

New Zirconium Phosphate Fluorides: Hydrothermal Synthesis and Crystal Structures

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A series of zirconium phosphate fluorides were synthesized and structurally characterized using different amines as templates. The compounds have the general formulas $[amH_n]_{1/n}[Zr_2(HPO_4)(PO_4)_2F] \cdot H_2O$ (1, am = ethylenediamine, $n = 2$; 2, am = *N*-methylethylenediamine, $n = 2$; 3, am = 1,3-diaminopropane, $n = 2$; 4, am = diethylenetriamine, $n = 3$) and $[amH_2]_{0.5}[Zr_2(HPO_4)_2(PO_4)F_2] \cdot 0.5H_2O$ (5, am = *N,N,N',N'*-tetramethylethylenediamine). In the structures of 2–4 with a Zr:F ratio of 2:1, there exists a three-dimensional arrangement of zirconium octahedra (one ZrO_6 and one ZrO_5F) and phosphate tetrahedra (two PO_4 and one HPO_4) connected via common oxygen atoms, whereas fluorine atoms and OH groups are terminal. These compounds crystallize in the “ZrPO-1” structure type, which contains channels along the *b* axis formed by eight-membered rings of alternating PO_4 tetrahedra and ZrO_6 or ZrO_5F octahedra, respectively. The protonated disordered templates occupy the channels. Half the water molecules are situated in the positions alternatively left free by the disordered templates and the other half are bonded via hydrogen bridges to the terminal OH groups of the HPO_4 tetrahedra. In contrast, the structure of 5 reveals a Zr:F ratio of 1:1, consequently forming a layer structure. The layers formed by ZrO_5F octahedra and PO_4 or HPO_4 tetrahedra, respectively, are linked by hydrogen bridges of type $O-H \cdots F$ and by weak H bonds over the protonated template. The similarities in connectivity pattern between Zr octahedra and P tetrahedra in all known zirconium phosphate fluorides and some zirconium phosphates are discussed. © 1998 Academic Press

INTRODUCTION

The search for new microporous compounds has led to widespread interest in a large range of several classes of metal phosphates. Besides others, zirconium phosphates are of great interest because of their potential regarding proton conductivity, ion exchange, and catalytic activity as reviewed by Clearfield *et al.* (1) and Alberti *et al.* (2). New opportunities in designing three-dimensional new network

structures were achieved by employing fluoride anions as mineralizer in hydrothermal synthesis methods (3, 4). Due to the use of fluoride, recently new fluorine-containing zirconium phosphates were obtained. To date, there exist examples where the Zr:F ratio in these structures is 1:2, 1:1, and 2:1. Thus, Clearfield *et al.* (5) reported the synthesis of a new layer structure of zirconium phosphate fluoride in dmso (dimethyl sulfoxide) as solvent with a Zr:F ratio of unity. Another example of a compound with a Zr:F ratio of 1:1 was reported by Xu *et al.* (6) on the basis of chemical analysis. However, subsequent single-crystal structure determination (7) revealed a double-stranded chain structure and proved the Zr:F ratio to be in fact 1:2. Recently, we succeeded in synthesizing the first zirconium phosphate fluoride with a three-dimensional cage structure and a Zr:F ratio of 2:1, $[(NH_3(CH_2)_2NH_3)_{0.5}[Zr_2(PO_4)_2(HPO_4)F] \cdot H_2O$, which was named “ZrPO-1” (8). Thus, there is clear evidence that the use of fluoride not only is of importance for improved crystallinity during hydrothermal synthesis but provides new structures and the prospect of obtaining compounds with possible applications. This is the case not only for zirconium phosphates but also for a series of other metal phosphates where fluoride was used as mineralizer. Thus, new gallium phosphate fluorides were synthesized with gallium having coordination numbers of 5 and 6 (9, 10) and even in one case ranging from 4 to 6 in the same structure (11). Whereas the few examples of zirconium phosphate fluorides contain fluoride terminally bonded, gallium phosphate fluorides show both kinds, terminal and often bridging fluoride ions, which seems to be the reason for a wider range of structure motifs in the latter case.

In this article we focus on systematic investigations of the synthesis conditions for hydrothermal preparations of some new zirconium phosphate fluorides using different amines as template molecules. As a result of this work four new examples of compounds belonging to the aforementioned substance class were synthesized and crystallographically characterized. Three of them are structurally very similar to the already described “ZrPO-1” with a Zr:F ratio of 2:1

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whereas the other one, having a layer structure, reveals a Zr:F ratio of 1:1.

EXPERIMENTAL

Synthesis

Reactants were purchased from commercial sources and used without further purification. The hydrothermal reactions were carried out in poly(tetrafluoroethylene)-lined steel containers under autogeneous pressure with a fill factor of approximately 60%. The following addition order of reactants was used for each reaction:

