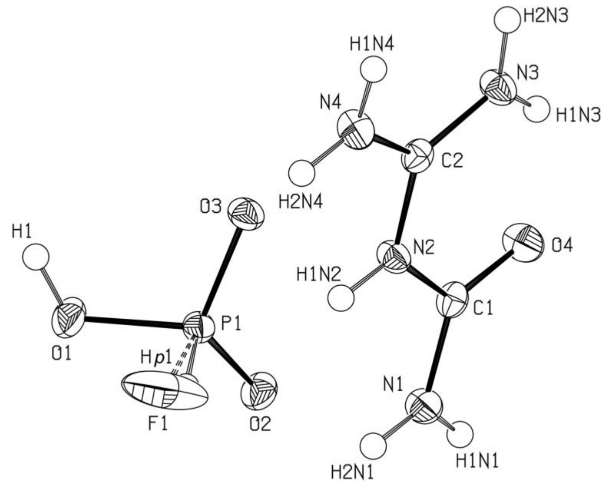


Figure 3
A view of (III), with displacement ellipsoids drawn at the 50% probability level.

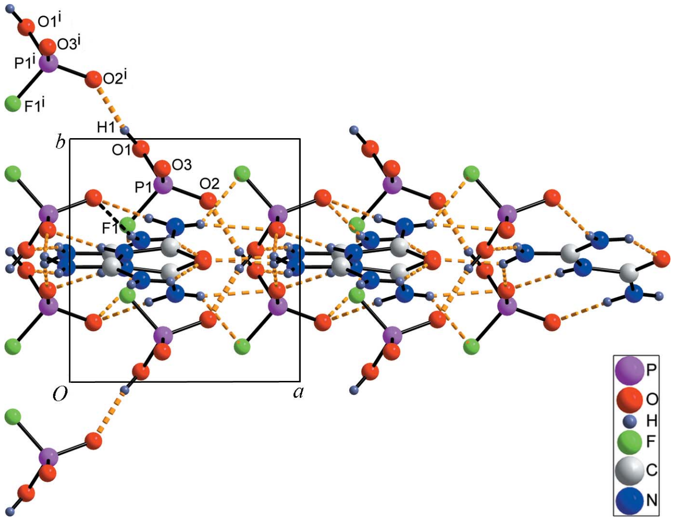


Figure 4
A view of the unit cell of (I) along the c axis. The strong O—H···O hydrogen bonds are in the [$\bar{1}$10] and [110] directions. [Symmetry code: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$.]

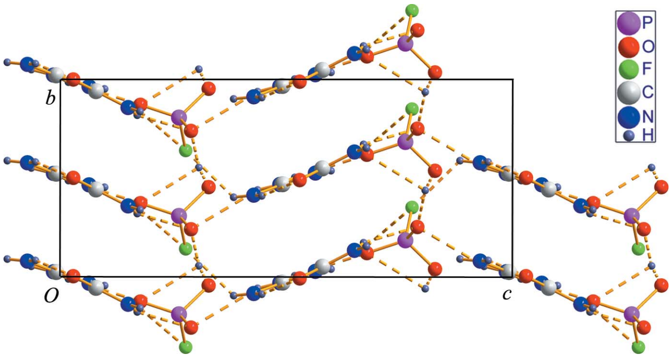


Figure 5
A view of the unit cell of (I) along the *a* axis, showing the hydrogen-bond pattern.

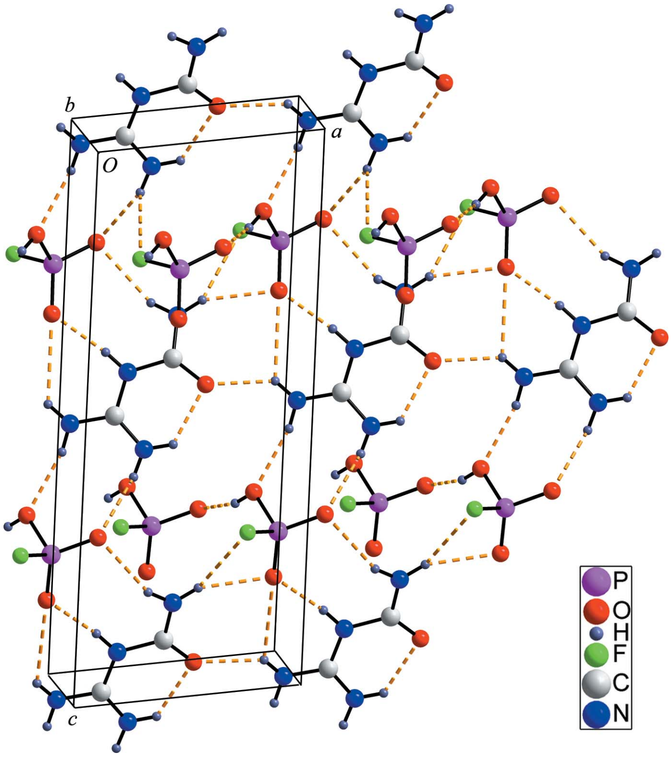


Figure 6
A section of (I) along the *b* axis, showing the hydrogen-bond pattern, including a weak hydrogen-bonding interaction with the F1 atom.

Fig. 7 shows the difference electron-density maps passing through the P1, O2 and F1 atoms in (I), (II) and (III), respectively. (In the case of the mixed crystals, these maps were calculated from the refined structural model from which the hydrido hydrogen had been excluded.) In contrast to (I), there is a build-up of electron density between atoms P1 and F1 in (II) and (III). This build-up of electron density can be attributed to the contribution of the hydrido H atoms.

