Synthesis and Crystal Structures of Zirconium Phosphate Fluorides with New 2D and 3D Structure Types

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Three new zirconium phosphate fluorides, $[amH_2]_{0.5}$ $[Zr_2(PO_4)(HPO_4)_2F_2] \cdot 0.5H_2O$ **(1)**, $[amH_2]_{1.5}[Zr_3(PO_4)_3F_6] \cdot$ $1.5H_2O$ **(2)** ($am = $ *trans*-1,4-diaminocyclohexane for **1** and **2**), and $[amH_2]_{0.5}[Zr_3(PO_4)_3(HPO_4)F_2] \cdot 1.5H_2O$ ($am = $ 2,2-dimethyl-1,3-diaminopropane) **(3)**, were synthesized under hydrothermal conditions and structurally characterized. Zr is octahedrally coordinated in all three structures. In **1**, the octahedra consist of ZrO_6 and ZrO_4F_2 units. Compound **2** is made exclusively of ZrO_4F_2. In **3**, there are three different types of Zr-octahedra, namely, ZrO_6, ZrO_5F, and ZrO_4F_2. The Zr octahedra and PO_4 tetrahedra are connected via non-OH oxygen atoms. In **1** and **2**, all F atoms are terminal, whereas in **3**, one of the two F atoms bridges between the ZrO_5F and ZrO_4F_2 octahedra. In structures **1** and **2** with higher F/Zr ratios, two-dimensional inorganic networks exist. The inorganic sheets are connected by the protonated templates via N−H···F and in **1** additionally by O−H···F hydrogen bonds. In **3**, the lower F/Zr ratio results in the formation of a three-dimensional inorganic framework with characteristic "double" channels in which the highly disordered templates are located. The existence of several structure types in the ZrPOF-*n* family is discussed on the basis of different template geometry and F/Zr ratios. © 2000 Academic Press

INTRODUCTION

In the last few years, a new class of compounds, the zirconium phosphate fluorides, has been described. Poojary *et al.* (1) were the first to report on the synthesis and crystal structure of a layered zirconium phosphate fluoride, $Zr(PO_4)F(OSMe_2)$. Zhao *et al.* (2) and Hursthouse *et al.* (3) synthesized and characterized a 1D double-stranded polymer having the composition $[enH_2]_{1.5}[Zr(PO_4)(HPO_4)F_2]$ and ZrO_4F_2 octahedra as a new building block. Recently, we reported the crystal structure of $[enH_2]_{0.5}[Zr_2(HPO_4)(PO_4)_2F] \cdot H_2O$ **(4)**. This compound represents the first organically templated 3D microporous zirconium phosphate fluoride and was designated as "ZrPOF-1." The special feature of this structure is the presence of both ZrO_6 and

ZrO_5F octahedra. The presence of fluorine in the coordination sphere of Zr leads to a variation in the connection of the ZrO_5F octahedra compared to the common ZrO_6 octahedra. Therefore, 3D structures exhibiting channels are formed. Further progress was achieved by varying the template molecules and the molar ratios of the reagents in the hydrothermal synthesis. This resulted in the synthesis of other new compounds belonging to the same class (5). Small variations of the amine template can lead to differences in the crystal symmetry or changes in the water content of compounds. The inorganic framework remains almost identical to that of ZrPOF-1. However, significant variations in the chain length or the type of branching in the amine molecule results in fundamental changes of the structure, sometimes forming layer structures (5).

Understanding the influence of the amine geometry on the structural type formed was a primary goal of further investigations. In a recent paper, some new zirconium phosphate fluorides having the structural type of ZrPOF-1 have already been described (6). In this paper, we report on the syntheses and structures of new zirconium phosphate fluorides. With these structures, the variety of structural types in the ZrPOF-*n* family is substantially increased.

EXPERIMENTAL

Preparation

The synthesis of compounds **1–3** was performed using commercially available products without further purification. The hydrothermal reactions were carried out in PTFE-lined steel containers under autogeneous pressure with a filling rate of about 60%. The following process is representative of the general procedure applied to each preparation. The amine was added to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ and the mixture was stirred vigorously. Phosphoric acid (85%) and hydrofluoric acid (40%) were added to the resulting thick paste. After reaction, the crystalline products were filtered, washed with distilled water

TABLE 1
Synthesis Conditions for the Preparation of Pure Zirconium Phosphate Fluoride Phases

