

The Crystal Structures of Hydrated Calcium and Ammonium Monofluorophosphates: CaPO₃F·2H₂O and (NH₄)₂PO₃F·H₂O

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With the primary intention of establishing the dimensions and configuration of the monofluorophosphate ion, the crystal structures of the calcium and ammonium salts have been determined by three-dimensional X-ray diffraction analysis. Data were measured on an automated diffractometer using Nb-filtered Mo $K\alpha$ radiation, $\lambda=0.71069$ Å. Both structures were established by direct phase determining techniques and refined by full-matrix least-squares analysis using anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms. All hydrogen atoms were located in difference maps and the hydrogen bonding in these structures could be unambiguously determined. The crystal data (at 25°C) and final R values are: CaPO₃F·2H₂O; $P\bar{1}$, $a=8.6497$ (7), $b=6.4614$ (6), $c=5.7353$ (4) Å, $\alpha=119.003$ (7)°, $\beta=110.853$ (7)°, $\gamma=94.146$ (8)°, $V=249.94$ Å³, $Z=2$, $\rho_c=2.313$ g.cm⁻³, $R=2.0\%$ (1254 observed data). (NH₄)₂PO₃F·H₂O; $P2_1/c$, $a=6.3042$ (5), $b=8.2942$ (7), $c=12.7597$ (10) Å, $\beta=98.415$ (8)°, $V=660.00$ Å³, $Z=4$, $\rho_c=1.530$ g.cm⁻³, $R=3.6\%$ (1721 observed data). The average dimensions of the PO₃F²⁻ ion are; P-F 1.585, P-O 1.506 Å, F-P-O 104.5 and O-P-O 114.0°.

Introduction

The PO₃F²⁻ ion has been suggested as a potentially ideal system for obtaining information about chemical-shift anisotropy and the sign of the F-P indirect dipolar coupling constant from n.m.r. line-shape analysis, and this has been done for BaPO₃F (Van der Hart, Gutowsky & Farrar, 1969). These authors were forced to use assumptions about both the symmetry of PO₃F²⁻ ion itself, and the structure of BaPO₃F, due to the lack of structural data on such salts. The only single-crystal work on a monofluorophosphate has been reported by Robinson (1958) on K₂PO₃F. However, his work was done on poor crystals and utilized only two-dimensional data. Serious overlap of atoms prevented a good refinement and, consequently, his results are given with rather large errors. The present work was done, primarily, in an effort to better establish the dimensions and configuration of the monofluorophosphate ion. Initially, only the CaPO₃F·2H₂O salt was available for study. Later the (NH₄)₂PO₃F·H₂O salt was made and its structure analyzed in order to confirm the PO₃F²⁻ dimensions and also to provide some information on the distortion of the anion in two different structures.

Experimental

Single crystals of the two colorless salts were supplied by T. C. Farrar and T. Tsang of the National Bureau of Standards. The CaPO₃F·2H₂O crystals were lath-shaped, elongated along [011] with (100) as the dominant face. Other visible faces were (11 $\bar{1}$), (001) and (010). (NH₄)₂PO₃F·H₂O crystallized as rectangular prisms, elongated along the a axis and bounded by

{011}. The Ca salt is stable in air, but the NH₄ salt slowly dehydrates in air and had to be enclosed in a thin-walled Pyrex capillary (0.03 mm wall thickness) for the data collection.

Preliminary symmetry and approximate cell dimensions were obtained from precession photographs. Measurements for the calculation of the final cell dimensions by least-squares refinement (Table 1) and the intensity data were collected on an automated three-circle counter diffractometer using Nb-filtered Mo radiation ($\lambda=0.71069$ Å). A 4° takeoff angle was used. The detector was a scintillation counter equipped with a pulse-height analyzer set to pass the central 90% of the Mo $K\alpha$ peak. Attenuation filters of Nb were used, where necessary, to keep all measurements within the linear response range of the equipment (<20,000 counts per sec). The recommendation of Alexander & Smith (1962), $2\theta \pm 0.5$ (1.8 + tan θ), was used for the scan range or background settings. All independent reflections up to $2\theta=60^\circ$ were measured. Standard reflections were monitored every 50 reflections and no deterioration in the crystals was detectable. The ob-

Table 1. *Crystal data* (25°C)

Figures in brackets are standard deviations.

	CaPO ₃ F·2H ₂ O	(NH ₄) ₂ PO ₃ F·H ₂ O
a	8.6497 (7) Å	6.3042 (5) Å
b	6.4614 (6)	8.2942 (7)
c	5.7353 (4)	12.7597 (10)
α	119.003 (7)°	—
β	110.853 (7)	98.415 (8)°
γ	94.146 (8)	—
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
Density (obs.)	—	1.528 g.cm ⁻³
Density (calc.)	2.313 g.cm ⁻³	1.530 g.cm ⁻³

servable threshold limit was chosen to be twice the standard deviation of a measurement. Specific details for the two crystals are as follows.

$\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$: crystal size, $0.04 \times 0.13 \times 0.35$ mm; $\mu_{\text{MoK}\alpha}$ 14.89 cm^{-1} ; cell dimension refinement from 22 reflections; cell contents derived from volume comparison with $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (Atoji & Rundle, 1958; Wooster, 1936); intensities measured by θ - 2θ scan at 2° 2θ per min with 30 sec background counts at scan extremities; aligned with the 342 reflection along φ

axis; 2 standard reflections; resultant independent data: 1254 observed and 193 unobserved reflections.