These features are related to the following peculiarities. In (I), the P1—F1 [1.564 (3) Å] distance is about the same as the longest P1—O1 distance of the hydrogenated O atom [1.560 (4) Å]; in other known structures, the P—F distances are routinely longer than the respective longest P—O distances (Table 2 and Fig. 8). Fig. 8 also shows that the P—F distance is sensitive to the hydroxy O—H distance of hydrogen fluorophosphonate, *i.e.* to the degree of hydrogenation of such an O atom.

In structures (II) and (III), the P1—F1 bond lengths have been biased by the presence of the hydrido H atom (see Figs. 2 and 3) and therefore the P1—F1 lengths were restrained to the refined value in (I), *i.e.* to 1.564 (1) Å.

The P1—H*p*1 bond seems to be oriented almost in the same direction as that of P1—F1. Table 3 lists the components of the displacement parameters, as well as the equivalent isotropic displacement parameters for (I), (II), (III), (IV) and GUHP. [The structure (IV) has a similar composition to (III).] It can clearly be seen that the values of the equivalent isotropic displacement parameters of the corresponding atoms are quite similar except for F1 of (III). No splitting of the electron density of the atoms given in Table 3 was observed, in particular no splitting of the electron density took place in the region of F1 and H*p*1 in (III) and (IV) which have a similar composition. It should be added that the ratios of the components of the anisotropic displacement parameters in (III) (Table 3) are similar to those in (IV). Therefore, it seems that there is some quirk in (III) regarding the F1 atom. From the similar values of the equivalent isotropic displacement parameters in the series of structures in Table 3 it can be inferred that the P1 and the anionic O atoms are situated practically at the same positions in the mixed crystals. It is interesting that the proportions of the values of the components U^{22} and U^{33} of P1, O1, O2 and F1 seem to be interchanged for (I) and GUHP and that the displacement parameters of the anion in the mixed crystals (II), (III) and (IV) are rather similar to those in GUHP. On the other hand, the displacement parameters of the non-H atoms of the cation are even more similar (Table 3).

As to the cation, the disorder would presumably also affect its planarity in the title compounds. The χ^2 index regarding the plane fitted through all the non-H atoms of the cation tends to decrease from the hydrogen-phosphite-rich end towards the hydrogen-fluorophosphonate-rich end of the series: 6515.041 (GUHP), 8048.089 (III), 6270.070 (IV), 1403.672 (II) and 1139.577 (I). Also this trend, together with the data in Table 3, shows that the disorder of the anions minutely affects the positions of the cations in the mixed crystals of the title structures, otherwise one would expect an increase of these values in the mixed crystals together with the increase in the U_{eq} values of the non-H atoms of the cation.

The Flack parameter (Flack, 1983) has an unusual value of 0.36 (9) in the recalculated refinement of GUHP that confirmed the result by Fridrichová, Němec, Císařová & Němec (2010). [This significant inversion twinning was found in more samples and is related to spontaneous noncollinear second harmonic generation in GUHP; Kroupa & Fridrichová (2011).] In the title structures, it resulted in Flack parameters of 0.11 (5), 1.02 (5), 0.037 (2) and 0.91 (2) for (I), (II), (III) and (IV), respectively. This means that only in (I), *i.e.* in the pure fluorophosphonate, is the Flack parameter somewhat larger. [For the sake of easy comparison of the positional parameters in all the title structures, we have reported the non-inverted

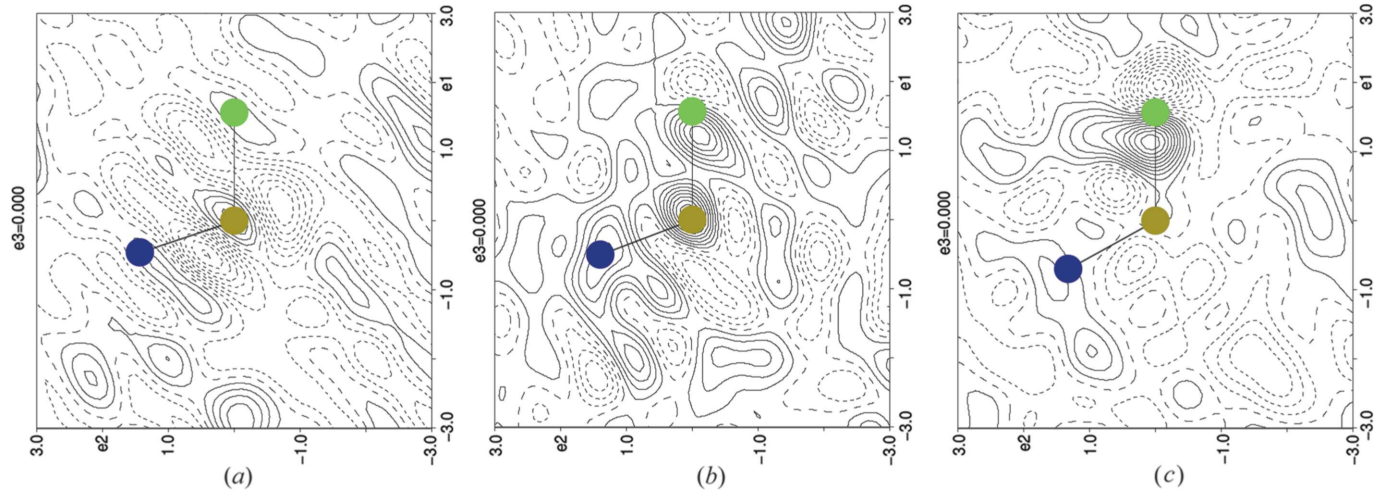


Figure 7

The difference electron-density map passing through the O2 (blue in the electronic version of the paper), P1 (khaki) and F1 (green) atoms in (I), (II) and (III). The contours are in intervals of 0.05 e Å^{-3}. The negative electron density is shown by dashed contours. The map was drawn using *JANA2006* (Petříček *et al.*, 2006). (*a*) For (I), the maximal electron densities in the vicinities of P1 and F1 are about 0.222 and 0.095 e Å^{-3}. The minimal electron densities between P1—F1 and outside F1 are −0.150 and −0.108 e Å^{-3}, respectively. (*b*) For (II), the maximal electron density is 0.387 e Å^{-3} in the region between P1 and F1. (*c*) For (III), the maximal electron density is 0.216 e Å^{-3} in the region between P1 and F1.