	Nominal molar ratios of reactants[a] and analytical data for the solid products		
	Compound **1**	Compound **2**	Compound **3**
$ZrOCl_2 \cdot 8H_2O$ (mol)	1	1	1
Amine (mol)	2	2	1
	trans-1,4-diamino-cyclohexane	trans-1,4-diamino-cyclohexane	2,2-dimethyl-1,3-diaminopropane
H_3PO_4 (mol)	5	3	3
HF (mol)	4	4	3–4
Reaction temperature (°C)	170	170	170
Reaction time (h)	120	120	240
C-content (w%) (determ./calc.)	3.2/6.27	12.1/12.27	2.6/3.89
H-content (w%)	1.90/1.93	3.0/3.11	1.65/1.57
N-content (w%)	2.4/2.44	4.8/4.81	1.83/1.82
F-content (w%)	6.6/6.61	12.3/13.04	4.9/4.92

[a] In all batches, the molar ratio H_2O/Zr was between 50 and 70.

and ethyl alcohol, and left to air-dry. More detailed information concerning the synthesis is given in Table 1. All compounds were obtained as fine white crystalline solids with an yield of about 30% based on the nominal amount of zirconium.

CHN-analyses were performed using conventional methods. Fluoride was determined with the method of Seel (7). The solid was decomposed with concentrated sulfuric acid at elevated temperature. The liberated fluoride was detected with a fluoride sensitive electrode.

For the three compounds, the phase purity was checked by XRD analysis using a Seifert-FPM XRD 7 diffractometer ($CuK\alpha$) in the 2θ range from 5° to 50° in steps of 0.01° with 6 s per step. Thermogravimetric measurements were carried out on a Netzsch STA-429 apparatus in the temperature range 20–700°C with a heating rate of 5 K/min.

X-Ray Crystallography

Data collections on small single-crystals were recorded on an IPDS (Fa. Stoe) image plate diffractometer at low temperatures using monochromated $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were not applied. The structures were solved by direct methods (SHELXS-97 (8)) and refined using SHELXL-93 (9). The crystallographic data and some details of the structure solutions and refinements are summarized in Table 2.

In structure **1**, all acidic H atoms and those of H_2O were localized and refined isotropically. The other H atoms (at C-atoms of the template) were placed in calculated

positions. Although several crystals of **2** were tested, all of them were of poor quality. Therefore, the H atoms were neither found nor calculated. Some peaks with nonnegligeable electron density were found near zirconium and phosphorus atoms, however, without any chemical meaning. For compound **3**, only very small single-crystals were available. Hence, the intensities measured were rather weak, especially for higher theta values. For this reason and due to the fact that the template was strongly disordered, the H atoms were neither located nor calculated.

Atomic coordinates and thermal paameters are given in Table 3. Bond distances in Zr octahedra and P tetrahedra are listed in Table 4. The full crystallographic data have been deposited at the Cambridge Crystallographic Data Center under CDS numbers 112257 (**1**), 112258 (**2**), and 112259 (**3**).

RESULTS AND DISCUSSION

Synthesis

The composition of the compounds, $[C_6H_{16}N_2]_{0.5}$ $[Zr_2(PO_4)(HPO_4)_2F_2] \cdot 0.5 H_2O$ (**1**), $[C_6H_{16}N_2]_{1.5}$ $[Zr_3(PO_4)_3F_6] \cdot 1.5 H_2O$ (**2**), and $[C_5H_{16}N_2]_{0.5} [Zr_3(PO_4)_3$ $(HPO_4) F_2] \cdot 1.5 H_2O$ (**3**), was determined by X-ray single-crystal investigations and was confirmed by elemental as well as thermogravimetric analyses (cf. Table 1). As can be

TABLE 2
Crystallographic Data and Details of Structure Refinements for Compounds 1–3

	Compound **1**	Compound **2**	Compound **3**
Empirical formula	$C_3H_{11}F_2NO_{12.5}$ P_3Zr_2	$C_9H_{27}F_6N_3O_{13.5}$ P_3Zr_3	$C_{2.5}H_{12}F_2$ $NO_{17.5}P_4Zr_3$
F_w	574.48	873.90	771.66
Space group	$C2/c$	$P\bar{1}$	$Pnnm$
a (Å)	16.754(4)	10.622(4)	15.168(5)
b (Å)	6.621(1)	10.668(4)	18.972(6)
c (Å)	27.094(6)	13.643(4)	6.628(2)
α (°)	90	68.48(4)	90
β (°)	90.57(2)	86.16(4)	90
γ (°)	90	68.10(4)	90
V (Å³)	3005(1)	1330.0(8)	1907(1)
Z	8	2	4
$\rho_{calc.}$ (g/cm³)	2.539	2.182	2.687
$\mu(MoK\alpha)$ (cm⁻¹)	17.94	14.39	20.50
Crystal size (mm)	$0.40 \times 0.10 \times 0.06$	$0.30 \times 0.08 \times 0.04$	$0.30 \times 0.07 \times 0.03$
Temperature (K)	160	130	150
θ(max) (°)	24.4	27.2	26.2
Total refl.	9274	10579	16082
Unique refl.	2382	5004	2061
Reflns. $I > 2\sigma(I)$	1797	2309	964
Refinable parameters	233	347	173
R_1	0.0234	0.0893	0.0340
R_2 (F^2)	0.0497	0.1635	0.0537

