Synthesis and structure of a new zirconium phosphate with double-stranded chains

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The zirconium phosphate $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5H_2en$ was prepared, and its structure was determined by X-ray diffraction analysis.

Key words: zirconium phosphate, X-ray diffraction analysis.

Crystalline zirconium orthophosphates, such as the α, β, γ varieties that are formed from aqueous media, are normally lamellar phases.[1,2] They consist of alternate layers of ZrO_6 octahedra and PO_4 tetrahedra with molecules of water arranged in interlamellar fashion. A range of other species may also be intercalated between the zirconophosphate sheets, and, in many instances, useful catalytic and other new solid-state properties may be developed.[3,4] The intercalation of amines by layered zirconium phosphates has been extensively investigated;[5] but, to our knowledge, no direct synthesis of amine-containing zirconium phosphates has yet been reported.

It is known that nonaqueous syntheses of amine-containing aluminum, gallium, and zinc phosphates often generate open-framework three-dimensional structures.[6–9] Occasionally, however, layered[10–11] and chain[12] alumino- and gallo-phosphates can also crystallize from nonaqueous media. In the present work we describe the predominantly nonaqueous synthesis of an ethylenediamine-containing zirconium phosphate, the structure of which is unique and which consists of double-stranded chains with alternating vertex-sharing tetrahedra and octahedra. The chains are vaguely reminiscent of those recently reported for α-Fe_2PO_5[13] except that there are face-sharing octahedra in the latter.

In the structure of the compound synthesized by us, two terminal F atoms, together with four O atoms, which belong to four PO_4 tetrahedra, coordinate to the Zr^{IV} central atom, forming a more or less regular ZrO_4F_2 octahedron (Fig. 1). The Zr atom and one of the phosphorus atoms (P(2)) are linked to each other through bridging O atoms in such a way that, in the overall structure, they are arranged by symmetry to form infinite double-stranded chains along the *b* axis. Three of the four oxygen atoms bound to P(2) are linked to three Zr atoms, and the fourth O atom is terminal. The other PO_4 group, consisting of P(1), O(1), O(2), O(3), and O(4), is linked to the Zr atom only *via* one oxygen (O(1)) atom. The O(2) and O(4) atoms are both terminal whereas O(3) belongs to a hydroxyl group.

The double-stranded chains are located in the *ab* plane parallel to one another to form disrupted layers, and the ethylenediamine molecules are accommodated between these layers (Fig. 2). It is noteworthy that the amine molecules are each protonated, and the hydrogen atom attached to O(3) obviously plays an important role in ensuring the structural stability: the short O—H···O

Table 1. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (×10³) for $[Zr(HPO_4)(PO_4)F_2] \times 1.5\ H_2en$

Atom	*x*	*y*	*z*	U_{eq}*
Zr	3838.7(3)	2243.4(6)	2213.5(3)	6.5(2)
P(1)	6306(1)	1915(2)	2387(1)	12(1)
P(2)	1329(1)	2263(2)	2191(1)	8(1)
F(1)	4514(2)	2235(3)	3676(2)	16(1)
F(2)	3186(2)	2372(4)	735(2)	20(1)
O(1)	5187(2)	2250(4)	1933(2)	14(1)
O(2)	6681(3)	2018(5)	3504(2)	21(1)
O(3)	6495(3)	−250(5)	2066(3)	30(1)
O(4)	6837(3)	3409(5)	1933(3)	29(1)
O(5)	1125(2)	4126(4)	2735(2)	14(1)
O(6)	1085(2)	381(4)	2691(2)	13(1)
O(7)	2454(2)	2240(4)	2332(2)	15(1)
O(8)	719(3)	2324(4)	1098(2)	16(1)
N(1)	6143(4)	9655(8)	4785(4)	21(1)
C(1)	6978(4)	8226(8)	5197(4)	21(1)
C(2)	6932(4)	6471(8)	4529(5)	25(1)
N(2)	6128(4)	5034(7)	4514(4)	22(1)
N(3)	6044(3)	6648(8)	734(4)	23(1)
C(3)	5008(4)	5961(7)	277(4)	21(1)

* U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table 2. Selected bond lengths (d/Å) and angles (φ/deg) for $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5\ H_2en$*