The amine was added to an aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the mixture was stirred for about 10 min. To the resulting thick gel phosphoric acid (85%) and hydrofluoric acid (40%) were added and the mixture was stirred again for about 10 min. After the reaction (reaction time 6 or 7 days) the crystalline products were filtered, washed with distilled water and alcohol, and finally dried at 60°C for 1 h. For detailed information, cf. Table 1. As already was observed in case of "ZrPO-1," the hydrothermal synthesis of these compounds depends very strongly on slight changes of the synthesis parameters. Consequently, a wide screening of the synthesis conditions was performed. In all cases described herein, the temperature, the filling capacity of the vessel, and, therefore, also the pressure were kept constant (190°C, 60% filled volume). Whereas the Zr to amine ratio was always kept constant at 1, the $\text{H}_3\text{PO}_4/\text{Zr}$ ratio was varied between 2 and 6 and the HF/Zr ratio between 2 and 4. Various amines were used as templates; the final structure type, however, was mainly related to "ZrPO-1." For instance, employing piperazine, 1,2-diaminopropane, or *N,N*-dimethylethylenediamine, we were able to synthesize new "ZrPO-1"-related compounds but until now failed to obtain single crystals large enough for structure

determination. In Table 1 the optimized conditions for the synthesis of mostly phase-pure compounds 1–5 are summarized. It was found that these conditions should be changed to some extent for growing larger single crystals. Additionally, the reaction times should be increased, too, at least up to 14 days.

X-Ray Crystallography

Data collections were performed on different diffractometers depending on the crystal size. The larger crystals (1 and 4) were measured on a STADI-4 (Fa. Stoe) four-circle diffractometer at room temperature whereas the smaller crystals (2, 3, and 5) were measured on an IPDS (Fa. Stoe) image plate diffractometer (2 and 5 at lower temperature). Absorption correction was not applied. The structures were solved by direct methods [SHELXS-86 (12)] and refined using SHELXS-93 (13). The crystallographic data and some details of the structure refinement are summarized in Table 2.

Although structures 1–4 are similar, two of them (1 and 2) have doubled *c* parameters and consequently twice the unit cell volumes in comparison with structures 3 and 4. Correspondingly, the glide plane *c* is not present in the last two structures. This results in a positional disorder of one of the three PO_4 tetrahedra when the refinement is performed in the space group *C2/m*. Disorder of such type was disregarded by refinement in the noncentrosymmetric space group *C2* for structure 3, but it was retained in structure 4 at all variations of the space group (*C2*, *Cm*, *C2/m*), so that the centrosymmetric space group has been used in the calculations in line with *E*-statistics.

In structures 1–4, the protonated templates and a part of the water molecules are strongly disordered over a few positions. In all cases the template disorder has been

TABLE 1
Synthesis Conditions for the Preparation of Phase-Pure Zirconium Phosphate Fluorides^a

Compound	Template	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	Amine	H_3PO_4	HF	H_2O	Conditions	Phase purity ^b
1	Ethylenediamine	1	1	2.5 ^c	2	50	<i>t</i> = 6 days; <i>T</i> = 190°C	Pure
2	<i>N</i> -Methylethylenediamine	1	1	3	4	50	<i>t</i> = 7 days; <i>T</i> = 190°C	Pure
3	1,3-Diaminopropane	1	1	3	2	50	<i>t</i> = 7 days; <i>T</i> = 190°C	Pure
4	Diethylenetriamine	1	1	4	2	50	<i>t</i> = 7 days; <i>T</i> = 190°C	Pure
5	<i>N,N,N',N'</i> -Tetramethylethylenediamine	1	1	5	4	50	<i>t</i> = 7 days; <i>T</i> = 190°C	Impurities < 5%

^aThe optimized initial molar gel compositions are given.

^bNo additional phases have been detected by XPD using an XRD-7 Fa.Seiffert for the phase analysis (>98.5%).

^cThis ratio is different from that given in ref. 8 but represents a more sufficient one for phase products.

TABLE 2
Crystallographic Data and Details of Structure Refinements

	1	2	3	4	5
Formula weight	536.43	539.41	540.42	526.42	575.48
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2</i>	<i>C2/m</i>	<i>C2/c</i>
<i>a</i> (Å)	17.277(3)	17.224(3)	17.340(3)	17.233(3)	21.647(4)
<i>b</i> (Å)	6.620(1)	6.630(1)	6.6053(8)	6.626(1)	6.648(2)
<i>c</i> (Å)	23.104(5)	23.181(5)	11.540(2)	11.523(2)	21.284(5)
β (deg)	94.21(3)	94.53(3)	95.41(2)	94.82(2)	103.03(3)
<i>V</i> (Å ³)	2635.4(8)	2638.9(8)	1315.9(4)	1311.1(3)	2984.1(10)
<i>Z</i>	8	8	4	4	8
ρ_{calc} (g cm ⁻³)	2.704	2.715	2.728	2.667	2.562
μ (MoK α)(cm ⁻¹)	20.28	20.26	20.32	20.31	18.07
Crystal size (mm)	0.4 × 0.2 × 0.1	0.3 × 0.1 × 0.05	0.3 × 0.2 × 0.08	0.4 × 0.2 × 0.1	0.30 × 0.1 × 0.08
Temperature (K)	293	180	293	293	200
Diffractometer	STADI-4	IPDS	IPDS	STADI-4	IPDS
θ_{max} (deg)	27.5	30	24	27.5	28.3
Total data	3017	13109	4488	3258	11031
Unique data	2961	2560	2011	1629	3461
Observed data with $I > 2\sigma(I)$	2785	1983	1993	1333	2155
No. of parameters	223	226	248	153	225
wR_2^a	0.1167	0.0987	0.0556	0.0602	0.0969
R_1^a	0.0401	0.0548	0.0195	0.0251	0.0391

^a R values are defined as $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \{\sum [w(F_o^2)^2]\}^{1/2}$ and $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

modeled using some soft restraints. The most simple type of disorder was found in structure **2** with two positions of the template cation $[\text{CH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ around an inversion center which correlated with two positions of water molecules. The only difference in the disorder type in structure **1** consists in the availability of four positions for disordered water instead of two. In structure **3**, there are three positions of the template in the channels—one on and two near the two-fold axis. Accordingly, the water molecule is distributed over four positions. In **4**, the template disorder over four positions seems to correlate with PO_4 disorder (see previous paragraph). The occupancy of the template positions ($\frac{1}{3}$) is based on the charge neutrality assuming that all three N atoms are protonated. Due to the longer chain of the template species, $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{3+}$, their disorder additionally influences the occupation of the small cavities by water, which is not the case for structures **1–3**. For structures **2** and **5**, the H atoms of coordinated water and HPO_4 groups could be localized and refined isotropically; other H atoms were put in calculated positions and refined in a riding mode.