TABLE 3
Atomic Coordinates and Thermal Parameters for Compounds 1–3

Atom	x	y	z	$U_{eq.}$ (Å^2)
		Compound 1		
Zr(1)	0.85353(2)	0.54226(6)	0.71152(1)	0.00080(6)
Zr(2)	0.70033(2)	0.03768(6)	0.59103(1)	0.00154(9)
P(1)	0.80555(5)	0.0422(2)	0.70587(3)	0.0029(2)
P(2)	0.75193(5)	0.5423(2)	0.59758(3)	0.0042(2)
P(3)	0.54460(5)	−0.0303(2)	0.67390(3)	0.0033(2)
F(1)	0.8071(1)	0.0344(4)	0.56060(7)	0.0152(5)
F(2)	0.6456(1)	0.0490(4)	0.52620(6)	0.0116(4)
O(1)	0.8572(1)	0.2318(4)	0.70646(8)	0.0070(6)
O(2)	0.7484(1)	0.0468(4)	0.74916(8)	0.0090(5)
O(3)	0.7597(1)	0.0265(4)	0.65779(8)	0.0113(6)
O(4)	0.8617(1)	−0.1402(4)	0.71159(7)	0.0047(5)
O(5)	0.7005(1)	0.7248(4)	0.58624(8)	0.0089(6)
O(6)	0.7867(1)	0.5565(4)	0.64940(8)	0.0082(5)
O(7)	0.7039(1)	0.3509(4)	0.59067(8)	0.0076(6)
O(8)	0.8278(2)	0.5409(5)	0.56517(9)	0.0134(6)
O(9)	0.5914(1)	0.0387(4)	0.62932(8)	0.0086(5)
O(10)	0.4605(1)	0.0583(4)	0.67122(7)	0.0063(5)
O(11)	0.5829(1)	0.0273(4)	0.72265(8)	0.0085(6)
O(12)	0.5395(1)	−0.2667(4)	0.67039(9)	0.0092(6)
O(13)	0.50	0.5232(6)	0.75	0.0112(9)
N	0.9544(2)	−0.0650(6)	0.5999(1)	0.0132(7)
C(1)	1.0004(2)	−0.0431(6)	0.5527(1)	0.0107(8)
C(2)	0.5100(2)	0.3282(6)	0.4661(1)	0.0116(9)
C(3)	0.9686(2)	−0.1977(6)	0.5155(1)	0.0118(9)
H(1)	0.898(2)	−0.036(6)	0.592(1)	0.016
H(2)	0.967(2)	0.019(7)	0.622(1)	0.016
H(3)	0.956(2)	−0.189(7)	0.612(1)	0.016
H(4)	0.463(3)	−0.546(8)	0.743(2)	0.04(1)
H(8)	0.831(3)	−0.472(7)	0.542(1)	0.016
H(12)	0.530(2)	−0.335(6)	0.697(1)	0.011
		Compound 2		
Zr(1)	0.1764(2)	0.3063(2)	0.1578(1)	0.0121(5)
Zr(2)	0.3728(2)	0.2436(2)	−0.1579(1)	0.0122(5)
Zr(3)	0.1973(2)	−0.1795(2)	−0.0423(1)	0.0113(5)
P(1)	0.1739(5)	0.5450(5)	−0.1054(4)	0.013(1)
P(2)	0.1323(5)	0.1348(5)	−0.0007(4)	0.013(1)
P(3)	0.5019(5)	0.1266(5)	0.1075(4)	0.013(1)
F(1)	0.204(1)	0.432(1)	0.2242(8)	0.022(2)
F(2)	0.183(1)	0.163(1)	0.3042(9)	0.026(3)
F(3)	0.522(1)	0.300(1)	−0.2294(8)	0.022(3)
F(4)	0.281(1)	0.304(1)	−0.2995(9)	0.027(3)
F(5)	0.084(1)	−0.021(1)	−0.1686(9)	0.029(3)
F(6)	0.303(1)	−0.331(1)	0.0875(9)	0.031(3)
O(1)	0.219(1)	0.667(1)	−0.111(1)	0.024(3)
O(2)	0.279(1)	0.454(1)	−0.1629(9)	0.016(3)
O(3)	0.035(1)	0.605(1)	−0.1619(9)	0.015(3)
O(4)	0.1701(1)	0.453(1)	0.009(1)	0.020(3)
O(5)	0.199(1)	0.204(1)	−0.0963(9)	0.017(3)
O(6)	0.185(1)	−0.029(1)	0.025(1)	0.018(3)
O(7)	−0.021(1)	0.202(1)	−0.026(1)	0.016(3)
O(8)	0.166(1)	0.158(1)	0.097(1)	0.022(3)
O(9)	0.626(1)	0.161(1)	0.116(1)	0.021(3)
O(10)	0.456(1)	0.173(1)	−0.008(1)	0.018(3)
O(11)	0.536(1)	−0.037(1)	0.164(1)	0.022(3)
O(12)	0.388(1)	0.211(1)	0.163(1)	0.018(3)