$(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$: crystal size, essentially spherical with a minimum diameter of 0.473 mm and a maximum diameter of 0.546 mm; $\mu_{\text{MoK}\alpha}$ 3.943 cm^{-1} ; cell dimension refinement from 16 reflections; density measured on a Berman balance; intensities measured by peak-height method using 10 sec counts for peak and each background, converted to integrated intensities by empirical curve; aligned with the 302 reflection along

Table 2. *Statistics*

Average	Observed		Theoretical	
	$\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$	Centro	Non-centro
$\langle E \rangle$	0.8042	0.8003	0.798	0.886
$\langle E^2 \rangle$	1.0000	1.0000	1.000	1.000
$\langle E^2 - 1 \rangle$	0.9545	0.9706	0.968	0.736
Distribution				
> 1.0	0.3406	0.3224	0.3173	0.3679
> 2.0	0.0332	0.0442	0.0455	0.0183
> 3.0	0.0000	0.0011	0.0027	0.0001

Table 3. *Final atomic parameters*

For uniformity all of the non-hydrogen positional parameters have been reported to five decimal places, the hydrogen positions to four decimal places and all thermal parameters to two decimal places. The reader should be guided by the estimated standard deviations in determining the actual number of significant figures for each parameter.

Estimated standard deviations in parentheses.

Temperature factors are of the form $\exp[-\frac{1}{4}(h^2a^*2B_{11} + k^2b^*2B_{22} + l^2c^*2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ or $\exp[-B \sin^2 \theta / \lambda^2]$.

	x/a	y/b	z/c	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$									
Ca	0.14522 (3)	0.31936 (5)	0.34790 (6)	0.96 (1)	0.79 (1)	0.94 (1)	0.26 (1)	0.40 (1)	0.56 (1)
P	0.14948 (4)	0.79913 (6)	0.36129 (7)	1.03 (1)	0.76 (1)	0.83 (1)	0.28 (1)	0.38 (1)	0.54 (1)
O(1)	0.06536 (14)	0.87650 (19)	0.14945 (23)	1.62 (4)	1.05 (4)	1.22 (4)	0.45 (3)	0.49 (3)	0.82 (3)
O(2)	0.27331 (14)	0.65093 (21)	0.29427 (25)	1.45 (4)	1.60 (4)	1.56 (4)	0.80 (3)	0.84 (3)	1.08 (3)
O(3)	0.03090 (14)	0.67808 (20)	0.42765 (26)	1.63 (4)	1.50 (4)	1.97 (4)	0.68 (3)	1.14 (4)	1.29 (4)
F(4)	0.73213 (14)	0.94418 (18)	0.33644 (21)	2.24 (4)	1.29 (3)	1.21 (3)	-0.02 (3)	0.21 (3)	0.31 (3)
O(5)	0.39174 (16)	0.19678 (26)	0.28442 (31)	1.36 (4)	2.01 (5)	2.20 (5)	0.62 (4)	0.71 (4)	1.01 (4)
O(6)	0.64687 (18)	0.38711 (28)	0.13755 (29)	1.67 (5)	3.18 (6)	1.46 (4)	-0.06 (4)	0.54 (4)	1.13 (4)
H(51)	0.3727 (40)	0.0684 (60)	0.1722 (72)	1.68 (63)					
H(52)	0.4966 (33)	0.2411 (43)	0.4294 (57)	0.49 (44)					
H(61)	0.5500 (49)	0.3492 (67)	0.0814 (81)	2.98 (75)					
H(62)	0.6792 (42)	0.3848 (58)	0.0077 (72)	2.35 (65)					
$(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$									
P	0.80346 (6)	0.42331 (5)	0.14299 (3)	2.17 (2)	1.73 (1)	1.38 (1)	0.02 (1)	0.31*(1)	0.06 (1)
F(1)	0.23275 (21)	0.07044 (14)	0.43699 (9)	5.37 (6)	2.89 (5)	3.16 (5)	-0.49 (4)	0.96 (4)	-1.40 (4)
O(2)	0.66492 (19)	0.46206 (15)	0.22655 (9)	2.86 (5)	2.62 (5)	2.07 (4)	0.27 (4)	0.77 (4)	-0.15 (4)
O(3)	0.72471 (20)	0.27942 (15)	0.07649 (9)	3.29 (5)	2.53 (5)	2.20 (4)	-0.25 (4)	0.18 (4)	-0.58 (4)
O(4)	0.03990 (19)	0.42313 (17)	0.18203 (10)	2.30 (5)	3.65 (6)	2.66 (5)	-0.08 (4)	0.30 (4)	-0.47 (4)
N(5)	0.67838 (26)	0.17531 (20)	0.35604 (12)	2.95 (6)	2.61 (6)	1.97 (5)	-0.11 (5)	0.38 (4)	0.28 (5)
N(6)	0.28881 (25)	0.18352 (19)	0.09996 (12)	2.82 (6)	2.30 (5)	2.19 (5)	-0.05 (5)	0.31 (4)	0.26 (4)
O(7)	0.17888 (52)	0.45778 (25)	0.39972 (15)	16.41 (24)	3.25 (8)	2.66 (7)	-1.82 (11)	-2.43 (10)	0.72 (6)
H(51)	0.5607 (42)	0.1218 (33)	0.3337 (20)	2.02 (51)					
H(52)	0.7591 (38)	0.1163 (30)	0.3450 (18)	1.50 (45)					
H(53)	0.6963 (39)	0.1973 (32)	0.4234 (22)	2.22 (53)					
H(54)	0.6746 (36)	0.2715 (30)	0.3208 (18)	1.25 (43)					
H(61)	0.2898 (35)	0.1061 (30)	0.1472 (18)	1.23 (43)					
H(62)	0.2254 (41)	0.1416 (33)	0.0326 (22)	2.51 (54)					
H(63)	0.4210 (40)	0.2183 (29)	0.0985 (18)	1.52 (46)					
H(64)	0.1962 (38)	0.2666 (31)	0.1188 (19)	1.84 (48)					
H(71)	0.8048 (51)	0.0559 (44)	0.0991 (26)	4.01 (77)					
H(72)	0.1421 (51)	0.4368 (39)	0.3360 (28)	3.92 (73)					