Bond	d	Bond	d	Bond	d
Zr—F(1)	1.998(3)	Zr—F(2)	2.016(3)	Zr—O(7)	2.031(3)
Zr—O(5a)	2.071(3)	Zr—O(1)	2.085(3)	Zr—O(6b)	2.088(3)
P(1)—O(2)	1.515(4)	P(1)—O(4)	1.518(4)	P(1)—O(1)	1.523(3)
P(1)—O(3)	1.560	P(2)—O(8)	1.521(3)	P(2)—O(6)	1.536(3)
P(2)—O(5)	1.540(3)	P(2)—O(7)	1.545(3)	N(1)—C(1)	1.482(7)
C(1)—C(2)	1.497(8)	C(2)—N(2)	1.484(7)	N(3)—C(3)	1.472(6)
C(3)—C(3c)	1.499(10)				

Angle	φ	Angle	φ
F(1)—Zr—F(2)	177.42(10)	F(1)—Zr—O(7)	93.13(12)
F(2)—Zr—O(7)	88.11(12)	F(1)—Zr—O(5a)	87.83(11)
F(2)—Zr—O(5a)	94.43(11)	O(7)—Zr—O(5a)	90.54(11)
F(1)—Zr—O(1)	92.83(12)	F(2)—Zr—O(1)	85.95(12)
O(7)—Zr—O(1)	174.05(13)	O(5a)—Zr—O(1)	89.73(11)
F(1)—Zr—O(6b)	86.40(11)	F(2)—Zr—O(6b)	91.30(11)
O(7)—Zr—O(6b)	91.49(11)	O(5a)—Zr—O(6b)	173.98(12)
O(1)—Zr—O(6b)	88.83(11)	O(2)—P(1)—O(4)	111.9(2)
O(2)—P(1)—O(1)	113.5(2)	O(4)—P(1)—O(1)	108.6(2)
O(2)—P(1)—O(3)	108.6(2)	O(4)—P(1)—O(3)	108.4(2)
O(1)—P(1)—O(3)	105.5(2)	O(8)—P(2)—O(6)	111.3(2)
O(8)—P(2)—O(5)	111.3(2)	O(6)—P(2)—O(5)	107.9(2)
O(8)—P(2)—O(7)	110.3(2)	O(6)—P(2)—O(7)	108.3(2)
O(5)—P(2)—O(7)	107.6(2)	P(1)—O(1)—Zr(1)	144.5(2)
P(2)—O(5)—Zr(1b)	144.5(2)	P(2)—O(6)—Zr(1a)	145.9(2)
P(2)—O(7)—Zr(1)	168.3(2)	N(1)—C(1)—C(2)	112.5(5)
N(2)—C(2)—C(1)	112.3(5)	N(3)—C(3)—C(3c)	109.7(6)

* Symmetry transformations used to generate equivalent atoms:
a: $-x+1/2$, $y-1/2$, $-z+1/2$; b: $-x+1/2$, $y+1/2$, $-z+1/2$; c: $-x+1$, $-y+1$, $-z$.

Table 3. Bond lengths (d/Å) and angles (φ/deg) involving H atoms for $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5\ H_2en$

Bond	d	Bond	d	Bond	d
N(1)—H(11)	0.84(5)	N(1)—H(12)	0.92(6)	N(1)—H(13)	0.69(5)
C(1)—H(21)	0.98(5)	C(1)—H(22)	0.94(8)	C(2)—H(31)	0.95(5)
C(2)—H(32)	1.09(5)	N(2)—H(41)	0.89(5)	N(2)—H(42)	0.96(6)
N(2)—H(43)	0.94(5)	N(3)—H(51)	0.92(6)	N(3)—H(52)	0.90(6)
N(3)—H(53)	1.16(10)	C(3)—H(61)	0.93(5)	C(3)—H(62)	1.15(5)