TABLE 3—Continued

Atom	x	y	z	$U_{eq.}$ (Å^2)
		Compound 2		
O(13)	0.180(2)	0.813(2)	0.252(1)	0.063(6)
O(14)[a]	−0.017(7)	0.040(7)	0.359(4)	0.09(2)
N(1)	0.506(2)	0.406(2)	0.210(1)	0.029(4)
N(2)	0.644(2)	0.100(2)	0.658(1)	0.038(5)
C(1)	0.556(3)	0.318(3)	0.323(2)	0.066(9)
C(2)	0.447(5)	0.374(7)	0.393(2)	0.11(2)
C(3)	0.503(5)	0.320(5)	0.508(3)	0.12(2)
C(4)	0.591(4)	0.192(4)	0.552(2)	0.09(1)
C(5)	0.694(5)	0.136(7)	0.463(4)	0.17(3)
C(6)	0.655(4)	0.201(4)	0.354(3)	0.09(1)
N(3)	0.011(2)	0.653(3)	0.278(2)	0.064(7)
C(7)	0.039(4)	0.557(3)	0.399(2)	0.060(8)
C(8)	−0.001(3)	0.429(3)	0.423(2)	0.055(8)
C(9)	−0.030(3)	0.660(3)	0.455(2)	0.054(7)
		Compound 3		
Zr(1)	0.90134(6)	0.11654(5)	0	0.0002(2).
Zr(2)	1.23125(7)	0.21653(6)	0	0.0002(2)
Zr(3)	0.49660(7)	0.18106(5)	0	0.0007(2)
P(1)	0.8911(2)	0.1573(1)	0.50	0.0020(6)
P(2)	1.0125(2)	0.2801(1)	0	0.0036(6)
P(3)	0.7206(2)	0.2307(1)	0	0.0011(4)
P(4)[a]	1.1205(2)	0.0598(2)	0.0755(6)	0.0027(9)
F(1)	0.3568(3)	0.1680(3)	0	0.007(2)
F(2)	0.4998(4)	0.0771(3)	0	0.008(1)
O(1)	0.7998(4)	0.1904(4)	0.50	0.006(2)
O(2)	0.9598(4)	0.2150(4)	0.50	0.006(2)
O(3)	0.9017(3)	0.1116(2)	0.6869(8)	0.005(1)
O(4)	0.9551(4)	0.2149(4)	0	0.007(2)
O(5)	1.1099(4)	0.2579(4)	0	0.007(2)
O(6)	0.9935(3)	0.3238(2)	0.1870(8)	0.007(1)
O(7)	0.7813(5)	0.1667(4)	0	0.006(2)
O(8)	0.6256(4)	0.2033(4)	0	0.004(2)
O(9)	0.7362(3)	0.2759(3)	0.1891(8)	0.007(1)
O(10)	1.0294(4)	0.0773(4)	0	0.011(2)
O(11)	1.1886(4)	0.1131(4)	0	0.007(2)
O(12)	1.1461(4)	−0.0143(4)	0	0.004(2)
O(13)[a]	1.1232(6)	0.0643(6)	0.308(1)	0.011(2)
O(14)	1.0	0	0.50	0.017(3)
N(1)[a]	0.50	0	0.359(6)	0.067(8)
N(2)[b]	0.339(1)	−0.002(1)	0.092(4)	0.009(6)
C(1)[a]	0.3226(6)	−0.0476(6)	0.300(2)	0.011(3)[c]
C(2)[a]	0.361(1)	−0.004(1)	0.50	0.015(5)[c]
C(3)[a]	0.3245(9)	0.0730(8)	0.50	0.028(4)[c]
C(4)[a]	0.465(2)	−0.010(2)	0.50	0.050(9)[c]

[a] Half occupancy of the corresponding position.
[b] Occupancy 0.25.
[c] U(iso).

seen from Table 1, there is very good agreement between calculated and experimental values except for the C-values for compounds **1** and **3**. From DTA/TG-measurements, distinct steps for water evolution were found with mass losses confirming the water content in the compounds. The destruction of the templates occurs in the temperature range of about 350 to 500°C for all three compounds. In compound **1**, the water evolution step overlaps with that of the