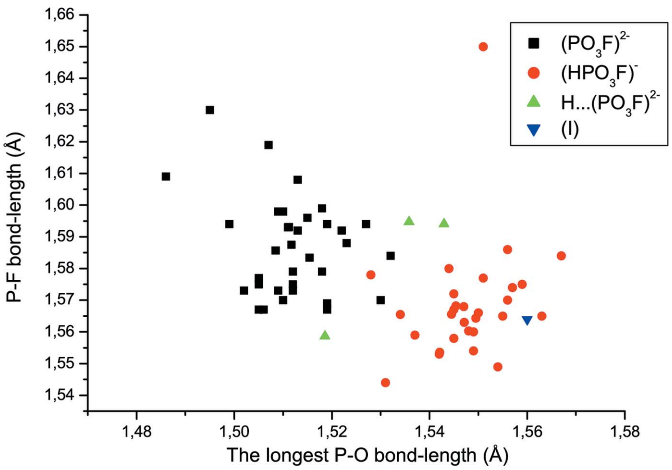


Figure 8

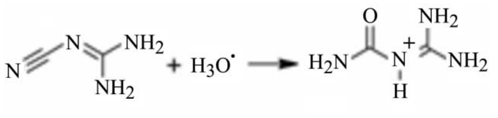
Plot of P—F *versus* the longest P—O bond lengths in the hydrogen fluorophosphonate and fluorophosphonate anions. The data correspond to those in Table 2. The plot was constructed by *Origin* (OriginLab, 2000). Note the position of the structures with an H atom situated at about the centre of the hydrogen bond, *i.e.* away from the donating O atom (these structures are denoted by a triangle). (I) is located at the extreme position.

structures for (II) and (IV), *i.e.* those with the Flack parameter → 1.]

Measurements of the second harmonic generation of light for the title structures are planned. Preliminary measurements have shown that GUHP is more efficient in the second harmonic generation of light than the nonhygroscopic mixed title structures, *i.e.* the structures with a preponderance of hydrogen phosphite. Since the structures are quite similar it is reasonable to seek the reason in the dipole moments of the anions. The calculation by the program *GAUSSIAN* (Frisch *et al.*, 2009) at the B3LYP/6–311G(d,p) level with optimization of the geometry of either anion situated in a vacuum yielded μ = 3.0454 and 3.1437 D for the hydrogen phosphite and hydrogen fluorophosphonate anions, respectively. The orientation of the dipole moments is about the same in both structures.

Experimental

The title structures were prepared by neutralization of stoichiometric amounts of solutions of 2-carbamoylguanidinium hydroxide and H_2PO_3F or the corresponding mixtures of these solutions with the prepared 2-carbamoylguanidinium hydrogen phosphite.



Scheme 2

2-Carbamoylguanidinium hydroxide was prepared from 2-carbamoylguanidinium hydrochloride hemihydrate by the exchange reaction on anex (Dowex Serva, type 2X8; ion exchange OI/OH, Entwicklungslabor, Heidelberg, Germany). 2-Carbamoylguanidinium chloride hemihydrate was first described at the beginning of the 20th century (Ostrogovich, 1911) and characterized by Scoponi *et al.* (1991). For the preparation of the title structures, it was prepared by acid hydrolysis of cyanoguanidine according to Scheme 2. A diluted water 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 light-grey and cloudy for a while and then an exothermal process occurred, accompanied by very intense boiling of the reaction mixture. At this moment, the heating was immediately interrupted and the reaction mixture was placed on a cold magnetic stirrer while it was still boiling due to the exothermal reaction and the mixture was stirred for another 15 min.

The liquid, which in the meantime had turned colourless again, was heated at the boiling point for 2 h, then the excess water was evaporated under vacuum and a white crystalline product was filtered off. It was purified by recrystallization from water and characterized by powder X-ray diffraction and found to be identical to the structure

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 reported by Scoponi *et al.* (1991), whereas the intense doublet of the CN^- group typical for cyanoguanidine was absent.

The solution of H_2PO_3F was prepared from the solution of $(NH_4)_2PO_3F{\cdot}H_2O$ that passed through the column of catex (Amberlite IR120, Fluka). $(NH_4)_2PO_3F{\cdot}H_2O$ was prepared according to the method described by Schülke & Kayser (1991) and the raw material of $(NH_4)_2PO_3F{\cdot}H_2O$ prepared by this method was recrystallized in order to get rid of contamination of $(NH_4)H_2PO_4$. The volume of the eluted solution of H_2PO_3F was about 50 ml in all cases. The solutions, from which crystals of the title compounds were to be grown, were placed in an evacuated desiccator over P_4O_{10}. The crystals appeared in about 7–10 d. The crystals of (I) and (II) deteriorated quickly on exposure to air, possibly because of the mother liquor that was on the surface of the crystals, while (III) with a composition rich in hydrogen phosphite was stable in air. The crystals (I) and (II) were placed in special glass capillaries (producer Wolfgang Müller, Schönwalde bei Berlin, Germany).

