The Synthesis and Crystal Structures of Two New Hydrated Sodium Monofluorophosphates: NaHPO$_3$F · 2.5 H$_2$O (I) and Na$_2$PO$_3$F · 10 H$_2$O (II)

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The structures of two new sodium salts of monofluorophosphoric acid, NaHPO$_3$F · 2.5 H$_2$O (I) and Na$_2$PO$_3$F · 10H$_2$O (II), were determined with single-crystal X-ray diffraction at 160 K. I is monoclinic with the space group $C2/c$, $a = 19.112(4)$, $b = 5.341(1)$, $c = 12.727(3)$ Å, $\beta = 110.18(3)°$, $V = 1219.4(4)$ Å^3, and $Z = 8$ ($R_1 = 0.0276$ and w$R_2 = 0.0647$). II crystallizes in the monoclinic space group, $P2_1/c$, $a = 11.380(3)$, $b = 10.234(2)$, $c = 13.051(4)$ Å, $\beta = 106.49(3)°$, $V = 1457.4(7)$ Å^3, and $Z = 4$ ($R_1 = 0.0266$ and w$R_2 = 0.0581$). The crystal structure of I contains hydrogen-bonded zigzag chains of HPO$_3$F tetrahedra. The fluorine atom does not participate in the hydrogen bonding system. In the structure of II, hydrogen bonds create a complex structure of water molecules connected to each other and to the PO$_3$F tetrahedron. The structure is isotypic to Na$_2$SO$_4$ · 10H$_2$O with two disordered hydrogen atoms instead of four. The fluorine atom acts as an acceptor in two of the hydrogen bonds. © 2001 Academic Press

Key Words: monofluorophosphate; hydrogen bonding; crystal structure; P–F bond.

INTRODUCTION

The class of compounds, metal monofluorophosphates, has been known for about 100 years. The first published work discussed a potassium and a rubidium hydrogen monofluorophosphate (1). The compositions of the compounds were determined with chemical analysis, but a confirmation of the P–F bond was not possible at that time. Since then, quite a bit of work has been done on monofluorophosphates (2). Neels and Grunze reported the synthesis of a sodium and other alkali metal hydrogen monofluorophosphates (3). The salts were characterized by ^{31}P and ^{19}F NMR spectroscopy and Guinier powder diffraction.

Monofluorophosphates are of interest for a structural comparison with the isoelectronic sulfates with emphasis on the hydrogen sulfates. Some hydrogen sulfates are well-known for their phase transitions resulting in high proton conductivity (5), thus leading to the question if the same could be true for the hydrogen monofluorophosphates. The first single-crystal structure was published very recently for cesium hydrogen monofluorophosphate (4). Interestingly enough, this compound has lattice constants similar to those of a high-temperature phase of cesium hydrogen sulfate (5).

In this paper, the structures of both sodium hydrogen monofluorophosphate 2.5 hydrate (compound **I**) and disodium monofluorophosphate decahydrate (compound **II**) are presented and discussed. The decahydrate is compared in detail to the isotypic structure of Glauber's salt, Na$_2$SO$_4$ · 10H$_2$O.

EXPERIMENTAL

Sample Preparation and Characterization

The sodium salt of monofluorophosphoric acid, NaHPO$_3$F · 2.5 H$_2$O (**I**), was prepared in a two-step synthesis involving cationic exchange (Amberlite IR 120 +, Aldrich) similar to that carried out by Neels and Grunze (3). The eluent (5.0 g, 35 mmol of Na$_2$PO$_3$F in 10 mL water) was passed over a 35-cm column. After complete cationic exchange, sodium carbonate (5.04 g, 48 mmol) was gradually added to the cooled eluate (ice/salt bath) until pH 3.73. The solution was freeze–dried. The raw product was recrystallized from aqueous solution by slow evaporation in a desiccator. Weathering was observed in the recrystallized product of **I**. Some crystals were washed with acetone and a brittle chalk white product was obtained due to dehydration.

Crystals of Na$_2$PO$_3$F · 10H$_2$O (**II**) were obtained by crystallizing commercial Na$_2$PO$_3$F from aqueous solution

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between 273 and 280 K. **II** was also synthesized via cationic exchange (10 g of Na_2PO_3F, 69 mmol) and the addition of Na_2PO_3F to pH 4.65. This raw product was crystallized from a 50:50 acetone/water mixture in the freezer. The crystals have an incongruent melting point of 283 ± 2 K.