The atom coordinates for structures **2–5** are listed in Table 3, and the relevant bond distances for **2** (the corresponding values for **3** and **4** are very similar) and **5** are presented in Table 4.

X-ray powder diffraction measurements were performed using a Seiffert-FPM XRD 7 (CuK α) in a 2θ range from 5 to 50° in steps of 0.01° with 6 s per step.

RESULTS AND DISCUSSION

Synthesis

The use of fluoride as mineralizer during the synthesis of microporous metal phosphates improves the crystal growth during hydrothermal synthesis. Obviously, the formation of zirconium phosphate fluorides proceeds via fluorozirconate intermediates.

Not surprisingly, in some cases fluoride was found to be incorporated into the framework, resulting in new metal phosphate fluorides. There are now a few examples of zirconium phosphate fluorides with three-dimensional cage structures as has already been found in the case of “ZrPO-1.” Although an extensive study of synthetic conditions was performed, it is still not entirely clear how different factors influence the formation of these compounds. Thus, sometimes under very similar synthesis conditions quite different compounds were formed. For instance, “ZrPO-1” was formed when ethylenediamine was used whereas under the same conditions, remarkable amounts of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (“ $\alpha\text{-ZrP}$ ”) were unexpectedly found besides the phosphate fluoride when 1,3-diaminopropane was used. Obviously, there is a strong competition between the formation of different solid phases which are all thermodynamically very similar. Probably the kinetic parameters (nucleation, crystal growth, etc.) are important and are strongly influenced by small changes of the synthesis parameters.

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic
Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Compounds 2–5

Atom ^a	x	y	z	U(eq) ^b
Compound 2, $[\text{CH}_3\text{NH}_2(\text{CH}_2)_2\text{NH}_3]_{0.5}[\text{Zr}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}] \cdot \text{H}_2\text{O}$				
Zr(1)	3591.7(2)	9985(1)	2997.5(2)	1.8(2)
Zr(2)	2201.3(2)	4945(1)	4253.9(2)	2.3(2)
P(1)	3080.2(7)	4986(3)	2931.2(5)	3.4(3)
P(2)	2690.7(7)	9973(3)	4304.4(5)	4.8(3)
P(3)	578.0(8)	5725(2)	3340.1(6)	5.3(3)
F	3303(2)	4854(6)	4585(1)	14(1)
O(1)	3625(2)	6824(7)	2932(2)	7(1)
O(2)	2531(2)	4954(7)	2373(1)	7(1)
O(3)	2599(2)	5098(7)	3452(2)	11(1)
O(4)	3591(2)	3094(7)	2965(2)	8(1)
O(5)	3162(2)	10096(7)	4898(2)	9(1)
O(6)	2185(2)	8089(7)	4280(2)	9(1)
O(7)	3260(2)	9914(7)	3829(2)	9(1)
O(8)	2156(2)	11814(7)	4223(2)	10(1)
O(9)	925(2)	4978(7)	2798(2)	10(1)
O(10)	1048(2)	5050(7)	3893(2)	9(1)
O(11)	−260(2)	4988(7)	3359(2)	10(1)
O(12)	599(3)	8080(7)	3362(2)	14(1)
O(13)	5000	5336(10)	2500	12(1)
O(14) ^a	5345(6)	8493(23)	5357(5)	47(4)
N	5579(3)	4673(11)	4522(2)	25(2)
C(1) ^a	5140(8)	2932(23)	4854(6)	21(3)
C(2) ^a	4991(9)	3524(25)	5482(7)	25(3)
C(3) ^a	4996(10)	5938(27)	4191(7)	27(3)
H	5991(46)	4975(133)	4783(34)	29(21)
H(1A) ^a	4635(8)	2634(23)	4637(6)	26
H(1B) ^a	5458(8)	1687(23)	4862(6)	26
H(2A) ^a	5490(9)	3895(25)	5689(7)	30
H(2B) ^a	4768(9)	2360(25)	5680(7)	30
H(12)	448(46)	8856(136)	3054(34)	27(22)
H(13)	4632(42)	6031(132)	2589(33)	22(20)
Compound 3, $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Zr}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}] \cdot \text{H}_2\text{O}$				
Zr(1)	8597.9(2)	8548.7(4)	1001.7(2)	2.9(1)
Zr(2)	7785.4(2)	8475.1(4)	6494.6(2)	4.0(1)
P(1)	7718.8(4)	8526(2)	3609.2(6)	6.1(2)
P(2)	6923.6(4)	8551(2)	−856.2(6)	4.8(2)
P(3)	9421.8(5)	7853(2)	8330.8(7)	7.0(2)
F	6710(1)	8387(6)	5778(2)	21(1)
O(1)	8939(1)	8494(7)	7228(2)	11(1)
O(2)	7478(1)	8543(7)	253(2)	10(1)
O(3)	8168(1)	8504(7)	4820(2)	10(1)
O(4)	9752(1)	8592(7)	1715(2)	14(1)
O(5)	9409(2)	5504(5)	8287(2)	20(1)
O(6)	8579(1)	5427(6)	924(2)	11(1)
O(7)	8286(1)	8587(7)	2671(2)	12(1)
O(8)	7820(1)	5340(6)	6511(2)	11(1)
O(9)	8619(1)	11690(6)	855(2)	10(1)
O(10)	7775(1)	11595(7)	6533(2)	13(1)
O(11)	9086(1)	8557(7)	−586(2)	14(1)
O(12)	7392(1)	8419(7)	8096(2)	14(1)
O(13)	10000(1)	13166(6)	0	20(1)
N(1) ^a	5695(9)	7973(36)	3688(16)	29(4)
N(2) ^a	5657(12)	8601(31)	3959(14)	29(4)
C(1) ^b	5000	5836(26)	5000	53(4)
C(2) ^a	5018(7)	7089(25)	6111(11)	47(3)