For (I), 1.18 g of $(NH_4)_2PO_3F{\cdot}H_2O$ and 0.936 g of 2-carbamoylguanidinium hydroxide were used. For (II), 1.18 g of $(NH_4)_2PO_3F{\cdot}H_2O$ and 0.936 g of 2-carbamoylguanidinium hydroxide were used, with 0.98 g of guanylurea hydrogen phosphite (GUHP). The composition of the initial solution corresponded to a 1.465:1 molar ratio of (I) and GUHP, while the stoichiometry derived from the refined structure in the obtained crystal was 3.16:1. For (III), 0.59 g of $(NH_4)_2PO_3F{\cdot}H_2O$ and 0.468 g of 2-carbamoylguanidinium hydroxide were used, with 2.152 g of GUHP. The composition of the initial solution corresponded to a 1:3 molar ratio of (I) and GUHP, while the stoichiometry derived from the refined structure was 1:7.69. For (IV), 1.18 g of $(NH_4)_2PO_3F{\cdot}H_2O$ and 0.936 g of 2-carbamoylguanidinium hydroxide were used, with 1.43 g of guanylurea hydrogen phosphite (GUHP). The composition of the initial solution corresponded to a 1:1 molar ratio of (I) and GUHP, while the stoichiometry derived from the refined structure was 1:4.43.

Compound (I)

Crystal data

$C_2H_7N_4O^+{\cdot}HFO_3P^-$
M_r = 202.09
Monoclinic, *Cc*
a = 6.6567 (3) Å
b = 6.9950 (3) Å
c = 16.2875 (7) Å
β = 97.467 (4)°
V = 751.97 (6) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 3.44 mm^{-1}
T = 120 K
0.38 × 0.13 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur Gemini ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min}$ = 0.605, $T_{\max}$ = 0.852
4342 measured reflections
1268 independent reflections
1222 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.080

Refinement

$R[F^2 > 3\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.117
S = 2.31
1268 reflections
132 parameters
11 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.68 e Å^{-3}
$\Delta\rho_{\min}$ = −0.54 e Å^{-3}
Absolute structure: Flack (1983), 607 Friedel pairs
Flack parameter: 0.11 (5)

Compound (II)

Crystal data

$C_2H_7N_4O^+{\cdot}0.76HFO_3P^-{\cdot}0.24H_2O_3P^-$
M_r = 197.8
Monoclinic, *Cc*
a = 6.6648 (2) Å
b = 6.9435 (2) Å
c = 16.2924 (4) Å
β = 97.185 (3)°
V = 748.04 (4) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 3.40 mm^{-1}
T = 120 K
0.41 × 0.28 × 0.21 mm

Data collection

Oxford Diffraction Xcalibur Gemini ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min}$ = 0.362, $T_{\max}$ = 0.484
3985 measured reflections
1257 independent reflections
1237 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.070

Refinement

$R[F^2 > 3\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.114
S = 2.96
1257 reflections
134 parameters
13 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.49 e Å^{-3}
$\Delta\rho_{\min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), 602 Friedel pairs.
Flack parameter: 1.02 (5)

Compound (III)

Crystal data

$C_2H_7N_4O^+{\cdot}0.115HFO_3P^-{\cdot}0.885H_2O_3P^-$
M_r = 186.2
Monoclinic, *Cc*
a = 6.67841 (16) Å
b = 6.78864 (13) Å
c = 16.2696 (4) Å
β = 96.588 (2)°
V = 732.75 (3) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 3.29 mm^{-1}
T = 120 K
0.41 × 0.24 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur Gemini ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min}$ = 0.452, $T_{\max}$ = 0.604
4272 measured reflections
1216 independent reflections
1200 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.024

Refinement

$R[F^2 > 3\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.047
S = 1.27
1216 reflections
137 parameters
13 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.10 e Å^{-3}
$\Delta\rho_{\min}$ = −0.13 e Å^{-3}
Absolute structure: Flack (1983), 566 Friedel pairs
Flack parameter: 0.037 (19)

All H atoms were discernible in difference electron-density maps of (I). In (I), (II) and (III), the isotropic amine H-atom displacement parameters have been constrained to $1.2U_{\rm eq}$ of the respective carrier N atoms, while the $U_{\rm iso}$(H) value for the hydrogen fluorophosphonate H atom was set at $1.5U_{\rm eq}$ of the carrier O atom. The positional parameters of the H atoms were restrained: O1—H1 = 0.820 (1) Å, and N—H = 0.860 (1) and 0.890 (1) Å for the primary and secondary amines, respectively. The H1N1—N1—H2N1, H1N3—N3—H2N3 and H1N4—N4—H2N4 angles were constrained to 120.00 (1)°. (This is substantiated by the primary amine C—N distances in the title

Table 1
Comparison of the hydrogen-bond patterns (Å, °) in (I), (II), (III) and in recalculated GUHP (Fridrichová, Němec, Císařová & Němec, 2010).

Also given are the N3—H2N3···H*p*1 and N3—H2N3···F1 interactions in (II) and (III).