A fluoride analysis was carried out on the recrystallized product of **I**. The sample was prepared according to Seel (6) and the content of fluoride was measured with a fluoride-sensitive electrode. The experimental value of 11.4% coincided with the theoretical value (11.38%) for $NaHPO_3F \cdot 2.5 H_2O$. For liquid ^{31}P and ^{19}F NMR spectroscopy, samples of the aqueous solutions (prior to freeze drying) were recorded on a Bruker DPX 300 spectrometer in FEP NMR tubes. The spectra were measured at frequencies of 121.5 MHz (^{31}P) and 282.4 MHz (^{19}F) with the internal standards 85% phosphoric acid and Freon-11, respectively. The ^{31}P and ^{19}F spectra of compounds **I** and **II** show a doublet for the monofluorophosphate anion at $\delta_p = -2.23$ ppm, $\delta_F = -74.2$ ppm with $J_{PF} = 898$ Hz for **I** and at $\delta_p = 0.06$ ppm, $\delta_F = -74.2$ ppm with $J_{PF} = 881$ Hz for **II**. This doublet signal confirms the presence of a P–F bond in solution, which remains intact during freeze–drying and a quick recrystallization. Weaker signals for phosphorus at about 1 ppm and fluorine at about -120 ppm, which can be assigned to PO_4^{3-} and F^-, respectively, were also observed in the spectra of both samples.

Single Crystal X-Ray Analysis

The single-crystal intensity measurements were carried out on a STADI-4 (Stoe) four-circle diffractometer (**I**) and an IPDS (Stoe) diffractometer (**II**) using $MoK\alpha$ radiation with a graphite monochromator ($\lambda = 0.71073$ Å). Due to its low decomposition temperature, the crystal of **II** was prepared for measurement under a stream of cool nitrogen. The crystallographic data and details of both data collections and analyses are given in Table 1. A numerical absorption correction was applied to the data set of **I** with a transmission difference of 10% ($T_{min} = 0.8454$, $T_{max} = 0.9741$).

Both structures were solved with SHELXS-86 (7) and refined with SHELXL-93 (8). All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were found with difference Fourier synthesis and refined isotropically. Two hydrogen atoms belonging to two water molecules, $O_w(5)$ and $O_w(11)$, in **II** were found to be disordered between two positions. The relative occupancies for the positions were refined to values of 0.667 for H(5B) and H(11B) and 0.333 for H(5C) and H(11C), which were then fixed. Atomic coordinates and displacement parameters for **I** and **II** are given in Table 2. Selected bond lengths are listed in Table 3. The hydrogen bond geometry is presented in Table 4. In order to compare **II** more thoroughly to the isotypic $Na_2SO_4 \cdot 10H_2O$ (**III**), a single crystal data set of this salt was recorded on the STADI-4 (Stoe) diffractometer at

180 K. Previous measurements were only carried out at room temperature (9, 10). Further details of all three crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411318 (**I**), CSD-411317 (**II**), and CSD-411348 (**III**).

RESULTS

$NaHPO_3F \cdot 2.5H_2O$ (**I**)

In the structure of $NaHPO_3F \cdot 2.5 H_2O$ (Fig. 1), there is one Na atom, one HPO_3F tetrahedron, and three crystallographically independent molecules of water. The Na atom is octahedrally coordinated by four water molecules ($O_w(4)$, $O_w(5)$, $O_w(5')$, and $O_w(6)$) and two O atoms shared with the tetrahedron (O(1) and O(1')) with an average Na–O bond length of 2.410 Å. The Na-octahedra alternately share one edge involving $O_w(5)$ and $O_w(5')$ and one face defined by $O_w(6)$, O(1), and O(1') to build up chains running along the c-axis. The bonding in the HPO_3F tetrahedron consist of two short P–O bonds (1.484(1) for P–O(1) and 1.508(1) Å for P–O(2)), a longer one for P–O(3) (1.563(2) Å), and a long P–F bond (1.565(1) Å). The lengths of the P–O(2) and P–O(3) bonds reflect the function of O(2) and O(3) in the hydrogen bonding system: O(2) as an acceptor and O(3) as a donor.

TABLE 1
Selected Experimental Data for $NaHPO_3F \cdot 2.5H_2O$ (I) and $Na_2HPO_3F \cdot 10H_2O$ (II)

	$NaHPO_3F \cdot 2.5H_2O$;	$Na_2PO_3F \cdot 10H_2O$;
Formula; molecular weight (g mol^{-1})	167.01	323.98
Sample color	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	19.112(4)	11.380(3)
b (Å)	5.341(1)	10.234(2)
c (Å)	12.727(3)	13.051(4)
β (°)	110.18(3)	106.49(3)
Cell volume (Å^3), Z	1219.4(4), 8	1457.4(7), 4
ρ_{calc} (g cm^{-3})	1.819	1.477
Crystal size (mm)	$0.8 \times 0.4 \times 0.4$	$0.5 \times 0.5 \times 0.4$
μ ($MoK\alpha$) (mm^{-1})	0.499	0.310
Diffractometer	STADI-4	IPDS
Temperature (K)	160	160
2θ Range for data collection (°)	3.0–60.0	3.8–56.3
Reflections collected	3906	14694
Unique reflections	1775	3422
Data/parameter	1312/103	2915/242
wR_2	0.0647	0.0581
R_1 [$I > 4\sigma(I)$]	0.0276	0.0266
GOOF (obs)	1.071	1.107
$\Delta\varsigma_{max}$, $\Delta\varsigma_{min}$ (e Å^{-3})	0.421, -0.339	0.320, -0.353