Table 4. CaPO₃F.2H₂O structure factors

The columns are h, 10F_o and 10F_c. An asterisk designates an unobservable reflection which has been assigned the estimated minimum observable F_o value.

Table with multiple columns of numerical data representing structure factors for various reflections. The table is organized into several vertical sections, each with its own set of column headers. The data includes values for h, 10F_o, and 10F_c for numerous reflections, with some values marked with an asterisk to indicate unobservable reflections.

Table 5. (NH₄)₂PO₃F.H₂O structure factors

The columns are *l*, 10*F*₀ and 10*F*_c. An asterisk designates an unobservable reflection which has been assigned the estimated minimum observable *F*₀ value.

Table with columns for reflection indices (h, k, l), intensity (F0), and structure factor (Fc). The table is organized into sections based on the l index (e.g., 00L, 20L, 40L, etc.). Each section contains multiple rows of data points, with some values in parentheses indicating estimated or unobservable values. The table is dense and spans the entire page.

Table 5 (cont.)

618•L	8 80	79	1 35	34	-5 13*	11	-9 40	41	4•9•L	5•9•L	4 34	-32	1 20	-26	0 13*	1	1 77	74	0•11•L	4 50	26				
-3 18	-19	10 19	16	3 27	-24	-3 13*	-7	-7 14	10	-9 18	16	-6 68	68	6 17	14	3 13*	-130	2 13*	2	3 116	115	1 25	-76	5 56	26
-2 99	100	11 96	-96	4 68	59	-2 106	108	-6 16	7	-8 45	86	-5 15*	-14	7 53	-50	4 14*	4	3 45	-53	4 14*	-9	2 57	54	2•11•L	
-1 22	18	1•9•L	5 13*	-5	-1 14	-17	-5 14	14	-7 51	50	-4 30	29	8 14*	-2	5 24	26	4 14*	10	5 79	-78	1 67	54	4 84	-62	
0 38	-44	7 22	22	1 20	18	-3 13*	1	-5 39	-40	-2 58	-62	-3 31	-27	9 107	-107	7 15*	152	6 14*	-1	6 15*	-10	4 84	-62	-3 15*	-7
2 51	-20	-11 18	12	8 53	-55	2 45	-47	-2 46	46	-4 42	-42	-1 50	47	1•10•L	8 33	31	7 44	45	4•10•L	1•11•L		-2 35	-23	2 24	-23
3 59	-58	-10 33	83	0 27	35	3 59	59	-1 15*	-7	-3 43	38	0 34	31	2•10•L	2 75	75	-9 31	28	3•10•L	-5 62	-58	-5 52	-51	1 47	-45
0•9•L	-8 105	-102	2•9•L	6 75	72	0 17*	42	-2 84	-84	1 22	23	-8 27	-29	0 14*	2	-7 55	-53	-4 14*	-13	-5 52	-174	0 49	-45	0 49	-45
1 13*	15	-6 100	-100	7 37	-36	3 13*	-10	1 51	-48	-6 14*	11	-7 29	31	-6 14*	-5	-2 14*	-5	-2 14*	-5	-3 72	71	3 48	-49		
2 15*	155	-5 13*	-3	-11 111	108	8 124	-106	4 20	20	2 21	-17	-5 74	-74	-6 14*	-3	-5 81	79	-1 23	-23	-2 20	-15				
4 60	-57	-3 16	12	-9 14*	-5	9 50	51	5 46	44	3 27	-27	-11 100	-100	-3 11	100	-4 31	-31	0 17	15	-1 14*	0				
5 69	68	-2 55	-56	-4 14*	-5	5 131	134	4 104	-104	0 15*	-11	-3 121	-120	-4 39	39	-3 35	35	1 53	-52	0 44	-44				
6 125	-124	-1 16	-13	-7 82	-82	7 23	-22	5 66	66	1 26	-24	-2 13*	6	-3 14*	-17	-2 21	21	2 26	-24	1 50	-47				
7 81	79	0 71	-71	-5 113	-114	-10 19	20	8 22	-24	6 29	28	3 39	37	0 13*	4	-1 18	19	0 14*	-4	3 99	99	3 24	-74		

the ϕ axis; 3 standard reflections; resultant independent data: 1721 observed and 195 unobserved reflections.

Lorentz and polarization but no absorption corrections were made. The maximum error from absorption was estimated to be 8% for the Ca salt and 1% for the NH_4 salt.

Structure determination and refinement

Both structures were solved by the direct phase determining method based on the symbolic addition method for centrosymmetrical structures (Karle & Karle, 1966). All computations were made using the computer programs from X-RAY 67 (Stewart, 1967). The atomic scattering factors used were Ca^{2+} and neutral P, N, O, F, and H as given in *International Tables for X-ray Crystallography* (1962).