	D—H	H—*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2$^{\mathrm{i}}$				
(I)	0.82 (6)	1.77 (6)	2.554 (5)	160 (6)
(II)	0.82 (5)	1.74 (5)	2.560 (5)	178 (8)
(III)	0.82 (2)	1.76 (2)	2.5776 (19)	173 (3)
GUHP	0.82 (3)	1.79 (3)	2.590 (2)	164 (3)
N1—H1N1···O3$^{\mathrm{ii}}$				
(I)	0.86 (3)	2.24 (3)	3.040 (7)	155 (4)
(II)	0.856 (19)	2.207 (16)	3.036 (5)	163 (4)
(III)	0.860 (7)	2.164 (6)	3.014 (2)	170.0 (18)
GUHP	0.860 (7)	2.181 (7)	3.037 (2)	174 (2)
N1—H2N1···O2$^{\mathrm{iii}}$				
(I)	0.86 (3)	2.36 (4)	3.179 (6)	160 (4)
(II)	0.86 (4)	2.31 (4)	3.160 (5)	167 (4)
(III)	0.861 (14)	2.200 (14)	3.056 (2)	173.5 (17)
GUHP	0.860 (15)	2.221 (15)	3.079 (2)	177 (2)
N2—H1N2···O3$^{\mathrm{iii}}$				
(I)	0.89 (4)	1.90 (5)	2.778 (6)	172 (6)
(II)	0.89 (4)	1.87 (4)	2.760 (5)	176 (7)
(III)	0.888 (15)	1.889 (15)	2.771 (2)	171.5 (17)
GUHP	0.889 (15)	1.898 (15)	2.780 (2)	171.9 (16)
N3—H1N3···O4				
(I)	0.860 (15)	2.03 (4)	2.643 (7)	128 (4)
(II)	0.861 (15)	1.99 (4)	2.642 (6)	132 (4)
(III)	0.860 (6)	1.980 (15)	2.639 (2)	132.5 (15)
GUHP	0.859 (6)	1.995 (16)	2.641 (3)	131.2 (16)
N3—H2N3···F1$^{\mathrm{iv}}$				
(I)	0.86 (3)	2.43 (5)	2.998 (6)	124 (5)
(II)	0.87 (4)	2.64 (5)	2.973 (6)	104 (3)
(III)	0.860 (16)	2.49 (4)	2.86 (3)	106.8 (18)
N3—H2N3···H*p*1				
(III)	0.86 (2)	2.59 (3)	2.95 (3)	106.5 (19)
N3—H2N3···O2$^{\mathrm{v}}$				
(I)	0.86 (3)	2.26 (4)	3.063 (6)	156 (5)
(II)	0.87 (4)	2.20 (4)	3.048 (6)	167 (4)
(III)	0.859 (15)	2.103 (14)	2.956 (2)	171.8 (13)
GUHP	0.858 (17)	2.088 (18)	2.941 (3)	172.3 (17)
N4—H1N4···O1$^{\mathrm{v}}$				
(I)	0.86 (3)	2.12 (4)	2.945 (6)	160 (5)
(II)	0.86 (3)	2.09 (3)	2.939 (6)	169 (5)
(III)	0.859 (11)	2.087 (11)	2.934 (2)	168.6 (19)
GUHP	0.861 (13)	2.098 (13)	2.954 (3)	173 (3)
N4—H2N4···O4$^{\mathrm{vi}}$				
(I)	0.86 (4)	2.07 (3)	2.698 (7)	129 (3)
(II)	0.86 (3)	2.14 (3)	2.706 (6)	123 (3)
(III)	0.860 (13)	2.123 (13)	2.695 (2)	123.4 (11)
GUHP	0.859 (14)	2.172 (14)	2.709 (2)	120.3 (12)
N4—H2N4···O3$^{\mathrm{iii}}$				
(II)	0.86 (3)	2.56 (3)	3.257 (6)	139 (3)
(III)	0.860 (13)	2.535 (13)	3.223 (2)	137.7 (11)
GUHP	0.859 (14)	2.509 (14)	3.214 (3)	140.0 (12)

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

Table 2
Lengths (Å) of the P—F and the longest P—O bonds in fluorophosphonates and hydrogen fluorophosphonates.