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2$) for NaHPO$_3$F · 2.5H$_2$O (I)
and Na$_2$PO$_3$F · 10H$_2$O (II)

	x	y	z	U_{eq}
NaHPO$_3$F · 2.5H$_2$O				
Na	0.02128(4)	0.91515(2)	0.37974(6)	0.0149(2)
P	0.16319(2)	0.15824(9)	0.28108(4)	0.0117(2)
F	0.21319(6)	0.0129(3)	0.3872(1)	0.0246(3)
O(1)	0.08396(7)	0.1121(3)	0.2673(1)	0.0166(3)
O(2)	0.18949(7)	0.0805(3)	0.1870(1)	0.0158(3)
O(3)	0.18254(8)	0.4378(3)	0.3152(1)	0.0202(3)
O$_w$(4)	0.12326(8)	0.6497(3)	0.48432(1)	0.0173(3)
O$_w$(5)	0.06758(8)	0.8010(3)	0.0343(1)	0.0173(3)
O$_w$(6)	0	0.5746(4)	0.25	0.0187(4)
H(1)	0.223(2)	0.488(7)	0.309(3)	0.06(1)
H(4A)	0.147(1)	0.609(5)	0.4434(2)	0.031(7)
H(4B)	0.148(2)	0.7097(6)	0.5381(2)	0.033(8)
H(5A)	0.080(2)	0.658(6)	0.015(2)	0.043(8)
H(5B)	0.107(2)	0.870(6)	0.079(3)	0.043(8)
H(6)	0.036(2)	− 0.523(6)	0.255(3)	0.051(9)
Na$_2$PO$_3$F · 10H$_2$O				
Na(1)	0.76241(5)	0.11186(5)	0.23800(4)	0.0157(1)
Na(2)	0.75240(5)	0.24128(5)	0.49222(4)	0.0165(1)
P	0.25291(3)	0.13984(3)	0.25237(2)	0.01163(9)
F	0.37462(9)	0.21322(8)	0.24354(7)	0.0276(2)
O(1)	0.24389(9)	0.18154(9)	0.36111(7)	0.0199(2)
O(2)	0.28235(9)	− 0.00249(9)	0.24331(7)	0.0215(2)
O(3)	0.01538(1)	0.19442(9)	0.16000(7)	0.0221(2)
O$_w$(4)	0.35763(9)	0.4508(1)	0.38699(8)	0.0198(2)
O$_w$(5)	0.8857(1)	− 0.0426(1)	0.35763(8)	0.0197(2)
O$_w$(6)	0.6478(1)	0.28448(9)	0.12452(8)	0.0176(2)
O$_w$(7)	0.8947(1)	0.1169(1)	0.11910(8)	0.0193(2)
O$_w$(8)	0.8532(1)	0.28569(9)	0.35744(8)	0.0176(2)
O$_w$(9)	0.6232(1)	0.1030(1)	0.35744(8)	0.0219(2)
O$_w$(10)	0.3867(1)	0.5761(1)	0.58246(8)	0.0216(2)
O$_w$(11)	0.8622(1)	0.4599(1)	0.05455(9)	0.0213(2)
O$_w$(12)	0.09907(9)	0.35056(9)	0.44299(8)	0.0187(2)
O$_w$(13)	0.3965(1)	0.14856(1)	0.56141(9)	0.0242(2)
H(4A)	0.330(2)	0.383(2)	0.378(1)	0.031(5)
H(4B)	0.354(2)	0.477(2)	0.442(2)	0.055(7)
H(5A)	0.872(2)	− 0.122(2)	0.348(2)	0.033(5)
H(5B)[a]	0.870(2)	− 0.021(2)	0.415(2)	0.018(6)
H(5C)[b]	0.958(7)	− 0.042(5)	0.377(4)	0.02(1)
H(6A)	0.671(2)	0.352(2)	0.160(2)	0.040(5)
H(6B)	0.573(2)	0.293(2)	0.098(2)	0.043(6)
H(7A)	0.967(2)	0.140(2)	0.140(2)	0.048(6)
H(7B)	0.898(2)	0.041(2)	0.102(2)	0.041(5)
H(8A)	0.825(2)	0.352(2)	0.330(2)	0.033(5)
H(8B)	0.929(2)	0.302(2)	0.382(2)	0.032(5)
H(9A)	0.558(2)	0.134(2)	0.327(2)	0.045(6)
H(9B)	0.615(2)	0.031(2)	0.375(1)	0.029(5)
H(10A)	0.367(2)	0.544(2)	0.633(2)	0.030(5)
H(10B)	0.459(2)	0.571(2)	0.605(2)	0.052(7)
H(11A)	0.834(2)	0.511(2)	0.085(2)	0.041(6)
H(11B)[a]	0.934(3)	0.459(3)	0.093(2)	0.031(7)
H(11C)[b]	0.839(5)	0.483(5)	− 0.026(5)	0.03(1)
H(12A)	0.139(2)	0.295(2)	0.416(1)	0.029(4)
H(12B)	0.118(2)	0.340(2)	0.506(2)	0.035(5)
H(13A)	0.354(2)	0.153(2)	0.499(2)	0.035(5)
H(13B)	0.364(2)	0.196(2)	0.598(2)	0.037(5)