Angle	φ	Angle	φ
C(1)—N(1)—H(11)	111(4)	C(1)—N(1)—H(12)	106(3)
H(11)—N(1)—H(12)	103(5)	C(1)—N(1)—H(13)	112(4)
H(11)—N(1)—H(13)	106(4)	H(12)—N(1)—H(13)	119(6)
N(1)—C(1)—H(21)	107(3)	C(2)—C(1)—H(21)	111(3)
N(1)—C(1)—H(22)	116(5)	C(2)—C(1)—H(22)	102(4)
H(21)—C(1)—H(22)	109(5)	N(2)—C(2)—H(31)	109(3)
C(1)—C(2)—H(31)	109(3)	N(2)—C(2)—H(32)	103(3)
C(1)—C(2)—H(32)	110(3)	H(31)—C(2)—H(32)	114(5)
C(2)—N(2)—H(41)	109(3)	C(2)—N(2)—H(42)	108(4)
H(41)—N(2)—H(42)	113(5)	C(2)—N(2)—H(43)	117(3)
H(41)—N(2)—H(43)	103(4)	H(42)—N(2)—H(43)	107(5)
C(3)—N(3)—H(51)	106(4)	C(3)—N(3)—H(52)	115(4)
H(51)—N(3)—H(52)	113(6)	C(3)—N(3)—H(53)	97(4)
H(51)—N(3)—H(53)	126(5)	H(52)—N(3)—H(53)	100(5)
N(3)—C(3)—H(61)	110(3)	C(3c)—C(3)—H(61)	111(3)
N(3)—C(3)—H(62)	110(3)	C(3c)—C(6)—H(62)	109(3)
H(61)—C(3)—H(62)	108(4)		