Compound	P—O	P—F
$\mathrm{CaPO_3F{\cdot}2H_2O}$[a]	1.515 (1)	1.583 (1)
$\mathrm{[Co(H_2O)_3](PO_3F)}$[b]	1.519 (2)	1.567 (2)
$\mathrm{[Cu(H_2O)_2](PO_3F)}$[c]	1.530 (7)	1.570 (6)
$\mathrm{CsHPO_3F}$[d]	1.528 (2)	1.578 (2)
$\mathrm{Cs_2PO_3F}$[e] (240 K)	1.506 (4)	1.608 (5)
$\mathrm{Cs_3(NH_4)_2(HPO_3F)_3(PO_3F)}$[d]	1.544 (6)	1.580 (5)
	1.545 (6)	1.572 (5)
	1.559 (6)	1.575 (6)
	1.551 (5)	1.577 (5)
	1.537 (8)	1.559 (7)
	1.547 (7)	1.568 (5)
	1.502 (4)	1.573 (6)
$\mathrm{(H_3NC_2H_6NH_3)(H_3PO_4)(HPO_3F)}$[f]	1.519 (1)	1.559 (1)
$\mathrm{KHPO_3F}$[g]	1.555 (4)	1.565 (3)
	1.567 (4)	1.584 (3)
	1.557 (3)	1.574 (3)
	1.545 (4)	1.567 (3)
$\mathrm{K_2PO_3F}$[h]	1.486 (6)	1.609 (6)
$\mathrm{K_3H(PO_3F)_2}$[g]	1.543 (4)	1.594 (5)
$\mathrm{K_3NaPO_3F}$[i]	1.495 (1)	1.630 (1)
$\mathrm{LiKPO_3F{\cdot}H_2O}$[j]	1.527 (7)	1.594 (5)
$\mathrm{LiNH_4PO_3F}$[k]	1.513 (4)	1.592 (3)
β-$\mathrm{Na_2PO_3F}$[l]	1.507 (9), 1.499 (9)	1.619 (8), 1.594 (8)
$\mathrm{Na(HPO_3F){\cdot}2.5H_2O}$[m]	1.563 (2)	1.565 (1)
$\mathrm{Na_2PO_3F{\cdot}10H_2O}$[m]	1.539 (1)	1.608 (1)
$\mathrm{(NH_4)_{0.926}K_{2.074}H(PO_3F)_2}$[n]	1.536 (1)	1.595 (1)
$\mathrm{(NH_4)_2PO_3F{\cdot}H_2O}$[a]	1.509 (1)	1.586 (1)
$\mathrm{(NH_4)_2[Cu(H_2O)_2](PO_3F)_2}$[o]	1.505 (4)	1.577 (4)
$\mathrm{(NH_4)_2PO_3F}$[p]	1.512 (1)	1.588 (1)
α-$\mathrm{NH_4HPO_3F}$[q]	1.545 (2)	1.558 (2)
	1.550 (2)	1.566 (2)
β-$\mathrm{NH_4HPO_3F}$[q]	1.547 (1)	1.563 (1)
	1.545 (1)	1.568 (1)
α-$\mathrm{RbHPO_3F}$[g]	1.556 (5)	1.570 (4)
	1.556 (5)	1.586 (5)
$\mathrm{Rb_2PO_3F}$[e] (290 K)	1.502 (3)	1.610 (3)
$\mathrm{SnPO_3F}$[r]	1.51 (7)	1.58 (3)
XESVEW[s]	1.551 (2)	1.650 (4)
XOMPAQ[t]	1.550 (1)	1.564 (1)
XOMPEU[t]	1.545 (1)	1.566 (1)
XOMPIY[t]	1.534 (2)	1.566 (2)
XOMPOE[t]	1.531 (3)	1.544 (3)
XOMPUK[t]	1.542 (2)	1.554 (2)
XOMQA*R*[t]	1.509 (4), 1.506 (4)	1.573 (3), 1.567 (5)
YUYKUY[u]	1.549 (3)	1.554 (4)
YEHFUY01[v]	1.519 (2)	1.594 (2)
(I)[w]	1.560 (4)	1.564 (3)
$\mathrm{(C_2H_7N_4O_1)_3(HFO_3P)(FO_3P)H_2O}$[x]	1.548 (2)	1.5603 (14)
	1.5118 (18)	1.5735 (18)
$\mathrm{(NH_4)_2(Ni(H_2O)_6(PO_3F)_2}$[y]	1.510 (1)	1.598 (1)
$\mathrm{(HOC(NH(CH_3))_2)(HPO_3F)}$[z]	1.542 (2)	1.553 (2)
$\mathrm{Na_5(N(CH_3)_4)(PO_3F)_3(H_2O)_{18}}$[z]	1.518 (2)	1.599 (2)
	1.512 (2)	1.579 (2)
	1.518 (2)	1.579 (2)
$\mathrm{(C(NH_2)_3)_2(PO_3F)}$[z]	1.505 (4)	1.575 (4)
	1.505 (4)	1.567 (5)
$\mathrm{(NH_4)Na(PO_3F)(H_2O)}$[aa]	1.509 (2)	1.598 (2)
$\mathrm{NH_4Ag_3(PO_3F)_2}$[ab]	1.523 (5)	1.588 (5)
	1.522 (5)	1.592 (5)
	1.515 (7)	1.596 (5)
$\mathrm{(C_2H_7N_4O_1)_2(FO_3P)2H_2O}$[ac]	1.5112 (17)	1.5931 (15)
	1.532 (6)	1.584 (4)
$\mathrm{Ag_2PO_3F}$[ad]	1.512 (3)	1.575 (3)
$\mathrm{Hg_2PO_3F}$[ae]	1.519 (6)	1.569 (9)

Notes: (*a*) Perloff (1972); (*b*) Durand *et al.* (1987); (*c*) Zeibig *et al.* (1991); (*d*) Prescott *et al.* (2000); (*e*) Fábry, Dušek, Fejfarová *et al.* (2006) (*f*) Fábry *et al.* (2005); (*g*) Prescott *et al.* (2003); (*h*) Payen *et al.* (1979); (*i*) Durand *et al.* (1975); (*j*) Galigné *et al.* (1974); (*k*) Durand *et al.* (1978); (*l*) Durand *et al.* (1974); (*m*) Prescott *et al.* (1999); (*n*) Fábry *et al.* (2003); (*o*) Berraho *et al.* (1992); (*p*) Krupková *et al.* (2002); (*q*) Prescott *et al.* (2002*a*); (*r*) Berndt (1974); (*s*) Samuel *et al.* (2001); (*t*) Prescott *et al.* (2002*b*); (*u*) Khaoulani Idrissi *et al.* (1995); (*v*) Fábry, Dušek, Krupková *et al.* (2006); (*w*) this work; (*x*) Fábry *et al.* (2012*a*); (*y*) Berraho *et al.* (1992); (*z*) Prescott (2001); (*aa*) Fábry *et al.* (2007); (*ab*) Weil (2007); (*ac*) Fábry *et al.* (2012*b*); (*ad*) Weil *et al.* (2007); (*ae*) Weil *et al.* (2004).

structures. They are pertinent to fairly planar primary amine groups, as was found by inspection of the CSD.) The *x* and *z* fractional coordinates of P1 have been fixed during the refinements of all the title structures in order to fix the origin. From the similarity of the lattice parameters to those of (I) as well as to those of GUHP,

Table 3
The components [U^{11}, U^{22}, U^{33}, U^{12}, U^{13} and U^{23} (Å^2)] of the anisotropic displacement parameters, as well as the equivalent isotropic displacement parameters $U_{\rm eq}$ (Å^2) of the non-H atoms in (I), (II), (III), (IV) and GUHP listed in order from the first to the fifth line within each block.