TABLE 4
Selected Bond Distances (Å) in Structures 1–3

1		2		3	
Zr(1)–O(1)	2.070(2)	Zr(1)–O(3)	2.09(1)	Zr(1)–O(3)	2.077(5)
Zr(1)–O(2)	2.021(2)	Zr(1)–O(4)	2.04(1)	Zr(1)–O(3a)	2.077(5)
Zr(1)–O(4)	2.107(3)	Zr(1)–O(8)	2.08(1)	Zr(1)–O(4)	2.037(7)
Zr(1)–O(6)	2.015(2)	Zr(1)–O(12)	2.09(1)	Zr(1)–O(7)	2.055(7)
Zr(1)–O(10)	2.110(2)	Zr(1)–F(1)	1.983(9)	Zr(1)–O(10)	2.081(7)
Zr(1)–O(11)	2.070(2)	Zr(1)–F(2)	2.01(1)	Zr(1)–O(12)	2.070(8)
Zr(2)–O(3)	2.056(2)	Zr(2)–O(2)	2.07(1)	Zr(2)–O(1)	2.049(7)
Zr(2)–O(5)	2.075(3)	Zr(2)–O(5)	2.10(1)	Zr(2)–O(5)	2.001(7)
Zr(2)–O(7)	2.075(3)	Zr(2)–O(10)	2.04(1)	Zr(2)–O(9)	2.067(6)
Zr(2)–O(9)	2.108(2)	Zr(2)–O(11)	2.09(1)	Zr(2)–O(9a)	2.067(6)
Zr(2)–F(1)	1.978(2)	Zr(2)–F(3)	1.97(1)	Zr(2)–O(11)	2.066(8)
Zr(2)–F(2)	1.975(2)	Zr(2)–F(4)	1.99(1)	Zr(2)–F(1)	2.114(6)
		Zr(3)–O(1)	2.11(1)	Zr(3)–O(2)	2.050(8)
		Zr(3)–O(6)	2.08(1)	Zr(3)–O(6)	2.077(5)
		Zr(3)–O(7)	2.09(1)	Zr(3)–O(6a)	2.077(5)
		Zr(3)–O(9)	2.12(1)	Zr(3)–O(8)	2.002(7)
		Zr(3)–F(5)	1.97(1)	Zr(3)–F(1)	2.136(5)
		Zr(3)–F(6)	1.95(1)	Zr(3)–F(2)	1.973(6)
P(1)–O(1)	1.525(3)	P(1)–O(1)	1.52(1)	P(1)–O(1)	1.521(7)
P(1)–O(2)	1.522(2)	P(1)–O(2)	1.56(1)	P(1)–O(2)	1.510(7)
P(1)–O(3)	1.510(2)	P(1)–O(3)	1.51(1)	P(1)–O(3)	1.522(5)
P(1)–O(4)	1.537(3)	P(1)–O(4)	1.52(1)	P(1)–O(3a)	1.522(5)
P(2)–O(5)	1.514(3)	P(2)–O(5)	1.52(1)	P(2)–O(4)	1.512(7)
P(2)–O(6)	1.517(2)	P(2)–O(6)	1.53(1)	P(2)–O(5)	1.537(7)
P(2)–O(7)	1.512(2)	P(2)–O(7)	1.52(1)	P(2)–O(6)	1.519(5)
P(2)–O(8)	1.552(3)	P(2)–O(8)	1.53(1)	P(2)–O(6a)	1.519(5)
P(3)–O(9)	1.517(2)	P(3)–O(9)	1.51(1)	P(3)–O(7)	1.523(7)
P(3)–O(10)	1.528(2)	P(3)–O(10)	1.52(1)	P(3)–O(8)	1.532(7)
P(3)–O(11)	1.512(2)	P(3)–O(11)	1.53(1)	P(3)–O(9)	1.537(5)
P(3)–O(12)	1.570(3)	P(3)–O(12)	1.55(1)	P(3)–O(9a)	1.537(5)
				P(4)–O(10)	1.507(7)
				P(4)–O(11)	1.529(8)
				P(4)–O(12)	1.541(8)
				P(4)–O(13)	1.542(11)

template. The same compound exhibits a broadened exothermic effect between 600 and 700°C which is accompanied by a subsequent loss of mass. This effect can be attributed to the oxidation of carbon still remaining in the structure cavities after only partial removal of the template at lower temperatures. For this reason, some amount of carbon in compounds **1** and **3** may have not been completely burned during elemental analysis.