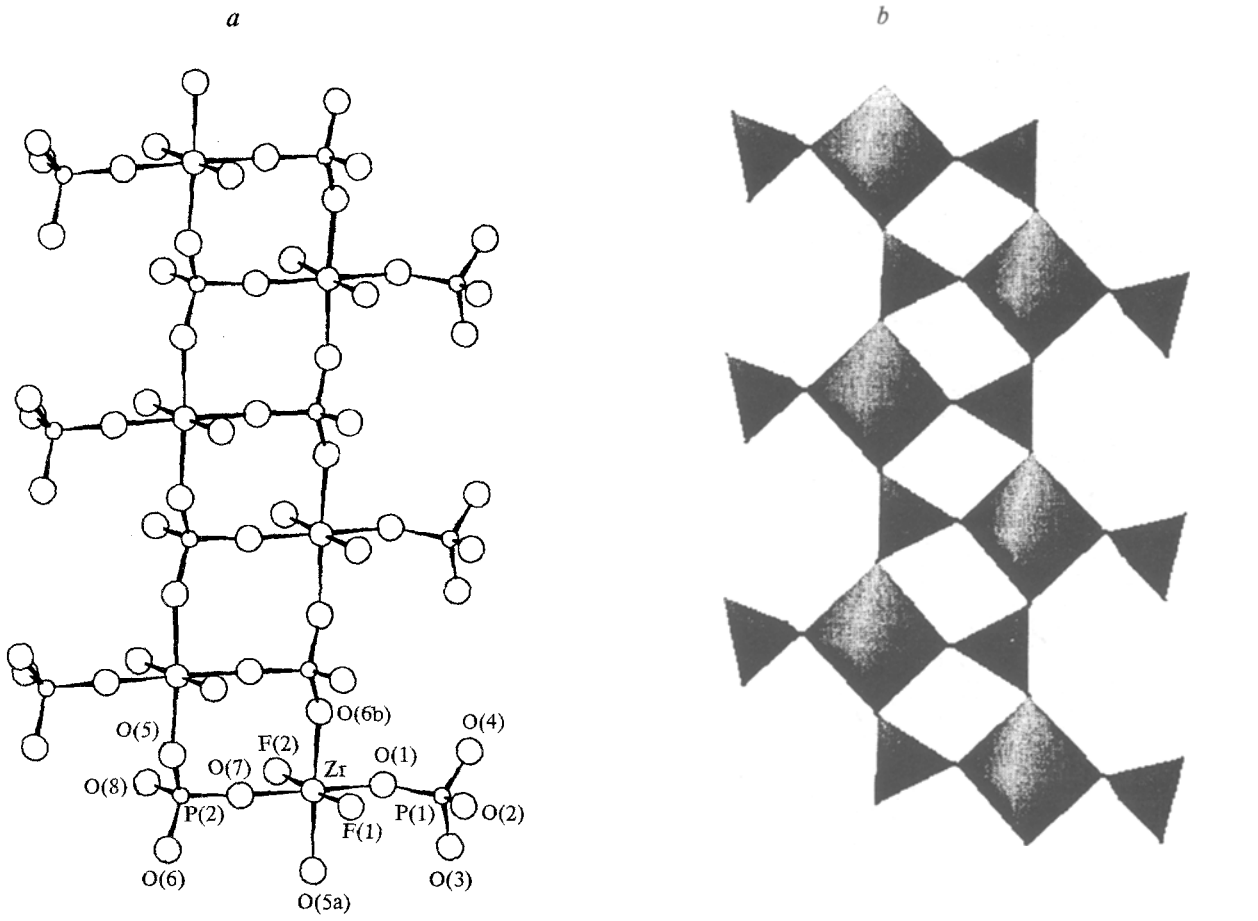

Fig. 1. Double-stranded chains of zirconium phosphate anions arranged along the *b* axis. The two F atoms, O(2), O(4), and O(8) are all terminal, whereas O(3) is chemically bound by a hydrogen. O(4) forms a strong H-bond with the hydroxyl group from another asymmetric unit.

Table 4. Anisotropic displacement parameters ($\times 10^3$) for $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5\ H_2en$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	7(1)	5(1)	8(1)	0(1)	3(1)	0(1)
P(1)	10(1)	14(1)	13(1)	−2(1)	5(1)	0(1)
P(2)	7(1)	6(1)	10(1)	1(1)	3(1)	0(1)
F(1)	18(2)	21(2)	8(1)	2(1)	0(1)	−1(1)
F(2)	21(2)	24(2)	11(2)	0(1)	2(1)	−1(1)
O(1)	12(2)	14(2)	16(2)	1(1)	6(2)	0(1)
O(2)	27(2)	24(2)	14(2)	2(1)	11(2)	3(2)
O(3)	19(2)	21(2)	37(2)	−20(2)	−7(2)	11(2)
O(4)	19(2)	39(2)	25(2)	10(2)	4(2)	−10(2)
O(5)	17(2)	9(2)	18(2)	−1(1)	8(2)	2(1)
O(6)	16(2)	6(2)	18(2)	2(1)	8(2)	−1(1)
O(7)	11(2)	16(2)	20(2)	1(1)	8(2)	0(1)
O(8)	20(2)	14(2)	13(2)	1(1)	2(2)	−1(1)
N(1)	26(3)	14(3)	24(3)	−3(2)	11(3)	−2(2)
C(1)	17(3)	22(3)	22(3)	3(2)	5(3)	−2(2)
C(2)	24(3)	16(3)	37(4)	1(3)	14(3)	−1(2)
N(2)	29(3)	16(3)	20(3)	0(2)	8(2)	−2(2)
N(3)	24(3)	21(3)	20(3)	−5(2)	4(2)	−5(2)
C(3)	20(3)	27(3)	16(3)	2(2)	5(3)	−3(2)

Table 5. Coordinates of hydrogen atoms ($\times 10^4$) and isotropic displacement parameters ($\times 10^3$) for $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5\ H_2en$

Atom	x	y	z	U_{iso}
H(11)	6094(37)	10451(74)	5218(41)	17(15)
H(12)	6336(41)	10486(83)	4365(42)	34(17)
H(13)	5686(40)	9164(72)	4609(39)	7(17)
H(21)	7598(37)	8994(60)	5311(35)	17(13)
H(22)	7003(58)	7590(88)	5793(59)	79(26)
H(3)	7161(56)	9226(95)	2483(54)	81(24)
H(31)	6816(41)	6956(70)	3879(42)	30(16)
H(32)	7608(42)	5567(74)	4821(41)	45(17)
H(41)	6192(36)	4692(66)	5131(41)	17(14)
H(42)	6171(42)	3901(84)	4110(45)	42(18)
H(43)	5472(43)	5514(73)	4262(40)	28(16)
H(51)	6373(45)	5610(87)	1132(47)	49(20)
H(52)	6115(47)	7830(87)	1058(49)	52(21)
H(53)	6163(61)	7166(94)	11(68)	96(27)
H(61)	4711(33)	5776(61)	755(36)	14(13)
H(62)	4560(46)	7165(69)	−272(45)	43(17)