All the experiments were carried out at 120 K (except for GUHP, where the experiment was carried out at 150 K). The presented values have been recalculated under similar conditions using the original data.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	$U_{\rm eq}$
P1	0.0193 (7)	0.0127 (5)	0.0210 (5)	0.0009 (5)	0.0033 (4)	−0.0003 (5)	0.0176 (3)
P1	0.0186 (6)	0.0196 (5)	0.0154 (5)	0.0012 (5)	0.0027 (4)	−0.0019 (5)	0.0178 (3)
P1	0.0150 (2)	0.0185 (2)	0.0129 (2)	0.0021 (2)	0.00253 (16)	−0.00059 (17)	0.0153 (1)
P1	0.0146 (2)	0.0210 (3)	0.0131 (2)	0.0020 (2)	0.00239 (15)	−0.0011 (2)	0.0162 (1)
P1	0.0276 (2)	0.0326 (2)	0.0253 (2)	0.00468 (18)	0.00466 (16)	−0.0016 (2)	0.0284 (1)
O1	0.034 (2)	0.0177 (16)	0.0242 (17)	0.0116 (15)	0.0067 (15)	0.0006 (13)	0.025 (1)
O1	0.035 (2)	0.0338 (19)	0.0201 (16)	0.0168 (15)	0.0090 (14)	0.0011 (14)	0.029 (1)
O1	0.0329 (9)	0.0343 (8)	0.0179 (7)	0.0198 (6)	0.0062 (6)	0.0037 (6)	0.0281 (5)
O1	0.0362 (9)	0.0380 (10)	0.0185 (7)	0.0233 (7)	0.0072 (6)	0.0041 (7)	0.0306 (5)
O1	0.0690 (12)	0.0599 (9)	0.0325 (9)	0.0396 (8)	0.0124 (8)	0.0066 (7)	0.0534 (6)
O2	0.024 (2)	0.0149 (15)	0.0345 (19)	0.0050 (14)	0.0079 (15)	0.0020 (14)	0.024 (1)
O2	0.028 (2)	0.0203 (15)	0.0229 (15)	0.0044 (14)	0.0047 (13)	0.0025 (14)	0.024 (1)
O2	0.0202 (8)	0.0228 (6)	0.0196 (7)	0.0056 (6)	0.0060 (6)	0.0021 (6)	0.0206 (4)
O2	0.0197 (8)	0.0245 (7)	0.0205 (7)	0.0056 (6)	0.0050 (6)	0.0026 (6)	0.0214 (4)
O2	0.0338 (8)	0.0432 (7)	0.0446 (9)	0.0137 (6)	0.0132 (7)	0.0037 (6)	0.0399 (5)
O3	0.016 (2)	0.0240 (18)	0.0290 (18)	0.0031 (14)	0.0042 (15)	0.0021 (14)	0.023 (1)
O3	0.0182 (17)	0.0288 (17)	0.0174 (15)	0.0023 (13)	0.0023 (12)	−0.0049 (13)	0.021 (1)
O3	0.0163 (7)	0.0242 (6)	0.0144 (6)	0.0017 (5)	0.0027 (5)	−0.0036 (5)	0.0182 (4)
O3	0.0158 (7)	0.0269 (8)	0.0142 (6)	0.0005 (6)	0.0022 (5)	−0.0043 (5)	0.01892 (1)
O3	0.0342 (7)	0.0504 (7)	0.0261 (7)	0.0048 (6)	0.0042 (6)	−0.0075 (6)	0.0368 (4)
F1	0.032 (2)	0.0214 (14)	0.0343 (16)	−0.0090 (13)	0.0042 (14)	−0.0054 (12)	0.029 (1)
F1	0.034 (3)	0.025 (2)	0.029 (2)	−0.0051 (16)	0.0035 (17)	−0.0042 (15)	0.029 (1)
F1	0.11 (3)	0.052 (10)	0.045 (12)	−0.018 (14)	0.023 (16)	−0.030 (8)	0.07 (1)
F1	0.052 (9)	0.033 (6)	0.033 (5)	−0.009 (4)	0.013 (5)	−0.017 (4)	0.0385 (9)
C1	0.012 (3)	0.022 (2)	0.025 (2)	0.002 (2)	0.001 (2)	0.0058 (18)	0.020 (1)
C1	0.022 (3)	0.016 (2)	0.020 (2)	−0.0017 (18)	0.0029 (19)	0.0039 (16)	0.019 (1)
C1	0.0136 (10)	0.0162 (8)	0.0179 (9)	0.0013 (7)	0.0035 (8)	0.0029 (7)	0.0157 (5)
C1	0.0127 (9)	0.0162 (10)	0.0194 (9)	0.0015 (8)	0.0032 (7)	0.0025 (8)	0.0160 (6)
C1	0.0251 (9)	0.0336 (9)	0.0348 (11)	0.0022 (7)	0.0047 (8)	0.0016 (7)	0.0310 (6)
N1	0.022 (3)	0.026 (2)	0.027 (2)	0.003 (2)	0.0066 (19)	−0.0010 (18)	0.025 (1)
N1	0.018 (2)	0.027 (2)	0.022 (2)	0.0044 (18)	0.0068 (16)	−0.0039 (16)	0.022 (1)
N1	0.0146 (9)	0.0245 (8)	0.0184 (8)	0.0015 (7)	0.0034 (7)	−0.0026 (6)	0.0190 (5)
N1	0.0150 (9)	0.0256 (9)	0.0179 (9)	0.0018 (7)	0.0029 (6)	−0.0025 (7)	0.0194 (5)
N1	0.0320 (9)	0.0517 (10)	0.0333 (11)	0.0029 (8)	0.0071 (7)	−0.0067 (8)	0.0387 (6)
O4	0.022 (2)	0.042 (2)	0.027 (2)	−0.0036 (18)	0.0021 (16)	−0.0073 (17)	0.031 (1)
O4	0.0170 (18)	0.041 (2)	0.0220 (17)	−0.0035 (15)	0.0035 (14)	−0.0048 (15)	0.027 (1)
O4	0.0130 (7)	0.0314 (7)	0.0219 (7)	−0.0013 (6)	0.0028 (6)	−0.0051 (6)	0.0220 (4)
O4	0.0131 (7)	0.0334 (9)	0.0214 (8)	−0.0012 (6)	0.0027 (6)	−0.0054 (6)	0.0226 (5)
O4	0.0235 (7)	0.0704 (10)	0.0431 (10)	−0.0028 (6)	0.0035 (7)	−0.0130 (7)	0.0457 (5)
N2	0.014 (2)	0.022 (2)	0.021 (2)	−0.0012 (17)	−0.0049 (16)	0.0017 (15)	0.020 (1)
N2	0.019 (2)	0.0202 (19)	0.0173 (17)	0.0001 (15)	−0.0024 (15)	−0.0011 (14)	0.019 (1)
N2	0.0137 (9)	0.0206 (7)	0.0142 (8)	−0.0010 (6)	0.0006 (6)	−0.0024 (6)	0.0162 (5)
N2	0.0145 (8)	0.0205 (9)	0.0152 (8)	−0.0006 (6)	0.0000 (6)	−0.0017 (6)	0.0169 (5)
N2	0.0233 (8)	0.0422 (8)	0.0255 (9)	−0.0019 (6)	0.0005 (6)	−0.0028 (6)	0.0305 (5)
C2	0.016 (3)	0.014 (2)	0.026 (2)	−0.0015 (19)	0.000 (2)	0.0057 (19)	0.019 (2)
C2	0.022 (3)	0.014 (2)	0.018 (2)	0.0006 (18)	−0.0008 (18)	0.0043 (17)	0.018 (1)
C2	0.0169 (11)	0.0138 (9)	0.0157 (9)	0.0015 (7)	0.0043 (8)	0.0033 (7)	0.0153 (6)
C2	0.0155 (10)	0.0134 (10)	0.0172 (10)	0.0011 (7)	0.0047 (8)	0.0025 (8)	0.0152 (6)
C2	0.0257 (9)	0.0320 (9)	0.0270 (11)	0.0012 (7)	0.0047 (8)	0.0043 (7)	0.0281 (6)
N3	0.020 (2)	0.028 (2)	0.0206 (19)	−0.0015 (19)	0.0016 (17)	−0.0011 (18)	0.023 (1)
N3	0.024 (2)	0.029 (2)	0.0151 (16)	0.0008 (17)	0.0005 (15)	−0.0022 (17)	0.023 (1)
N3	0.0149 (8)	0.0271 (8)	0.0146 (7)	0.0000 (6)	0.0024 (6)	−0.0024 (6)	0.0188 (5)
N3	0.0148 (8)	0.0296 (10)	0.0143 (7)	0.0007 (7)	0.0023 (6)	−0.0021 (7)	0.0195 (5)
N3	0.0295 (9)	0.0559 (10)	0.0261 (9)	−0.0003 (7)	0.0028 (7)	−0.0054 (7)	0.0372 (5)
N4	0.020 (3)	0.030 (2)	0.023 (2)	−0.0031 (18)	0.0031 (18)	−0.0023 (17)	0.024 (1)
N4	0.016 (2)	0.031 (2)	0.0197 (18)	−0.0011 (17)	0.0036 (15)	0.0004 (16)	0.022 (1)
N4	0.0143 (9)	0.0279 (8)	0.0171 (8)	−0.0011 (6)	0.0038 (6)	0.0006 (6)	0.0196 (5)
N4	0.0152 (9)	0.0269 (10)	0.0184 (8)	−0.0005 (7)	0.0027 (6)	−0.0001 (7)	0.0201 (5)
N4	0.0243 (9)	0.0570 (10)	0.0391 (12)	−0.0032 (7)	0.0078 (8)	−0.0013 (8)	0.0398 (6)