[a]Occupancy of 0.667.
[b]Occupancy of 0.333.

TABLE 3
Selected Bond Distances (Å)

NaHPO₃F·2.5H₂O (I)	d	Na₂PO₃F·10H₂O (II)	d
Na–O(1)	2.461(2)	Na(1)–O$_w$(4)	2.445(1)
Na–O(1′)	2.403(2)	Na(1)–O$_w$(5)	2.380(1)
Na–O$_w$(4)	2.406(2)	Na(1)–O$_w$(6)	2.433(1)
Na–O$_w$(5)	2.398(2)	Na(1)–O$_w$(7)	2.450(1)
Na–O$_w$(5′)	2.395(2)	Na(1)–O$_w$(8)	2.398(1)
Na–O$_w$(6)	2.395(2)	Na(1)–O$_w$(9)	2.473(1)
		Na(2)–O$_w$(6)	2.373(1)
		Na(2)–O$_w$(7)	2.439(1)
		Na(2)–O$_w$(8)	2.400(1)
		Na(2)–O$_w$(9)	2.440(1)
		Na(2)–O$_w$(10)	2.464(1)
		Na(2)–O$_w$(11)	2.426(1)
P–O(1)	1.484(1)	P–O(1)	1.513(1)
P–O(2)	1.508(1)	P–O(2)	1.5069(9)
P–O(3)	1.563(2)	P–O(3)	1.505(1)
P–F	1.565(1)	P–F	1.6082(9)

In the hydrogen bonding system, HPO₃F tetrahedra are connected to each other by a strong hydrogen bond O(3)–H(1)···O(2) (2.571 Å) (Table 4) to form columns around a twofold screw axis at ($\frac{1}{4}$, y, $\frac{1}{4}$). These columns run in the b-direction as zigzag chains of P-tetrahedra. They are held together by weaker hydrogen bonds (2.793(2) to 2.980(2) Å) with the water molecules to form a 3D network. In the a-direction, one hydrogen bond, O$_w$(6)–H(6A)···O(1) bridges the chains of HPO₃F tetrahedra together. Hydrogen bonds also link the chains parallel to the c-axis. The O$_w$ atoms act mainly as donors in the hydrogen bonds: O$_w$(4)–H(4A)···O(2), O$_w$(4)–H(4B)···O$_w$(3), O$_w$(5)–H(5B)···O$_w$(2), and O$_w$(5)–H(5A)···O$_w$(4). The F atom is not involved in any hydrogen bonding. The P–F bond points away from the NaO₆ octahedra (Fig. 1).

Na₂PO₃F·10H₂O (II)

The Na₂PO₃F·10H₂O structure consists of the following crystallographically independent atoms and units: two Na atoms, one PO₃F tetrahedron, and 10 molecules of water (Fig. 2a). Eight of the 10 O$_w$ atoms participate in the octahedral coordination of the Na atoms. The two different Na octahedra are linked together by edge-sharing (O$_w$(6)–O$_w$(7) and (O$_w$(8)–O$_w$(9)) and alternate in chains parallel to the c-axis. The Na–O bond lengths range from 2.380(1) to 2.473(1) Å.