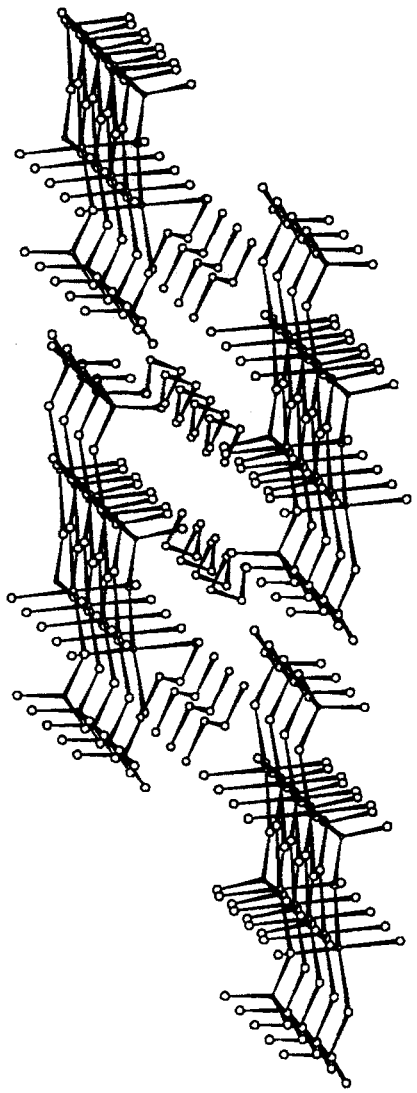

Fig. 2. Structure of $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5\ H_2en$ viewed along the *b* axis. Chains of zirconium phosphate anions are connected *via* H-bonds (not shown), forming disrupted macroanionic layers. Protonated ethylenediamine molecules are located between these disrupted layers.

bond involving the terminal O(4) atom from the neighboring chain efficiently converts the zirconium—phosphate chains into a layered structure. The O(3)—H distance is 1.00 Å and that of the O(4)···H hydrogen bond is 1.50 Å.

The Zr—O bond lengths fall within 2.031—2.088 Å (average 2.069 Å), and the two Zr—F distances are 1.998 and 2.016 Å, respectively, *i.e.*, they are only slightly shorter than the Zr—O distances. The P—O bond lengths for the $P(1)O_4$ group are in the range 1.515—1.560 Å (average 1.529 Å), and the P(1)—O(3) bond, the O atom of which is involved in a hydrogen bond, is the longest of them. The P—O distances for the $P(2)O_4$ tetrahedron vary over a narrower range (1.521—1.545 Å, average 1.536 Å).

Taking into account that small amines and other protonated small molecules can also be accommodated between the chains of this new zirconium phosphate structure, it would be instructive to explore the dielectric and conducting properties of such materials.

Experimental

The new zirconium phosphate was prepared from an ethylene glycol medium by crystallization of a zirconium phosphate gel containing ethylenediamine as the structure-directing template. For this, $ZrOCl_2 \cdot xH_2O$ and NH_4F were successively added to a solution of H_3PO_4 (85%) and ethylenediamine (en) in ethylene glycol (EG), and the mixture was stirred vigorously. A homogeneous gel with an empirical composition of ZrO_2 : 2.5 P_2O_5 : 5.3 en : 3.0 NH_4F : 2.0 HCl : 60 EG : 4.0 H_2O was formed. The gel was placed in a Teflon-lined stainless steel autoclave and heated at 140 °C for 10 days under autogeneous pressure. The solid product was separated by filtration, washed with distilled water, and dried at ~20 °C.

A single crystal with dimensions 0.15×0.10×0.06 mm was selected for structural characterization. Diffraction data were collected at 150 K[14] on an Enraf-Nonius FAST four-circle diffractometer with Mo-$K\alpha$ radiation. The scanning range was 2.46 to 24.91°. A total of 5311 reflections were collected, of which 1948 were independent. The structure was solved by a direct method (SHELX-S)[15] and refined by a full-matrix least-squares method (SHELX-93)[16] to $R = 0.355$ and $R_W = 0.0855$ [$I > 2\sigma(I)$] with 236 parameters; the residual factors for all of the data were $R = 0.0487$ and $R_W = 0.0874$, respectively. Absorption correction was introduced. Crystal data: $[Zr(HPO_4)(PO_4)F_2] \cdot 1.5H_2en$, $M = 413.35$, monoclinic symmetry, space group $P2_1/n$, $a = 14.220(2)$, $b = 6.639(1)$, $c = 14.349(2)$ Å, $\beta = 109.32(1)°$, $d_{calc} = 2.148$ g cm^{-3}, $Z = 4$, μ(Mo-$K\alpha$) = 1.175 mm^{-1}, $\lambda = 0.71069$ Å. The atomic coordinates, bond lengths and angles, and thermal parameters and their estimated standard deviations are listed in Tables 1—5.

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