An important factor influencing the product formation is the molar ratio of the reactants. Thus, in the case of **1** and **2**, the same template was used. The molar ratios of $ZrOCl_2$ to H_3PO_4 in the starting reaction mixture were 1/5 and 1/3, respectively. Accordingly, the Zr/P ratio in the solid product is 2/3 in **1**, but 3/3 in **2**. In addition, compound **1** was prepared from a more acidic solution leading to the presence of both HPO_4^{2-} and PO_4^{3-} in the final solid. In the structure of compound **2**, only PO_4^{3-} units are present. Consequently, more fluorine had to be incorporated into the structure of the latter. In an experiment performed with

the intermediate Zr/H_3PO_4 ratio 1/4, a mixture of compounds **1** and **2** was obtained.

Compound **3** was prepared with a moderate yield of about 30%, when the HF concentration was not higher than that given in Table 1. At higher HF concentrations, the yield decreased significantly. However, larger single-crystals could only be obtained from mixtures with Zr/F ratios higher than 1/6–1/7. At constant HF concentrations but higher nominal H_3PO_4 content (Zr/H_3PO_4 < 1/3), $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) was found to be the main solid product.

Structures

The structure of compound **1**, $[amH_2]_{0,5}[Zr_2(PO_4)(HPO_4)_2F_2] \cdot 0.5H_2O$, with am = trans-1,4-diaminocyclohexane, is closely related to the layer structure of the compound with am = N,N,N′,N′-tetramethylethylenediamine, ZrPOF-2, already reported in (5). It contains ZrO_6 and ZrO_4F_2 octahedra. The two terminal fluorine atoms are in *cis*-position. In both compounds, **1** and ZrPOF-2 described in (5), the PO_4 to HPO_4 ratio is 1/2 instead of 2/1 for all compounds related to the ZrPOF-1 type. As shown in Fig. 1, the water situated in the small cavities is a twofold H-donor (O13–H4···O4) and twofold as H-acceptor (O12–H12···O13) with one of the $PO_3(OH)$ groups functioning as an H-donor. The other $PO_3(OH)$ group is involved in the hydrogen bond O8–H8···F2 (O···F distance 2.59 Å) connecting the layers. The template molecules are located between the layers and are fixed by two hydrogen bonds N–H1···F1 (N···F distance 2.76 Å).

In compound **2**, $[amH_2]_{1,5}[Zr_3(PO_4)_3F_6] \cdot 1.5H_2O$ with the same amine as **1**, the different composition also results in a layer structure, however, with quite different structural features of the inorganic framework (Fig. 2). In contrast to **1**, only ZrO_4F_2 octahedra and PO_4 tetrahedra were found in **2**. In two of the three crystallographically different ZrO_4F_2 octahedra, the two F atoms are in *cis*-position, whereas they are in *trans*-position in the third octahedron. All six F atoms are terminal. Due to the absence of ZrO_6 octahedra in structure **2**, the characteristic linear Zr–P–Zr polyhedra arrangement with a typical length of 6.6 Å can not be formed contrary to all other structures of zirconium.

The protonated template, 1,4-diammoniumcyclohexane ion, is situated between the inorganic sheets. They are connected by several N···F hydrogen bonds with lengths ranging from 2.60 to 2.97 Å as well as a few N···O hydrogen bonds (2.78–3.05 Å). The water molecules are also located in the interlayer space. They are attached by O···F (2.83–2.98 Å) and O···O (2.96 Å) hydrogen bonds only to one of the sheets and act as hydrogen donors. There are also some hydrogen bonds between the template (donor) and water (acceptor) at N···O distances of 2.84–2.88 Å. Some of the hydrogen bonds are shown in Fig. 2.
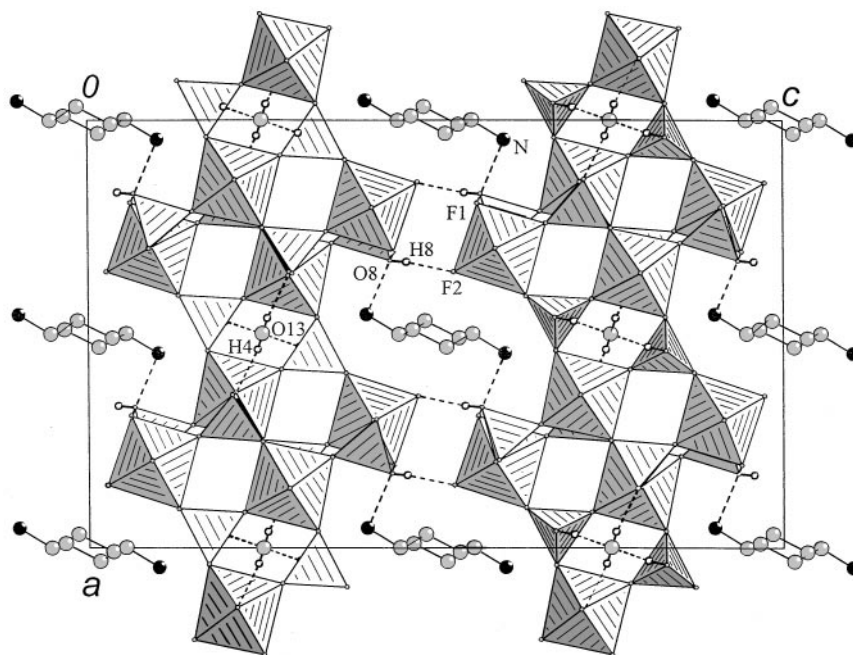
FIG. 1. Projection of structure **1** in the *b* direction. Hydrogen bonds are presented as dashed lines.