TABLE 3—Continued

Atom ^a	x	y	z	U(eq) ^b
C(3) ^c	4956(9)	10211(19)	4342(10)	25(3)
C(4) ^c	5155(10)	8315(37)	6346(13)	44(4)
O(15) ^b	4686(8)	5054(23)	4149(11)	38(3)
O(16) ^b	4702(9)	1451(39)	4552(17)	78(7)
Compound 4, $[\text{NH}_3(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]_{0.33}[\text{Zr}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}] \cdot 0.94\text{H}_2\text{O}$				
Zr(1)	2213.6(2)	0	8503.6(3)	8.9(1)
Zr(2)	1401.7(2)	0	4008.5(3)	7.7(1)
P(1)	2304.8(7)	0	1398.8(9)	11.3(2)
P(2)	3078.3(6)	0	5845.7(9)	9.3(2)
P(3)	573.4(9)	692(3)	6695(1)	13.2(3)
F	3309(2)	0	9162(3)	31(1)
O(1)	1724(2)	0	2338(3)	19(1)
O(2)	1848(2)	0	192(3)	17(1)
O(3)	2822(1)	1872(4)	1525(2)	19(1)
O(4)	2535(2)	0	4724(2)	14(1)
O(5)	2587(2)	0	6880(3)	22(1)
O(6)	3605(1)	1863(4)	5887(2)	17(1)
O(7)	−253(2)	0	6730(3)	21(1)
O(8)	922(2)	0	5610(3)	20(1)
O(9)	1052(2)	0	7798(3)	18(1)
O(10)	548(4)	3018(10)	6726(6)	38(1)
O(11) ^d	5000	0	5000	48(5)
O(12) ^e	5254(17)	3262(49)	391(25)	172(19)
N(1) ^f	4462(7)	323(81)	1071(9)	67(11)
N(2) ^g	4763(22)	0	4349(26)	249(45)
C(1) ^f	4999(21)	1803(59)	646(15)	140(13)
C(2) ^g	4906(21)	0	2225(22)	145(20)
C(3) ^g	4305(21)	0	3202(22)	83(10)
Compound 5, $[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2]_{0.5}[\text{Zr}_2(\text{HPO}_4)_2(\text{PO}_4)_2\text{F}_2] \cdot 0.5\text{H}_2\text{O}$				
Zr(1)	511.9(2)	2279.0(6)	1424.7(2)	3.8(1)
Zr(2)	2477.6(2)	−2680.2(6)	1541.5(2)	3.4(1)
P(1)	816.3(6)	−2740(2)	1217.8(6)	7.1(3)
P(2)	2828.6(6)	−2690(2)	3262.7(6)	4.8(3)
P(3)	910.0(6)	1551(2)	3119.8(6)	7.6(3)
F(1)	243(1)	2413(4)	465(1)	16(1)
F(2)	2317(1)	−2715(4)	601(1)	12(1)
O(1)	485(2)	−834(4)	1368(2)	11(1)
O(2)	1518(2)	−2722(4)	1526(2)	10(1)
O(3)	486(2)	−4559(5)	1451(2)	9(1)
O(4)	766(2)	−2908(5)	479(2)	16(1)
O(5)	2723(2)	−2701(4)	2529(2)	9(1)
O(6)	2525(2)	−834(4)	3493(2)	8(1)
O(7)	3545(2)	−2673(4)	3574(2)	8(1)
O(8)	2535(2)	−4566(4)	3495(2)	9(1)
O(9)	1560(2)	2287(5)	3458(2)	9(1)
O(10)	422(2)	2248(4)	3490(2)	9(1)
O(11)	724(2)	2213(5)	2418(2)	11(1)
O(12)	960(2)	−803(5)	3152(2)	15(1)
O(13)	0	−3052(7)	2500	18(1)
N	1658(2)	2313(6)	−516(2)	13(1)
C(1)	2226(3)	3229(7)	−72(2)	15(1)
C(2)	1420(3)	484(7)	−234(2)	18(1)
C(3)	1143(3)	3870(8)	−674(3)	21(1)
H(4)	367(29)	−2728(75)	219(29)	23
H(12)	664(29)	−1428(86)	2931(28)	23
H(13)	137(29)	−3839(82)	2245(27)	28