Normalized structure factor computations, Σ_2 relations and the symbolic addition procedure were performed using the *DATFIX*, *SIGMA2* and *PHASE* programs respectively. The resulting statistical averages are given in Table 2 and they generally confirm the centrosymmetrical choice. The distribution of E values for the Ca salt appears to be ambiguous in this respect, but this is probably due to the strong rational dependence on k being even or odd (e.g. for $E \geq 1.0$, 413 reflections had k even and 80 had k odd; for $E \geq 1.5$, 215 had k even and 12 had k odd). This rational dependence resulted in initial E maps in which all atoms at x, y, z had ghost images at $x, y + \frac{1}{2}, z$ but gave no other apparent difficulties in the structure solution.

For the $\text{CaPO}_3\text{F} \cdot 2\text{H}_2\text{O}$ solution, the *PHASE* program was used to establish phases for all reflections with $|E| \geq 1.0$ from relationships having a probability of 0.95 or greater. In addition to the three origin-determining reflections $70\bar{3}$, $4\bar{2}3$ and $2\bar{7}6$, which were assigned positive phases, the reflections 205 and 641 required assigned phases to establish the phases for 394 of the 486 reflections with $|E| \geq 1.0$. E maps were computed for the four possibilities. The phase sets with phases 205 and 641 both + or both - gave unreasonable maps and were discarded immediately. The phase set based on 205(-) and 641(+) revealed Ca and P positions (peak heights 36 and 32, respectively) plus 7 pairs of peaks in the 5-9 peak height range for the 6 lighter atoms expected, while the phase set based on 205(+) and 641(-) gave Ca and P peaks (35 and 34 peak heights, respectively) plus 8 pairs of peaks in the

5-9 peak height range. Both sets were treated to cycles of structure factor and electron density calculations starting with Ca, P and four O as phosphate ligands and adding water molecules one at a time to the strongest unassigned peak in each cycle. Both sets ended up with the expected two molecules of water in the asymmetric unit. The two possibilities were then subjected to isotropic least-squares refinement (based on Ca, P and six O) and bond distance calculations. The structure based on 205(-) and 641(+) stopped refining at $R=30\%$ and revealed unreasonably short O-O distances ($\sim 1.5 \text{ \AA}$) between some oxygen atoms of neighboring phosphate groups, while the model based on 205(+) and 641(-) which was refined to $R=6\%$, exhibited no abnormal distances and was accepted as the correct structure.

The P-O bond distances of the correct structure, at this stage, were one of 1.58 \AA and three $\sim 1.51 \text{ \AA}$. While it was felt that the longer distance almost certainly represented the P-F distance, additional confirmation was sought by testing each of the phosphate ligands as a fluorine atom for two additional cycles of isotropic least-squares refinement. Fortunately, the only model to give an improved R value (5.2%) corroborated the bond length indication and that ligand was accepted as the fluorine. A difference map at this point suggested that some of the atoms had anisotropic motion, so three cycles of anisotropic least-squares refinement were run which reduced the R value to 2.6%. Another difference map now clearly indicated the hydrogen atom positions and these were added to the atom list for the final cycles of full-matrix least-squares refinement with the non-hydrogen atoms having anisotropic thermal parameters and the hydrogen atoms having isotropic thermal parameters. This refinement ended with a conventional $R=2.0\%$ and a weighted $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 2.9%, based on observed data only. The final standard deviation of an observation of unit weight was 0.3051. The data were weighted $w^{1/2} = 60/(sF_o)$ for reflections with $sF_o \geq 60$ and $w^{1/2} = 1$ for reflections with $sF_o < 60$, where $s =$

$$\frac{1}{0.22554} \text{ and } F_o \text{ is the observed structure factor. The}$$

final parameters are listed in Table 3.

The $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$ structure determination was more straightforward, requiring only the assignment of the three origin-determining reflections $1, 10, \bar{7}$,

2,1,13 and 245 as positive to establish phases for 415 of 461 reflections with $E \geq 1.2$ (using a minimum probability of 0.95). The initial E map showed the P atom (peak height 28) plus eight smaller peaks (peak height 5–11) for the expected seven additional atoms. By using the P atom and five O atoms, based on the five strongest peaks, for structure factor and electron-density calculations the false peak was eliminated. This was followed by two cycles of isotropic least-squares refinement, based on one P and seven O atoms, resulting in a R of 12.4%. Bond distance calculations were then used to assign the F and N atoms. The unique long P–ligand distance was accepted as determining the F atom. Of the three non-ligand atoms two had tetrahedral surroundings and one had a planar trigonal coordination, all within possible hydrogen-bonding distances. The latter was chosen as the water molecule since the trigonal plane is a common coordination for water, but would be unusual for an NH_4 group. The tetrahedrally surrounded atoms were accepted as N atoms. With the assignment of one P, one F, four O and two N atoms, isotropic least-squares refinement reduced the R value to 11.6% and anisotropic refinement reduced it to 5.4%. A difference map at this point revealed the ten H atoms and was otherwise featureless. A final full-matrix least-squares refinement using anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogens resulted in a final conventional R value of 3.6% and a weighted R' of 4.2%, both based on observed data only. The final standard deviation of an observation of unit weight was 0.4793. The data were weighted $w^{1/2} = 100/(sF_o)$ for reflections with $sF_o \geq 100$ and $w^{1/2} = 1$ for reflections with $sF_o < 100$, where $s = 1/0.23761$ and F_o is the observed structure factor. The final parameters are listed in Table 3. The observed and calculated structure factors for $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$ are given in Tables 4 and 5 respectively.