TABLE 4
Hydrogen Bond Geometry (Å,°)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
NaHPO₃F·2.5H₂O (I)				
O(3)–H(1)···O(2)	0.85(3)	1.73(3)	2.571(2)	172(3)
O$_w$(4)–H(4A)···O(3)	0.83(3)	2.17(3)	2.980(2)	164(2)
O$_w$(4)–H(4B)···O(2)	0.76(3)	2.11(3)	2.842(2)	165(3)
O$_w$(5)–H(5A)···O$_w$(4)	0.86(3)	1.94(3)	2.793(2)	171(3)
O$_w$(5)–H(5B)···O(2)	0.86(3)	2.03(3)	2.883(2)	170(3)
O$_w$(6)–H(6A)···O(1)	0.84(3)	2.14(3)	2.912(2)	152(3)
Na₂PO₃F·10H₂O (II)				
O$_w$(4)–H(4A)···O(1)	0.76(2)	2.26(2)	3.023(2)	177(2)
O$_w$(4)–H(4B)···O$_w$(10)	0.78(2)	2.03(2)	2.790(2)	163(2)
O$_w$(5)–H(5A)···O(3)	0.83(2)	1.90(2)	2.727(1)	174(2)
O$_w$(5)–H(5B)···O$_w$(11)	0.85(3)	1.95(3)	2.790(2)	170(2)
O$_w$(5)–H(5C)···O$_w$(11)	0.79(7)	1.98(7)	2.771(2)	172(5)
O$_w$(6)–H(6A)···O(2)	0.83(2)	1.93(2)	2.753(1)	173(2)
O$_w$(6)–H(6B)···O$_w$(13)	0.82(2)	2.02(2)	2.827(2)	165(2)
O$_w$(7)–H(7A)···O(3)	0.83(3)	2.14(3)	2.952(2)	168(2)
O$_w$(7)–H(7B)···O$_w$(12)	0.82(2)	2.03(2)	2.851(1)	177(2)
O$_w$(8)–H(8A)···O(2)	0.79(2)	1.99(2)	2.767(2)	167(2)
O$_w$(8)–H(8B)···O$_w$(12)	0.85(2)	1.94(2)	2.782(2)	175(2)
O$_w$(9)–H(9A)···F	0.79(2)	2.21(2)	3.003(2)	176(2)
O$_w$(9)–H(9B)···O$_w$(13)	0.81(2)	2.03(2)	2.842(2)	176(2)
O$_w$(10)–H(10A)···O(2)	0.82(2)	1.99(2)	2.793(2)	164(2)
O$_w$(10)–H(10B)···O$_w$(4)	0.80(3)	2.07(2)	2.836(2)	162(2)
O$_w$(11)–H(11A)···O(1)	0.78(2)	2.16(2)	2.927(2)	167(2)
O$_w$(11)–H(11B)···O$_w$(5)	0.83(4)	1.96(4)	2.771(2)	163(2)
O$_w$(11)–H(11C)···O$_w$(5)	1.04(6)	1.84(6)	2.790(2)	149(5)
O$_w$(12)–H(12A)···O(1)	0.87(2)	1.94(2)	2.802(2)	174(2)
O$_w$(12)–H(12B)···O(3)	0.80(2)	1.97(2)	2.760(2)	175(2)
O$_w$(13)–H(13A)···F	0.82(2)	1.90(2)	2.837(2)	172(2)
O$_w$(13)–H(13B)···O(1)	0.84(2)	2.08(2)	2.718(2)	149(2)
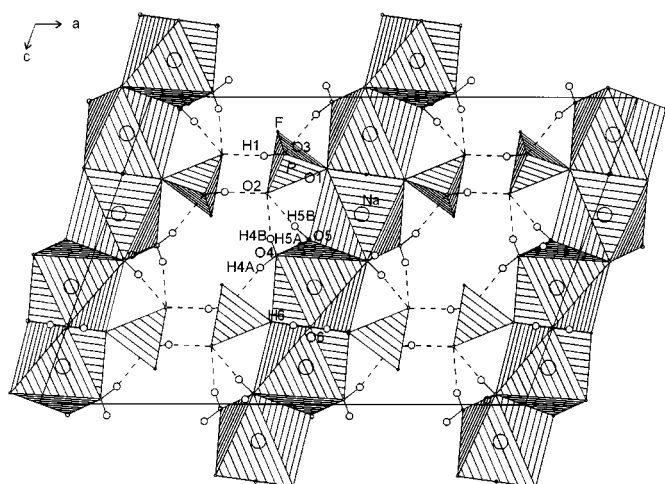
FIG. 1. Polyhedral representation of the structure of **I** down the *b*-axis, showing the chains of sodium octahedra and phosphorus tetrahedra. Dashed lines show the hydrogen bonds.

The PO$_3$F tetrahedron has three short P–O bonds with an average length of 1.508 Å and one long P–F bond (1.6082(9) Å). This confirms the existence of a sodium dibasic salt. Slightly shorter P–O bonds (average length, 1.484 Å) and similar P–F bonds (average length, 1.609(7) Å) are found in K$_2$PO$_3$F(11). Two different tetrahedra are present in the nonisotypic structure of Na$_2$PO$_3$F with average lengths for P–O of 1.493 Å and for P–F of 1.606 Å (12). The longer P–O bonds in **II** compared to those in these salts can be explained by the extensive amount of hydrogen bonds that each of the three O atoms participates in.