TABLE 3—Continued

Atom ^a	x	y	z	U(eq) ^b
H(N)	1771(2)	1942(6)	− 895(2)	16
H(1A)	2113(3)	3629(7)	336(2)	18
H(1B)	2354(3)	4454(7)	− 275(2)	18
H(2A)	1746(6)	− 565(18)	− 168(14)	27
H(2B)	1035(9)	− 9(29)	− 530(8)	27
H(2C)	1322(15)	831(13)	180(8)	27
H(3A)	771(7)	3289(17)	− 967(14)	32
H(3B)	1295(6)	5024(24)	− 883(15)	32
H(3C)	1027(12)	4313(39)	− 277(3)	32

^a Occupancies: a, 0.50; b, 0.25; c, 0.375; d, 0.161; e, 0.309; f, 0.333; g, 0.167.

^b U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Although in the meantime some examples of zirconium phosphate fluorides have been discovered, it is still difficult to derive definitive relationships between synthesis conditions and compounds formed. From the extended synthetic work performed, it seems that, in general, the formation of unwanted “ α -ZrP” can be suppressed by decreasing the H_3PO_4 and HF content in the reaction mixture. A further tendency is that normally larger single crystals are formed by increasing the HF to Zr or amine ratio. However, this is sometimes accompanied by the facilitated formation of other products, very often “ α -ZrP.” Nevertheless, under the synthesis conditions given in Table 1 phase-pure compounds were obtained as proven by XPD measurements (Fig. 1).

Structures

As can be seen from Table 2 the structures of **1–4** are very similar with virtually identical a and b parameters as well as the same values for β whereas the c parameter for **3** and **4** is

nearly exactly half that of **1** and **2**. On the contrary, **5** reveals a different structure type where only the b -parameter corresponds to that of the other structures. This is due to the fact that all the compounds have a common feature of tetrahedra–octahedra connectivity in one crystallographic direction, which will be discussed in detail in the following paragraphs.

First, the closely related structures **1–4**, which have a composition of the general formula $[amH_n]_{1/n}[Zr_2(HPO_4)(PO_4)_2F] \cdot H_2O$, will be discussed. In all these structures there exists a three-dimensional arrangement of zirconium octahedra (one ZrO_6 and one ZrO_5F) and phosphate tetrahedra (two PO_4 and one HPO_4) connected via common oxygen atoms. Both fluorine atoms and OH groups are terminal and consequently do not participate in the polyhedra connectivity (cf. Fig. 2). In the subsequent discussion, the structure of **2** will be described in more detail because it shows less complicated template disorder compared with the others. The characteristic feature of the structure is that most atoms of the inorganic framework (2 Zr, 2 P, F, and 7 of 12 O) are situated nearly exactly in the planes parallel to xOz at $y = 0$ and $y = 0.5$ (see Table 3 for **2**). Due to this special arrangement all these atoms remain very close to the same plane after their symmetry transformation by the c glide plane. In this way flat polyhedra bands that are infinite in the c direction are formed. Within the same band each PO_4 tetrahedron (P(1) and P(2)) connects two Zr octahedra whereas the HPO_4 tetrahedron (P(3)) links three Zr octahedra. Due to the fact that the bandwidth in the x direction is less than one a translation, it creates empty space between bands lying at the same level. It should be emphasized that eight-membered cyclic arrangements of alternating tetrahedra and octahedra form holes in the bands with a diameter of approximately 6.5 Å. The three-dimensional structure is built up by such bands which are connected to each other via the PO_4 tetrahedra. Besides the already described connectivity function of these tetrahedra

TABLE 4
Relevant Bond Lengths (Å) for Compounds **2** and **5**

Compound 2			Compound 5				
Zr(1)–O(1)	2.102(5)	P(1)–O(1)	1.538(4)	Zr(1)–F(1)	1.996(3)	P(1)–O(1)	1.525(3)
Zr(1)–O(2)	2.054(3)	P(1)–O(2)	1.541(3)	Zr(1)–O(1)	2.073(3)	P(1)–O(2)	1.512(4)
Zr(1)–O(4)	2.063(5)	P(1)–O(3)	1.518(4)	Zr(1)–O(3)	2.104(3)	P(1)–O(3)	1.543(3)
Zr(1)–O(7)	2.054(3)	P(1)–O(4)	1.530(5)	Zr(1)–O(7)	2.041(3)	P(1)–O(4)	1.556(4)
Zr(1)–O(9)	2.082(4)	P(2)–O(5)	1.544(4)	Zr(1)–O(10)	2.070(3)	P(2)–O(5)	1.527(4)
Zr(1)–O(11)	2.087(4)	P(2)–O(6)	1.522(5)	Zr(1)–O(11)	2.060(4)	P(2)–O(6)	1.530(3)
Zr(2)–F	1.991(3)	P(2)–O(7)	1.532(3)	Zr(2)–F(2)	1.953(3)	P(1)–O(7)	1.543(4)
Zr(2)–O(3)	2.035(4)	P(2)–O(8)	1.531(4)	Zr(2)–O(2)	2.071(3)	P(2)–O(8)	1.530(3)
Zr(2)–O(5)	2.109(4)	P(3)–O(9)	1.517(4)	Zr(2)–O(5)	2.048(3)	P(3)–O(9)	1.510(3)
Zr(2)–O(6)	2.085(5)	P(3)–O(10)	1.529(4)	Zr(2)–O(6)	2.098(3)	P(3)–O(10)	1.525(3)
Zr(2)–O(8)	2.078(5)	P(3)–O(11)	1.527(4)	Zr(2)–O(8)	2.072(3)	P(3)–O(11)	1.522(4)
Zr(2)–O(10)	2.094(3)	P(3)–O(12)	1.563(5)	Zr(2)–O(9)	2.084(3)	P(3)–O(12)	1.569(3)