Results and discussion

For both crystals the numbering of the light non-hydrogen atoms is arbitrarily in the order that they were accepted in the structure determination. The first four are the phosphate ligands in both compounds and the higher numbered oxygen atoms are from water molecules. Hydrogen atoms are numbered with the number corresponding to the atom to which they are covalently bound plus an arbitrary identifying digit.

$\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ structure

The $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ structure can be considered to be composed of ionically bonded sheets, parallel to (100), which are held together by hydrogen bonds. The linkage within a sheet can be seen most clearly in Fig. 1 and the intersheet bonding in Fig. 2. There is a strong resemblance to the structure of gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, (Wooster, 1936; Atoji & Rundle, 1958) with the differences being attributable to the F atom's non-parti-

cipation in the Ca coordination or hydrogen bonding. In the gypsum structure the Ca atom is coordinated to eight oxygens (six oxygens from four sulfate groups plus two water oxygens); there are two types of sulfate oxygens, an O(I) which coordinates to S, one Ca and accepts two hydrogen bonds, and an O(II) which bonds to S and two Ca ions; there is only one type of water molecule which coordinates to one Ca and provides H for two hydrogen bonds, one within a sheet and one between sheets.

In the calcium fluorophosphate structure the F replaces one of the O(I) type oxygen atoms without performing its function in satisfying the cation or hydrogen bonding. The Ca ion is coordinated to seven oxygen atoms of which five are from four different phosphate groups and two are water molecules. The distances are given in Table 6 and are well within the normal range (2.29–2.80 Å) observed in other compounds for 7-coordinated Ca (*International Tables for X-ray Crystallography*, 1962, p. 260). The closest Ca–F approach is 3.031 Å, which is comparable to Ca–P and Ca–H distances in the structure so it must be considered outside the Ca coordination sphere.

The deviations of PO_3F^{2-} group from an ideal C_{3v} symmetry appear to be real and in accordance with the stresses imposed by the structure. There is one edge [O(2)–O(3)] of the PO_3F^{2-} group which is shared with a Ca coordination polyhedron. This results in a shortened O–O distance and a smaller O–P–O angle relative to the other comparable distances and angles in the anion. O(1) and O(3) have the same environment corresponding to O(II) of the gypsum structure. Their P–O distances are essentially the same (1.503 and 1.506 Å) and significantly shorter than the P–O(2) distance of 1.515 Å. Atoji & Rundle (1958) found this same difference of 0.016 Å in the sulfate anion between S–O(1)

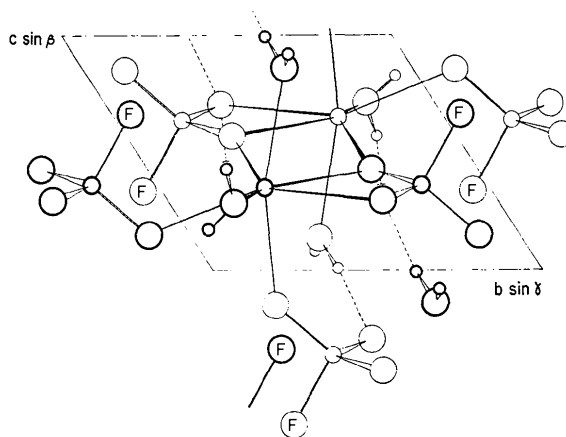


Fig. 1. $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ structure projected down a axis. Largest circles are O and F, medium ones are Ca and P, and smallest ones are H. Ca coordination is indicated by solid bonds, P and water O coordination by open bonds, and hydrogen bonding by dashed lines. F indicates the fluorine atom. Bonds ending in an arc represent bonding to an atom in the cell below.

Table 6. $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ bond distances and angles

The superscripts indicate the transformations applied to the x, y, z values given in Table 3: (i) $x, y-1, z$; (ii) $-x, 1-y, -z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 2-y, 1-z$; (vi) $1-x, 1-y, -z$.

Calcium distances

Ca—O(1 ⁱ)	2.441 (1) Å
Ca—O(1 ⁱⁱ)	2.350 (1)
Ca—O(2)	2.540 (2)
Ca—O(3)	2.487 (1)
Ca—O(3 ⁱⁱⁱ)	2.315 (2)
Ca—O(5)	2.413 (2)
Ca—O(6 ^{iv})	2.417 (1)

Anion distances and angles

P—O(1)	1.506 (1) Å	F(4 ^v)—P—O(1)	102.68 (6)°
P—O(2)	1.515 (1)	F(4 ^v)—P—O(2)	105.03 (6)
P—O(3)	1.503 (2)	F(4 ^v)—P—O(3)	106.13 (7)
P—F(4 ^v)	1.583 (1)	O(1)—P—O(2)	115.64 (8)
O(1)—O(2)	2.557 (2)	O(1)—P—O(3)	116.48 (7)
O(1)—O(3)	2.558 (2)	O(2)—P—O(3)	109.52 (8)
O(1)—F(4 ^v)	2.413 (1)		
O(2)—O(3)	2.465 (2)		
O(2)—F(4 ^v)	2.459 (1)		
O(3)—F(4 ^v)	2.468 (2)		

Water molecules and hydrogen bonding

O(5)—H(51)	0.72 (3) Å	H(51)—O(5)—H(52)	107 (3)°
O(5)—H(52)	0.89 (2)		
H(51)—H(52)	1.29 (3)		
O(5)—O(2 ^{iv})	2.738 (2)	O(5)—H(52)—O(2 ^{iv})	172 (4)
H(52)—O(2 ^{iv})	1.86 (2)		
O(6)—H(61)	0.75 (4)	H(61)—O(6)—H(62)	114 (4)
O(6)—H(62)	0.88 (5)		
H(61)—H(62)	1.37 (7)		
O(6)—O(2 ^{vi})	2.706 (3)	O(6)—H(62)—O(2 ^{vi})	174 (2)
H(62)—O(2 ^{vi})	1.83 (5)		

and S—O(II) distances, but were reluctant to claim the difference as being significant since their standard deviations of the distances were 0.01 Å. However, if the standard deviations of the present work are at all realistic, the observed longer P—O bond involving O(2), which has the same environment as their O(I), suggests that their results may be more valid than those indicated by the statistical significance criterion.