The elaborate system of 20 hydrogen bonds in **II** forms a 3D network with hydrogen supplied by the 10 molecules of crystal water (Table 4). The hydrogen bonds have lengths between 2.718(2) and 3.023(2) Å. The acceptor O atoms of the PO$_3$F tetrahedron, namely O(1), O(2), and O(3), are respectively hydrogen-bonded to 3, 3, and 4 molecules of crystal water (see Table 4). The F atom participates in only two hydrogen bonds with O$_w$(9) and O$_w$(13). The eight water molecules, O$_w$(4) to O$_w$(11), are all hydrogen-bonded to one of the O/F atoms in the tetrahedron and another O$_w$ atom. The O$_w$(12) and O$_w$(13) water molecules, which are not involved in the Na coordination, connect PO$_3$F tetrahedra to each other parallel to the *c*-axis (Fig. 2a). Two closed tetramers are formed with water molecules via hydrogen bonding around two inversion centers: O$_w$(4) with O$_w$(10) and O$_w$(5) with O$_w$(11) (Fig. 2b). The hydrogen bonds O$_w$(4)–H(4B)···O$_w$(10) and O$_w$(10)–H(10B)···O$_w$(4) form the first tetramer. In the second tetramer between O$_w$(5) and O$_w$(11), two disordered hydrogen bonds connect these water molecules to each other. The major positions of the disordered hydrogen atoms have an occupancy of 0.667. The disordered bonds are O$_w$(5)–H(5B)···O$_w$(11) and

(a)

(b)
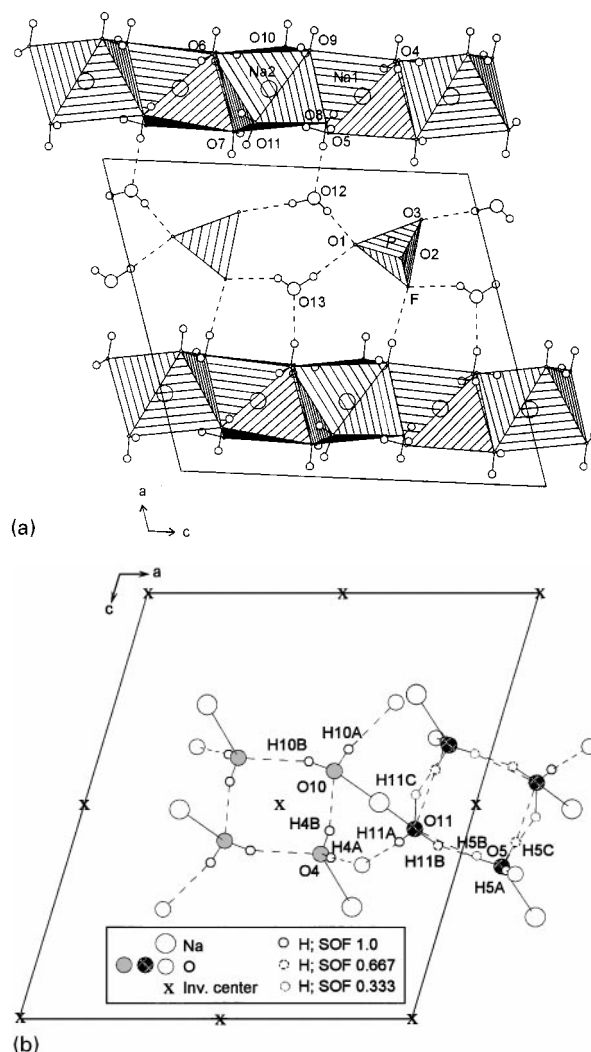
FIG. 2. (a) One of the layers in the structure of **II** projected down the *b*-axis. Sodium octahedra and connected phosphorus tetrahedra run parallel to the *c*-axis. Only the major component of the disordered H(5) and H(11) atoms are shown. (b) Projection of the two tetramers in the structure of **II** along the *b*-axis. The hydrogen bonds and anchoring bonds to the Na atoms and O(1)–O(3) are shown. Inversion centers are included for clarity.

O$_w$(11)–H(11B)···O$_w$(5) with the minor components H(11C) and H(5C), respectively. Both H-bonded ring systems are fixed in the structure by bonds to Na atoms and O atoms of the PO$_3$F tetrahedra.

DISCUSSION AND COMPARISON TO THE SULFATES

The most predominant similarities between **I** and **II** are the PO$_3$F tetrahedra and the bonding of the O atoms; however, the F atoms vary in their bonding. The P–O(2) bond length (1.508(1) Å) in **1** is identical to the average P–O length in **II** (1.5083 Å). All of these O atoms participate in three or more hydrogen bonds as acceptors. In comparison,