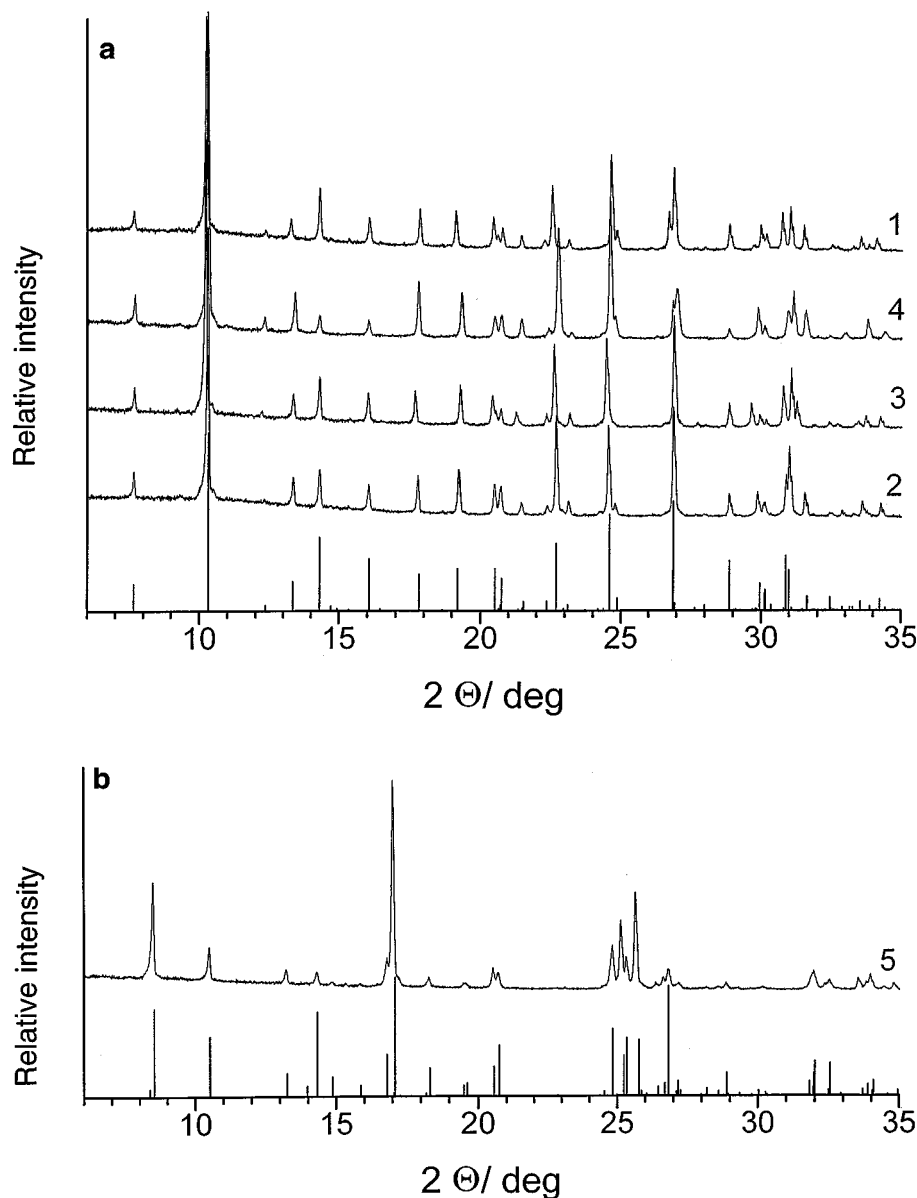


FIG. 1. X-ray powder diffraction patterns for compounds 1–4 (a) and 5 (b) in comparison with the calculated diagrams using single-crystal data of compounds 2 (a) and 5 (b).

within the same band, they are edge-connected to Zr octahedra of the upper and lower bands, resulting in a translation period of 6.63 Å in the *y* direction. The adjacent bands in the *y* direction are shifted by $0.5a$ so that the eight-membered holes overlap with the empty space between the bands above and below. Thus, channels in the *y* direction are present in the structure with bottlenecks due to the eight-membered polyhedra rings.

The protonated amine occupies these channels between two bottlenecks. The nitrogen atoms of the amine are linked to the F atoms via hydrogen bridges (N–H ... F, 2.73 Å). The

organic template cation is disordered between two positions around an inversion center. For each orientation of the template cation, the remaining empty space is occupied by a water molecule which appears disordered as well (occupancy factor 0.5). The oxygen of the other water molecule on the twofold axis is tetrahedrally linked to the inorganic framework via hydrogen bridges acting two times as the H donor (O(13)–H(13) ... O(1), 2.82 Å) and two times as H acceptor (O(13) ... H(12), 2.64 Å). Thus, the water molecules occupy two different positions in the channels and in the small cavities with a 1:1 ratio. Structure 1 differs from