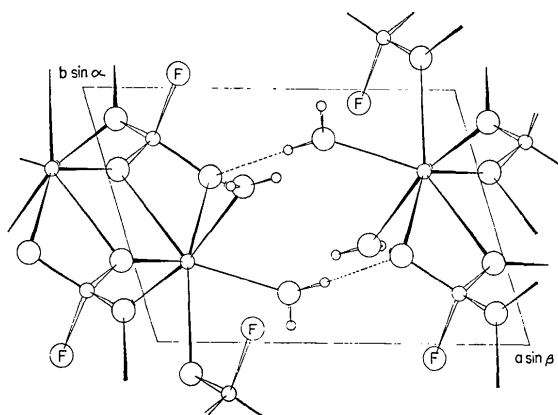


Fig. 2. $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ structure projected down the c axis. Bonding representations are the same as for Fig. 1.

Of considerable interest is the modification of the role of the water molecule hydrogen bonding relative to the gypsum structure. As mentioned above, the water molecule in gypsum utilizes both its hydrogen atoms in hydrogen bonding, one within a sheet and the other between sheets. The substitution of F in one of the sites which used to accept hydrogen bonds results in two crystallographically distinct water molecules, each of which utilizes only one hydrogen to provide half the hydrogen bonding function that was accomplished in gypsum. The O(5) water molecule provides only the intersheet hydrogen bond and the O(6) water molecule only the intrasheet hydrogen bond. The occurrence of a water molecule not utilizing all of its hydrogen atoms for hydrogen bonding has been observed in the $\text{MgSO}_4\cdot 4\text{H}_2\text{O}$ structure (Baur, 1964). The author is not aware of any structure other than $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ in which all of the water molecules use only one hydrogen bonding. If the hydrogen atoms had not been found directly it would have been tempting to infer an erroneous bonding scheme since there are O—O and O—F distances involving the water molecules that are possible hydrogen bonding distances, e.g. O(5)—F(4) = 2.942 [H(51)—F(4) = 2.69], O(5)—O(1) = 2.983 [H(51)—O(1) = 2.78], O(5)—O(6) = 3.254 [H(51)—O(6) = 2.55], O(6)—F(4) = 3.117 [H(61)—F(4) = 2.46] and O(5)—O(6) = 3.005 Å [H(61)—O(5) = 2.50 Å]. The minimum distance between a hydrogen atom and any of these atoms is 2.46 Å which is too long to be considered a hydrogen bond of any significance. Adjusting for the fact that the O—H distances in a water molecule (as listed in Tables 6 and 7) are very short relative to the internuclear distance that would be found by a neutron diffraction study (Hamilton & Ibers, 1958), does not seriously change the picture. Extending the water O—H bond to 0.96 Å, which is the value found in an isolated water molecule, reduces the above hydrogen-neighbor distances to H(51)—F(4) = 2.64, H(51)—O(1) = 2.75, H(51)—O(6) = 2.31, H(61)—F(4) = 2.29, H(61)—O(5) = 2.39 Å. The last three distances might be considered to be short enough to represent very weak hydrogen bonds, but are certainly outside the range of normal hydrogen bond values. Additional evidence for the non-hydrogen bonding or very weak hydrogen bonding behaviour can be seen in the water molecule O—H distances. The distances to H(51) and H(61), which are the nonparticipating hydrogen atoms, are, on average 0.15 Å shorter than the distances to the hydrogen-bonded hydrogens.

 $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$ structure

The ammonium fluorophosphate structure provides a more symmetrical environment for the fluorophosphate anion and a much more efficient arrangement of hydrogen bonds utilizing all of the hydrogen atoms. The structure is shown in Fig. 3. Each ammonium ion is tetrahedrally coordinated. N(5) is hydrogen bonded to oxygen atoms from four fluorophosphate anions while N(6) donates its hydrogen atoms to oxygens

Table 7. $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$ distances and angles

The superscripts indicate the transformations applied to the x, y, z values given in Table 3: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1+x, y, z$; (iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

Anion

P—F(1 ⁱ)	1.586 (1) Å	F(1 ⁱ)—P—O(2)	104.31 (7)°
P—O(2)	1.508 (1)	F(1 ⁱ)—P—O(3)	104.05 (6)
P—O(3)	1.506 (1)	F(1 ⁱ)—P—O(4 ⁱⁱ)	104.88 (7)
P—O(4 ⁱⁱ)	1.501 (1)	O(2)—P—O(3)	112.95 (7)
F(1 ⁱ)—O(2)	2.444 (2)	O(2)—P—O(4 ⁱⁱ)	114.53 (7)
F(1 ⁱ)—O(3)	2.437 (2)	O(3)—P—O(4 ⁱⁱ)	114.57 (8)
F(1 ⁱ)—O(4 ⁱⁱ)	2.447 (2)		
O(2)—O(3)	2.513 (2)		
O(2)—O(4 ⁱⁱ)	2.531 (2)		
O(3)—O(4 ⁱⁱ)	2.530 (2)		