isostructurality of the mixed crystals (II) and (III) could be inferred. Therefore, the model of (I), adapted for the simultaneous presence of hydrogen fluorophosphonate and hydrogen phosphite, has been used for the refinement of (II) and (III) as well as of (IV). The occupational parameters of the hydrido H*p*1 and F1 atom have been constrained so that their sum equalled 1. The P1—F1 distances have been restrained to 1.564 (1) Å, as in (I). The need for this restraint was called for by the electron densities around the F1 and hydrido H atom that has been smeared (Figs. 7*b* and 7*c*, *cf.* Fig. 7*a*). From the mean for 48 hits for the hydrogen phosphite anion that had been found in the CSD, the P—H distance was restrained to 1.295 (1) Å. This value corresponds excellently to the refined value of the P—H distance in GUHP (Fridrichová, Němec, Císařová & Němec, 2010), where it was found to be 1.30 (2) Å after a new refinement of the structure by the present authors using similar refinement conditions to those employed for (I). The isotropic displacement parameter $U_{\rm iso}$(H*p*1) was set at 1.2$U_{\rm eq}$(P1).

In the case of (II), this feature of the electron density caused the refinement of the F1 and hydrido H atoms to be correlated and in order to overcome this obstacle the hydrido H atom was assumed to be situated exactly along the P1—F1 bond. The P1—H*p*1 distance was set equal to 0.828 times the P1—F1 distance, while P1—F1 was restrained to 1.564 (1) Å, in accordance with the distance observed in (I) (*cf.* Fig. 6). Moreover, in the case of (II), 24 reflections for which $|I_{\rm o} - I_{\rm c}| > 10\sigma(I)$ have been omitted.

The structure of (IV) has been refined under the same conditions as those of (III) using 638 Friedel pairs in the refinement.

For all 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.*, 1997); 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3422). Services for accessing these data are described at the back of the journal.

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