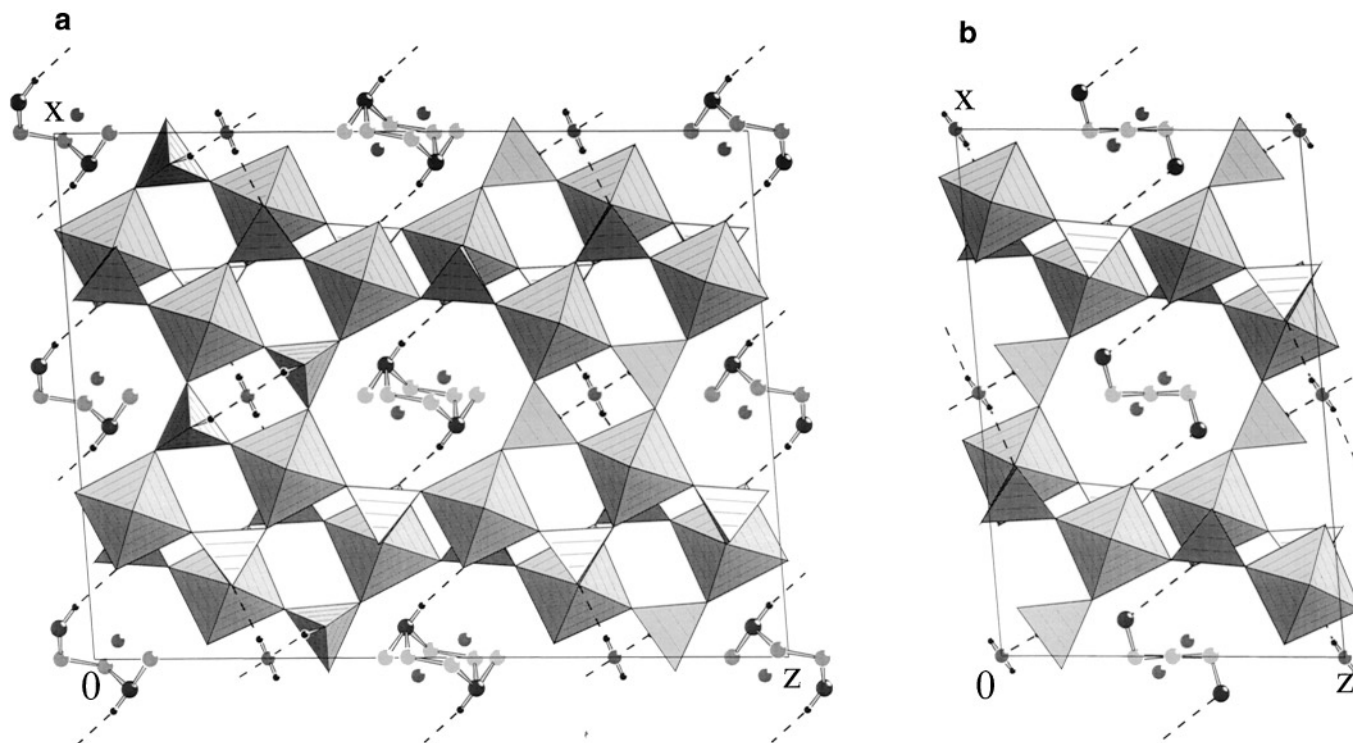


FIG. 2. Crystal structures of compounds **2** (a) and **3** (b). For **2**, the template cations and the water molecules in the channels are shown in one of two disordered orientations (at $z = 0$ and $z = 1$) or in both disordered orientations (at $z = 0.5$). For **3**, the template cations and the water molecules in the channels are shown in one of three disordered orientations.

2 only by the size of the protonated template (enH_2 instead of N -methylethylenediammonium) providing more possible positions for water in the channels (four instead of two) (8).

As a whole, the framework of structure **3** is similar to that of **2**. The most essential distinction is an orientation of OH groups of the P(3) tetrahedra in the same direction instead of alternating orientations in **2** (compare Fig. 2). On the contrary, the P(3) tetrahedra in **4** have both orientations, however, statistically disordered by a mirror plane. Due to the larger size of the template, both water positions are affected, being not fully occupied. The occupancy refinement resulted in values of 0.309 in the channels and 0.161 in the cavities, respectively, which corresponds to the overall composition $[\text{NH}_3(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]_{0.33} [\text{Zr}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}] \cdot 0.94\text{H}_2\text{O}$ with a little lower content of water compared to **1–3**. However, this could not be proved by chemical analysis due to the small deviation of the stoichiometric coefficient for water from 1.

Structure **5**, $[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2]_{0.5} [\text{Zr}_2(\text{HPO}_4)_2(\text{PO}_4)\text{F}_2] \cdot 0.5\text{H}_2\text{O}$, represents a new structure type of layered zirconium phosphate fluorides. It contains more fluorine ($\text{Zr}:\text{F} = 1:1$); therefore, both Zr atoms are octahedrally coordinated by five O atoms and one F atom. However, the charge of the anionic part remains the same (-1) due to the replacement of one PO_4^{3-} group by