the shorter P–O(1) bond in **I** (1.484(1) Å) is equivalent to the average P–O lengths in K_2PO_3F (1.484 Å), in which the O atoms also coordinate K atoms (11). All of the O atoms in **I** and **II** except for O(1) in **II** are involved in a total of four bonds: to the P atom, to the Na atom/s, and/or as a hydrogen donor/acceptor. However, the most interesting observation up until now is in the bonding of the F atoms. In both structures presented, the F atom does not coordinate with the alkali metal cation. On the other hand, Cs–F coordination was found in the $CsHPO_3F$ structure recently reported (4). Alkali metal coordination by fluorine is also present in the Na_2PO_3F salt (12), but Ca–F bonds were not found in the hydrate of the calcium salt, $CaPO_3F \cdot 2H_2O$ (13). Comparing the nonisotypic sodium compounds, Na_2PO_3F, **I** and **II**, with that of calcium (calcium and sodium have comparable ionic radii; $R_{Ca} = 1.00$ Å and $R_{Na} = 1.02$ Å (14)), it seems that fluorine does not coordinate the alkali metal cation, when there is a sufficient number of oxygen atoms in the structure, usually supplied by the crystal water. The amount of crystal water in the structure also influences the role of fluorine in the hydrogen bonding system. In the hydrates of the monofluorophosphates, $CaPO_3F \cdot 2H_2O$ (13), $(NH_4)_2PO_3F \cdot H_2O$ (13), $LiKPO_3F \cdot H_2O$ (15), and $CuPO_3F \cdot 2H_2O$ (16), and the hydrogen monofluorophosphates, $CsHPO_3F$ (4) and **I**, fluorine is not involved in the hydrogen bonding system. However in structure **II**, which has a high amount of crystal water and thus an excessive number of hydrogen atoms, the F atom is not only bonded to the P atom, but also participates in two hydrogen bonds as an acceptor. Valency differences between oxygen and fluorine could explain the differences in the crystal structures of these monofluorophosphates.

A comparison to the isoelectronic sulfates shows that **I** is not isotypic to any of the known sodium hydrogen sulfates, α-$NaHSO_4$ (17), β-$NaHSO_4$ (18), or the monohydrate (19), because of differences in composition. On the other hand, structure **II** is isotypic to the corresponding sulfate, $Na_2SO_4 \cdot 10H_2O$ (Glauber's salt; **III**) (9,10). The P–F bond corresponds to the S–O(6) bond in (14). Identical bridging of the Na octahedra and the tetrahedra to each other via two water molecules are general structural features of both **II** and **III**. The lengths of the hydrogen bonds in **III** (2.75 to 3.01 Å) (10) are similar to those found in **II**. A difference between the two structures is the bond lengths in the tetrahedron. In **III**, all the S–O bond lengths are within the narrow range of 1.4–1.5 Å (10). The PO_3F tetrahedron is distorted with three short P–O bonds and a long P–F bond.

The structure of **III** was studied at room temperature with X-ray (9) and neutron (10) single-crystal diffraction. In the crystal structure analysis of (9), disordered hydrogen bonds were assumed to be present in both tetramers of water molecules. The authors correlated the possible disorder in the structure to a residual entropy, which was found earlier

experimentally (20). In the neutron diffraction study (10), the exact position of the hydrogen atoms was determined. In this structural study, both the SO_4 tetrahedron and the hydrogen atoms in the ring systems were disordered. The two orientations for the SO_4 tetrahedron are rotated about 30° around one of the S–O bond axes. The disorder of the rings and tetrahedron was confirmed as the source for the zero point entropy. The refined occupancies were 0.5 for both positions of the disordered hydrogen atoms in the rings and 0.753/0.247 for the major and minor configurations of the disordered, tetrahedral O atoms.

The degree of disorder found in **II** and **III** measured at room temperature (10) differs, slightly affecting the hydrogen bonding system. In **II**, disorder is found in only one of the tetramers with $O_w(5)$ and $O_w(11)$. Disordering of the PO_3F tetrahedron is questionable. Very weak peaks with bond distances of 1.481, 1.423, and 1.869 Å from the P atom were found shifted 23.2 to 30.2° from O(2), O(3), and F, respectively. This weak disorder is rotated about the P–O(1) axis, which is not equivalent to the S–O axis of rotation in the sulfate. An additional refinement of the occupancies yielded values of about 0.97/0.03 compared to the occupancies in **III** of 0.753/0.247 (10). Therefore, this second orientation of the PO_3F tetrahedron was neglected in the final refinement of **II**. The disorder of the $O_w(5)/O_w(11)$ ring also varies from that in **III** (10) in the assigned occupancies. In **II**, the occupancies calculated for the disordered hydrogen atoms are 0.667 and 0.333 instead of an equal distribution between the two positions. One explanation for the discrepancies in disorder between the two isotypic structures could be the measurement temperature (160 K for **II** and 296.5 K for **III** (10)).