Ammonium ions, water and hydrogen bonding

N(5)—H(51)	0.88 (3) Å	H(51)—N(5)—H(52)	110 (2)°
N(5)—H(52)	0.91 (3)	H(51)—N(5)—H(53)	114 (2)
N(5)—H(53)	0.87 (3)	H(51)—N(5)—H(54)	109 (2)
N(5)—H(54)	0.91 (3)	H(52)—N(5)—H(53)	106 (2)
N(5)—O(2)	2.890 (2)	H(52)—N(5)—H(54)	111 (2)
N(5)—O(2 ⁱⁱⁱ)	2.873 (2)	H(53)—N(5)—H(54)	107 (2)
N(5)—O(4 ⁱⁱⁱ)	2.832 (2)		
N(5)—O(3 ^{iv})	2.810 (2)		
H(51)—O(2 ⁱⁱⁱ)	2.01 (3)	N(5)—H(51)—O(2 ⁱⁱⁱ)	167 (2)
H(52)—O(4 ⁱⁱⁱ)	1.97 (3)	N(5)—H(52)—O(4 ⁱⁱⁱ)	157 (2)
H(53)—O(3 ^{iv})	1.94 (3)	N(5)—H(53)—O(3 ^{iv})	173 (3)
H(54)—O(2)	1.98 (2)	N(5)—H(54)—O(2)	172 (2)
N(6)—H(61)	0.88 (2)	H(61)—N(6)—H(62)	108 (2)
N(6)—H(62)	0.96 (3)	H(61)—N(6)—H(63)	110 (2)
N(6)—H(63)	0.88 (3)	H(61)—N(6)—H(64)	107 (2)
N(6)—H(64)	0.96 (3)	H(62)—N(6)—H(63)	112 (2)
N(6)—O(3)	2.918 (2)	H(62)—N(6)—H(64)	107 (2)
N(6)—O(4)	2.827 (2)	H(63)—N(6)—H(64)	112 (2)
N(6)—O(2 ⁱⁱⁱ)	2.858 (2)		
N(6)—O(7 ^v)	2.804 (2)		
H(61)—O(2 ⁱⁱⁱ)	1.99 (2)	N(6)—H(61)—O(2 ⁱⁱⁱ)	168 (2)
H(62)—O(7 ^v)	1.87 (3)	N(6)—H(62)—O(7 ^v)	164 (2)
H(63)—O(3)	2.04 (3)	N(6)—H(63)—O(3)	172 (2)
H(64)—O(4)	1.88 (3)	N(6)—H(64)—O(4)	169 (2)
O(7)—H(71 ⁱ)	0.82 (4)	H(71 ⁱ)—O(7)—H(72)	104 (3)
O(7)—H(72)	0.83 (3)		
H(71 ⁱ)—H(72)	1.30 (5)		
O(7)—O(4)	2.802 (2)		
O(7)—O(3 ^{iv})	2.743 (2)		
H(71)—O(3)	1.93 (4)	O(7 ⁱⁱⁱ)—H(71)—O(3)	170 (3)
H(72)—O(4)	1.98 (3)	O(7)—H(72)—O(4)	171 (3)

from three anions and also to the water molecule. The water molecule is trigonally coordinated. In addition to accepting a hydrogen bond from N(6), it donates its hydrogens to oxygen atoms from two anions. Each anion oxygen accepts three hydrogen bonds: O(2) from three ammonium ions, and O(3) and O(4) from two ammonium ions and the water molecule. Here again, the F atom appears to be completely satisfied by its bond to the P atom and is not involved in any hydrogen bonding. This bonding arrangement is identical to that found in $(\text{NH}_4)_2\text{SO}_3\cdot \text{H}_2\text{O}$ (Battelle & Trueblood, 1965) and, with the omission of the F atom, the fluorophosphate and sulfite structures are isostructural.

All the distances and angles are in the normal range for previously reported compounds, e.g. N—H...O 2.73–3.22 Å (*International Tables for X-ray Crystallog-*

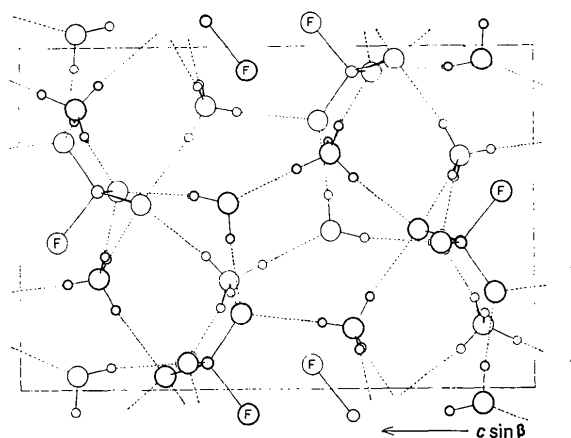


Fig. 3. $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot \text{H}_2\text{O}$ structure projected down the a axis. Largest circles are N, O or F (indicated by F), medium circles are P, and smallest circles are H. Covalent bonding is indicated by solid lines and hydrogen bonding by dashed lines. Bonds ending in an arc represent bonding to an atom in the cell below.

raphy, 1962, p. 273). It might be noted that there is an N(6)—F distance of 2.898 Å which would appear to be a potential hydrogen-bonding approach, but no H is closer than 2.64 Å to the fluorine atom.