HPO_4^{2-} (P(1)). Now this group can link three Zr octahedra only (instead of four in **1–4**). The structural functions of P(2) and P(3) do not change and, thus, belong to the building blocks containing four ZrO_5F octahedra which are further linked in the b direction in the same way as in structures **1–4** (Fig. 3). These blocks are not connected with each other in the x_0z plane due to the presence of several terminal groups such as F and OH. That results in the absence of eight-membered rings typical for structures **1–4**. Here, layers parallel to the xy_0 plane are formed with the most terminal groups directed toward the interlayer space. The adjacent layers are held together by hydrogen bonds of the type $\text{O}(4)\text{--H}(4) \cdots \text{F}(1)$ (2.63 Å) and, additionally, by weak bifurcated H bridges over the template cation, $\text{N--H}(1) \cdots \text{O}(12)$ (3.06 Å) and $\text{N--H}(1) \cdots \text{O}(6)$ (3.12 Å). The comparatively short $\text{F}(2) \cdots \text{F}(2)$ distance of 2.86 Å probably results from van der Waals interactions. In all structures the Zr–F distances (mean value 1.98 Å) are noticeably shorter than Zr–O distances (mean value 2.08 Å, Table 4). Although the structures of **1–4** differ remarkably from that of **5**, it should be emphasized that the linkage type of Zr octahedra and P tetrahedra found in structures **1–5** represents a common feature of all known zirconium phosphate fluorides. This connectivity type has been found in the double-stranded chain structure of $(\text{NH}_3(\text{CH}_2)_2\text{NH}_3)_{1.5} [\text{Zr}(\text{HPO}_4)(\text{PO}_4)]$

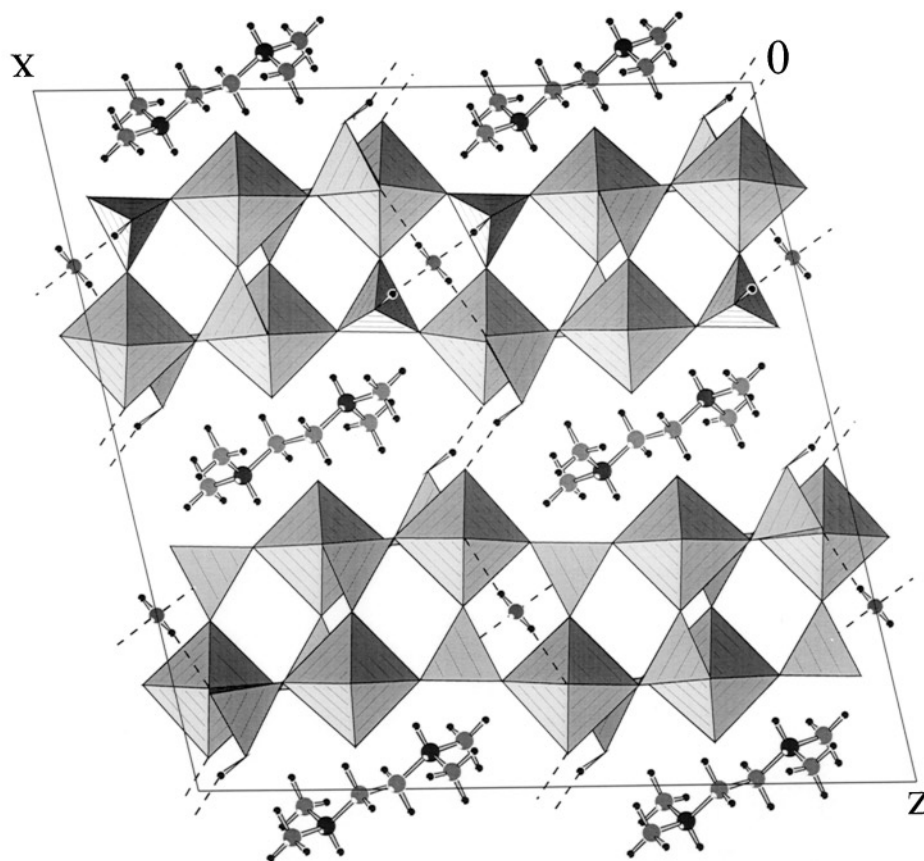


FIG. 3. Crystal structure of compound 5. Weak H bonds between template cations and inorganic double layers are not shown.

F₂] with a Zr:F ratio of 1:2 (7) as well as in the layer structure of Zr(PO₄)F·dmsO, determined from powder data (5). Correspondingly, the unit cell parameters along the specific linkage direction (*b*) are 6.62 and 6.61 Å, respectively. Owing to the tetragonal unit cell of the latter structure, there exists a second direction with a translation period of 6.61 Å. This typical value in the narrow range of 6.61–6.63 Å can be simply calculated as a sum of the lengths of the O–Zr–O diagonal of a Zr octahedron (4.2 Å) and the O···O edge of a PO₄ tetrahedron (2.4 Å). Moreover, such a linkage occurs also in the structures of zirconium phosphates, for example, in the Zr(PO₄)(H₂PO₄)·2H₂O (*γ*-ZrP) with *b* = 6.63 Å (14), which has a layer structure.

Presently, it can be concluded that the structure type of different zirconium phosphate fluorides strongly depends on the Zr:F ratio changing from a cage structure at higher values (2:1) over a layer structure at a 1:1 ratio to a double-stranded chain structure at a low ratio of 1:2.

It was shown that **1** can be reversibly dehydrated in the temperature range between 160 and 200°C without remarkable changes of the inorganic framework. Moreover, smaller molecules such as ammonia are able to enter the empty space of the structure instead of water (15). Finally, it should

be mentioned that first attempts to remove the organic template molecule under maintenance of the inorganic framework by thermal treatment failed. At least a part of the structure becomes remarkably rearranged as was shown by the XRD analysis. Further investigation has to be carried out in this regard.

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