The structure of compound **3**, $[amH_2]_{0.5}[Zr_3(PO_4)_3(HPO_4)F_2] \cdot 0.5H_2O$ with *am* = 2,2-dimethyl-1,3-diaminopropane, contains three different Zr octahedra, ZrO_6, ZrO_5F, and ZrO_4F_2, and four crystallographically different

FIG. 2. Projection of structure **2** along the *a* axis. Dashed lines represent selected N ⋯ F and O ⋯ F hydrogen bonds.

P tetrahedra. PO_4 units account for three of the P tetrahedra. The last P tetrahedra is a $PO_3(OH)$ group. The latter is disordered with a mirror plane resulting in the opposite orientation of the P–OH bonds. A similar disorder type of $PO_3(OH)$ groups was found earlier in some structures of the ZrPOF-1 type (5, 6). The decrease of the F/Zr ratio causes the formation of a three-dimensional structure with channels running along the *c*-axis. The length of the *c*-axis, 6.628 Å, is again defined by the characteristic Zr–P–Zr polyhedra arrangement. As can be seen in Fig. 3, the bottlenecks of these channels are formed by six Zr octahedra and four P tetrahedra instead of four Zr octahedra and four P tetrahedra typical for structures of the ZrPOF-1 family. Therefore, the shape of the cross section resembles a pair of eyeglasses and can be regarded as a "double channel". The reason for this peculiarity can be sought in the existence of the F atom bridging two Zr octahedra. It is worthwhile to note that the $Zr–F_{bridge}$ bonds are longer (2.114(6) and 2.136(5) Å) than the $Zr–F_{terminal}$ bond (1.973(6) Å).
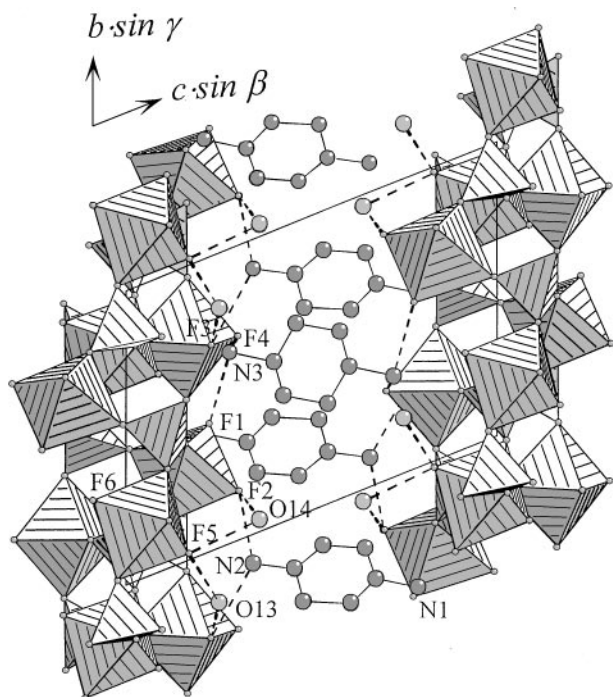
The template molecules in the channels of structure **3** are strongly disordered; however, they typically have N ⋯ F contacts (2.80–2.93 Å) due to the formation of hydrogen bonds. Water (O14) is situated in the small cavities (at *y* = 0.5 and *x* = 0.25 or 0.75) fixed by four hydrogen bonds (pairs of $O14_{donor} \cdots O3$, 2.87 Å and $O14_{acceptor} \cdots O13$, 2.57 Å) in the same way as in the structure of compound **1**. An additional water in the channels could not be located due to the disordering. However, the presence of approximately one additional water molecule in the formula is
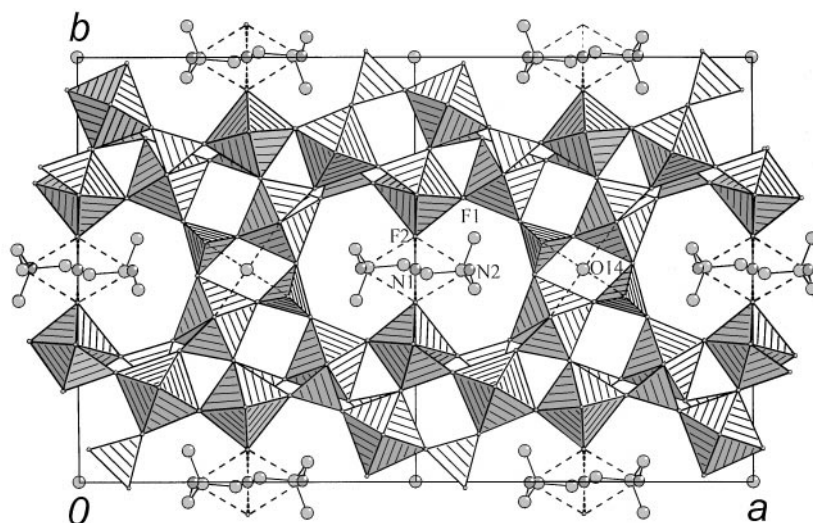
FIG. 3. Projection of structure **3** in the *c* direction. For clarity, only parts of the disordered template molecules are shown. Dashed lines represent O⋯O and N⋯F hydrogen bonds.