The PO_3F^{2-} ion

The primary purpose of this work was to establish the dimensions of the fluorophosphate ion. These values have been collected in Table 8 along with the average values for each type of bond or angle. The average values agree quite well and overall averages of P—F (1.585), P—O (1.506 Å), O—P—F (104.5) and O—P—O (114.0°) probably define well the expected average configuration of the PO_3F^{2-} ion in a crystal. The greater distortion of the PO_3F^{2-} ion in $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ appears to be real and attributable to its crystallographic environment. The reduction of the O—P—F angles below the ideal tetrahedral angle with the corresponding increase in the O—P—O angles, has been regularly found in most substituted phosphate anions, e.g. PO_3NH_3^- (Hobbs, Corbridge & Raistrick, 1953) and $\text{PO}_3(\text{OH})^{2-}$ (Baur & Khan, 1970), although it is not obvious in HPO_3^{2-} (Corbridge, 1956; Handlovič, 1969). The P—O distances found in the present work

Table 8. Fluorophosphate distances and angles

	Averages are given in parentheses.			
	Ca salt	NH_4 salt	Ca salt	NH_4 salt
P—F			102.68°	104.31°
or			105.03	104.05
O—P—F	1.583 Å	1.586 Å	106.13	104.88
			(104.61)	(104.41)
P—O	1.506	1.508	115.64	112.95
or	1.515	1.506	109.52	114.57
O—P—O	1.503	1.501	116.48	114.53
	(1.508)	(1.505)	(113.88)	(114.02)

agree well with those found in many comparable phosphates cited by Baur & Khan (1970) in which the short P–O distances range from 1.48 to 1.53 Å.

References

- ALEXANDER, L. E. & SMITH, G. S. (1962). *Acta Cryst.* **15**, 983.
 ATOJI, M. & RUNDLE, R. E. (1958). *J. Chem. Phys.* **29**, 1306.
 BATTELLE, L. F. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **19**, 531.
 BAUR, W. H. (1964). *Acta Cryst.* **17**, 863.
 BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584.
 CORBRIDGE, D. E. C. (1956). *Acta Cryst.* **9**, 991.
 HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 64. New York: Benjamin.
 HANDLOVIČ, M. (1969). *Acta Cryst.* **B25**, 227.
 HOBBS, E., CORBRIDGE, D. E. C. & RAISTRICK, B. (1953). *Acta Cryst.* **6**, 621.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 204. Birmingham: Kynoch Press.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 ROBINSON, M. T. (1958). *J. Phys. Chem.* **62**, 925.
 STEWART, J. M. (1967). Technical Report 67-58, Computer Science Center, Univ. of Maryland.
 VAN DER HART, D. L., GUTOWSKY, H. S. & FARRAR, T. C. (1969). *J. Chem. Phys.* **50**, 1058.
 WOOSTER, W. A. (1936). *Z. Kristallogr.* **94**, 375.

Acta Cryst. (1972). **B28**, 2191

The Crystal Structure of Ammonium Monofluorophosphate: $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$

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The crystal structure of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ has been determined by single-crystal X-ray methods using multiple-film equi-inclination Weissenberg data. The unit cell is monoclinic with $a = 6.298 \pm 0.027$, $b = 8.311 \pm 0.015$, $c = 12.702 \pm 0.012$ Å, $\beta = 98.58 \pm 0.13^\circ$. The space group is $P2_1/c$ and the density calculated for $Z = 4$ is 1.536 g.cm^{-3} , experimental 1.52 g.cm^{-3} . The structure was refined by least-squares methods to a final value of R of 0.128. The data and results of this determination are compared with those of an independent determination by Perloff by the method of normal-probability plot analysis. Substitution of fluorine into the orthophosphate anion results in a decrease of the P–O distance and increase in the O–P–O angle.

Introduction

The monofluorophosphate ion is used commercially as a toothpaste additive ('Colgate') as a decay inhibitor. A study of the crystal structure of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ was undertaken, since, to understand the mechanism of decay inhibition, it is necessary to know the structure and reactivities of the monofluorophosphate ion.

Experimental

Crystals of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ were prepared by recrystallizing a sample of commercial diammonium monofluorophosphate (Alfa Inorganics, Inc.) from aqueous solution.

The crystal chosen for data collection was approximately cylindrical, 0.3 mm in diameter and 1.4 mm in length, and was mounted with the long dimension coincident with the axis of rotation. Multiple-film equi-inclination Weissenberg data were collected for layer lines $0kl$ through $3kl$ with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å). Intensities were estimated

visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects.

The unit cell was found to be monoclinic with $a = 6.298 \pm 0.027$, $b = 8.311 \pm 0.015$, $c = 12.702 \pm 0.012$ Å, and $\beta = 98.58 \pm 0.13^\circ$. The lattice constants were determined from a powder pattern indexed with the aid of the single-crystal data. Standard deviations in the lattice constants were estimated by a least-squares analysis.

The Laue symmetry is $2/m$ and the space group was found to be $P2_1/c$. The density calculated for $Z = 4$ was 1.536 g.cm^{-3} . The experimental density was determined by flotation to be 1.52 g.cm^{-3} .

Structure determination

The structure was determined by standard techniques and was refined by least-squares methods using 593 observed reflections with weights assigned according to:

$$w = \frac{1}{\sigma} = \frac{A}{F_o} \quad \text{for } I_o \geq \sqrt{AI_{\min}}$$