For this reason, a single crystal analysis of **III** was done at 180 K. Although the same type of disorder is found at this temperature, the new occupancies of the different configurations were refined to 0.938/0.062 for the tetrahedron and 0.569/0.431 for one of the tetramers and thus vary from those found at room temperature. The disorder in the second tetramer (0.5/0.5) is independent of the temperature. It can be concluded that the temperature has a significant influence on the disorder of the tetrahedron in **III**. However, the disorder of the tetramers seems to be less temperature-dependent, because a similar disorder of the tetramers was found at 296.5 K. Fluorine seems to be the controlling factor for the variation in disorder of the tetrameric hydrogen atoms in the structures of **II** and **III**. Thus the replacement of SO_4 with PO_3F leads to interesting and subtle variations in the hydrogen bonding system. The F atom bonds to two water molecules just like that found for the corresponding O atom in sulfate. However, it does not participate in a third bond found in sulfate. By substituting an O atom with a F atom, disorder has been reduced in the structure and hydrogen bonding of the tetrameric water molecules to the PO_3F tetrahedron slightly varied.

The thermal stability of **II** was investigated directly on the IPDS diffractomer between 230 and 285 K. The same unit cell was determined for exposures taken up to 280 K. One exposure at 285 K showed that the crystal breaks down to powder. Powder rings at higher d-values were too diffuse to interpret; however, the d-values observed in the range of 2.00–1.356 Å could be assigned to Na_2PO_3F (21).

In conclusion, the crystal structures of $NaHPO_3F \cdot 2.5H_2O$ and $Na_2PO_3F \cdot 10H_2O$ demonstrate the effects of fluorine in the place of oxygen on the isotypy between these salts and the sulfates. The sodium hydrogen monofluorophosphate differs in its composition to those of the sulfate system. The extra molecules of crystal water seem to be necessary to coordinate the Na atom completely, because one of the O atoms present in the sulfate has been replaced with fluorine. $Na_2PO_3F \cdot 10H_2O$ is isotypic to the corresponding sulfate, $Na_2SO_4 \cdot 10H_2O$. Fluorine participates in the hydrogen bonding system, forming two of the three hydrogen bonds found for the corresponding O atom in the sulfate. This was not true for $CsHPO_3F$ (4), which has an equivalent formula to hydrogen sulfates, but is not isotypic to them. In this cesium structure, fluorine does not participate in the hydrogen bonding system. Therefore, the difference in valency between fluorine and oxygen seems to affect the hydrogen bonding system and thus the isotypy of hydrogen monofluorophosphates and hydrogen sulfates.

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REFERENCES

1. R. F. Weinland and J. Alfa, *Ber. Dtsch. Chem. Ges. B* **31,** 123 (1898).
2. D. A. Palgrave, *in* "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry" (J. W. Mellor, Ed.), Vol. 8, Suppl. 3, p. 843. Longmans, Green, London, 1971.
3. J. Neels and H. Grunze, *Z. Anorg. Allg. Chem.* **360,** 284 (1968).
4. H. A. Prescott, S. I. Troyanov, and E. Kemnitz, *Z. Kristallogr.* **215,** 240 (2000).
5. V. Varma, N. Rangavittal, and C. N. R. Rao, *J. Solid State Chem.* **106,** 164 (1993).
6. F. Seel, *Angew. Chem.* **76,** 532 (1964).
7. G. N. Sheldrick, **SHELXS-86,** Program for Crystal Structure Determination, Univ. Göttingen, Germany, 1990.
8. G. M. Sheldrick, **SHELXL-93,** Program for the Refinement of Crystal Structures, Univ. Göttingen, Germany, 1993.
9. H. W. Ruben, D. H. Templeton, R. D. Rosenstein, and I. Olovsson, *J. Am. Chem. Soc.* **83,** 820 (1961).
10. H. A. Levy and G. C. Lisensky, *Acta Crystallogr. B* **34,** 3502 (1978).
11. J. L. Payen, J. Durand, and L. Cot, *Can. J. Chem.* **57,** 886 (1979).
12. J. Durand, L. Cot, and J. L. Galigne, *Acta Crystallogr. B* **30,** 1565 (1974).
13. A. Perloff, *Acta Crystallogr. B* **28,** 2183 (1972).
14. A. F. Wells, "Structural Inorganic Chemistry," p. 313. Clarendon, Oxford, 1984.
15. J. L. Galigne, J. Durand, and L. Cot, *Acta Crystallogr. B* **30,** 697 (1974).
16. M. Zeibig, B. Wallis, F. Möwius, and M. Meisel, *Z. Anorg. Allg. Chem.* **600,** 231 (1991).
17. C. Werner, S. I. Troyanov, H. Worzala, and E. Kemnitz, *Z. Anorg. Allg. Chem.* **622,** 337 (1996).
18. E. J. Sonneveld and J. W. Visser, *Acta Crystallogr. B* **34,** 643 (1978).
19. M. Catti, G. Ferraris, and M. Franchini-Angela, *Atti. Accad. Sci. Torino Cl. Fis. Mat. Nat.* **109,** 531 (1975).
20. G. Brodale and W. F. Giauque, *J. Am. Chem. Soc.* **80,** 2042 (1958).
21. PDF-No. 18-1215, JCPDS-ICDD, PCPDFWIN, **Version 1.30,** August 1997.