consistent with thermogravimetric data and the determined H content. A similar disordered position interchange of the protonated template and water in the channels is known for some other structures of the ZrPOF-1 type (4–6).

The inorganic frameworks of all three structures differ from each other as well as the compounds related to ZrPOF-1. However, all zirconium phosphate fluorides known up to now do have some structural features in common. Zr atoms are always octahedrally coordinated either exclusively by oxygen or by both oxygen and fluorine atoms. All non-OH oxygen atoms of the PO_4 tetrahedra are involved in Zr–O–P bridges. In most structures except for structure **2**, a typical linear arrangement of Zr and P polyhedra is formed and results in a short translation period of ca. 6.6 Å along one axis.

As shown earlier, the variation of the amine does not have a strong influence on the structure of the inorganic framework in several cases (5). However, using N,N,N′,N′-tetramethyl-ethylenediamine, where both amine groups are dimethylated, a zirconium phosphate fluoride with layer structure was obtained. In new investigations, the use of 1,4-diaminocyclohexane with the same number of C atoms as N,N,N′,N′-tetramethylethylenediamine leads to the formation of two different compounds, both having a layer structure. However, with 2,2-dimethyl-1,3-diaminopropane which has one C-atom less than the aforementioned template and a different structure, an entirely new 3D cage structure was obtained. The number of known structures for zirconium phosphate fluorides is still too small to draw general conclusions concerning the influence of the template molecules on the structure formed. It seems that by using templates having a short C-atom chain, the formation of structures similar to ZrPOF-1 is favored. Even by use of

other zirconium sources, ZrPOF-1 can be obtained as it has been reported recently in (10), where $Zr(OPr)_4$ was used instead of $ZrOCl_2 \cdot 8H_2O$ as starting compound. Small templates containing chain fragments fill the channels of the structure, often together with water. Larger templates not only can occupy channels but also can penetrate into the small cavities. In contrast, templates with a bulky and/or branched geometry demand more space than available in the channels of ZrPOF-1. Therefore, larger channels are formed. Finally, this can result in a separation of structural units into sheets.

Due to the increasing number of examples for the ZrPOF phases, it seems reasonable to continue the "ZrPOF"-notation for this class of compounds. Due to significant structural differences between each other and ZrPOF-1, compounds **1**, **2**, and **3** can be regarded as representatives of ZrPOF-2, ZrPOF-3, and ZrPOF-4, respectively.

In conclusion, it can be stated that the transition from 3D to 2D structures is strongly dependent on the F to Zr ratio in the solid. With low F/Zr ratios of 1/2 (ZrPOF-1) or 2/3 (ZrPOF-4), three-dimensional structures are formed. With increasing F/Zr ratios, layer structures seem to be more stable. Thus, in the case of F/Zr = 1/1 in ZrPOF-2, layer structures are formed. A layer structure is also known for the F/Zr ratio 2/1 in ZrPOF-3. However, the transition to lower dimensional structures can proceed further to a one-dimensional double stranded chain structure, which was described in (3). The decrease in dimensionality for higher F/Zr ratios could be accounted for by the increased number of terminal F atoms in the structure. In addition, the size and geometry of the template has a certain influence on the formation of the structure of ZrPOF phases. Thus, small and/or chain-like amines can be incorporated into the

channels in the inorganic three-dimensional framework of ZrPOF-1 type. The use of branched or space-demanding amines seems to be favorable for the formation of either 3D structures with larger channels (ZrPOF-4) or layer structures (ZrPOF-2 and ZrPOF-3).

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