Journal of Solid State Chemistry **166,** 265–270 (2002)
doi:10.1006/jssc.2002.9569

Synthesis and Structure of a New Layered Zincophosphate $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$, Intercalated with Quintuply Protonated Tetraethylenepentamine

Yunling Liu, Wang Liu, Yan Xing, Zhan Shi, Yunlong Fu, and Wenqin Pang[1]

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jinlin University, Changchun 130023, People's Republic of China

Received November 1, 2001; in revised form February 15, 2002; accepted March 1, 2002

A new two-dimensional zinc phosphate $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$ has been synthesized hydrothermally using tetraethylenepentamine (TEPA) as structure-directing agent and its structure was determined by means of single-crystal X-ray diffraction. The title compound crystallizes in the orthorhombic system, space group $Pca2_1$ (No.29) with lattice parameters $a = 18.6286(12)$ Å, $b = 8.0804(5)$ Å, $c = 22.5019(15)$ Å, $V = 3387.1(4)$ Å^3, $Z = 4$, $R_1 = 0.0389$ and $wR_2 = 0.0862$ [4042 observed reflections with $I > 2\sigma(I)$]. The structure involves a network of ZnO_4, PO_4, and $PO_3(OH)$ tetrahedra forming macroanionic inorganic layers with eight-membered apertures. The charge compensation is achieved by the quintuply protonated TEPA molecule in interlamellar space, which interact with the inorganic layers via hydrogen bonding. © 2002 Elsevier Science (USA)

Key Words: **hydrothermal synthesis; zinc phosphates; structure-directing agent; layered structure.**

INTRODUCTION

The interest in zincophosphates has been steadily growing after the discovery of the first microporous zinc phosphates with zeolite-like topologies (1). Since then, a large number of zincophosphates with zero-, one-, two- and three-dimensional structures have been synthesized and characterized (2–5). The structures of these compounds are built mainly from tetrahedral PO_4 and ZnO_4 but examples of ZnO_6 and ZnO_5 subunits are also known (6). Interesting features, such as 3-rings and infinite –Zn–O–Zn–O– chains are shown by the inorganic component of various examples of zincophosphates. The recently reported zincophosphates possessing helical channels and the largest pores are particularly noteworthy (7–9). Up to now, 3-, 4-, 5-, 6-, 8-, 10-, 12-, 16-, 20-, and 24-membered rings have been found in the structures of zincophosphates (10, 11). In addition, it seems that diamines or triamines are more effective than monoamines in the formation of zincophosphates with open architecture (7–14). Recently, several new open-framework zinc phosphates have been synthesized hydrothermally in the presence of tetramine or polyamine (11, 15–17).

In recent years, we have devoted efforts toward the synthesis of transition metal phosphates with novel topologies (18–22). In the case of zinc, we obtained two new layered zincophosphates employing the triethylenetetramine and 1-, 4-, 8-, 11-tetraazacyclotetradecane (cyclam) as templates, respectively (5, 23). In this paper, we describe the synthesis and structure of a new layered zincophosphate $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$, using tetraethylenepentamine as the structure-directing agent.

EXPERIMENTAL

Synthesis and Characterization

The title compound was hydrothermally prepared from a mixture of zinc acetate dihydrate (99%, Shanghai Chemical Reagent Factory), phosphoric acid (85 wt%, Beijing Chemical Plant), tetraethylenepentamine (TEPA, 90%, Shenyang Chemical Reagent Factory) and distilled water. The molar ratio of the initial mixture was $1.0Zn(Ac)_2$:2.0 H_3PO_4:0.7TEPA:$80H_2O$. In a typical synthesis, 2.44 g of zinc acetate dihydrate was first dispersed into 15 mL H_2O, then 1.5 mL H_3PO_4 was slowly added, followed by dropwise addition of 1.4 mL TEPA with stirring. The final mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 393 K for 2 days under autogenous pressure. The resulting rod-like crystal product as a single phase (in about 80% yield based on the Zn source) was recovered by filtration, washed thoroughly with distilled water and dried at room temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count

[1]To whom correspondence should be addresed. Fax: + 86-431-5671974. E-mail: wqpang@mail.jlu.edu.cn.

0022-4596/02 $35.00

time was 4 s. The element analyses were performed on a Perkin-Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The infrared (IR) spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A Perkin-Elmer DTA 1700 differential thermal analyzer was used to obtain the differential thermal analysis (DTA), and a Perkin-Elmer TGA 7 thermogravimetric analyzer to obtain thermogravimetric analysis (TGA) curves in an atmospheric environment with a heating rate of 10°C min^{-1}.

Determination of Crystal Structure

A rod-like crystal with dimensions of approximate $0.20 \times 0.05 \times 0.05$ mm was mounted on a glass fiber. The intensity data were collected on a Siemens Smart CCD diffractometer. The numbers of collected reflections and independent reflections were 15,562 and 4761, respectively. Data processing was accomplished with the SAINT processing program (24). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 (25). The zinc and phosphorus atoms were first located and the carbon, nitrogen, oxygen atoms were found in difference Fourier maps. The hydrogen

TABLE 1
Crystal Data and Structure Refinement for $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$

Empirical formula	$C_8\ H_{39}\ N_5\ O_{29}\ P_6\ Zn_6$
Formula weight	1247.48
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit-cell dimensions	$a = 18.6286(12)$ Å, $\alpha = 90°$ $b = 8.0804(5)$ Å, $\beta = 90°$ $c = 22.5019(15)$ Å, $\gamma = 90°$
Volume	3387.1(4) $Å^3$
Z	4
Density (calculated)	2.446 $Mg\,m^{-3}$
Absorption coefficient	4.579 mm^{-1}
$F(000)$	2496
Crystal size	$0.20 \times 0.05 \times 0.05$ mm^3
θ range for data collection	1.81–23.25°
Limiting indices	$-19 \le h \le 20,\ -8 \le k \le 8,$ $-24 \le l \le 24$
Reflections collected/unique	15562/4761 [R(int) = 0.1048]
Completeness to $\theta = 23.25$	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.3087 and 0.1969
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4761/1/488
Goodness-of-fit on F^2	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$, $wR_2 = 0.0862$
R indices (all data)	$R_1 = 0.0493$, $wR_2 = 0.0898$
Largest diff. peak and hole	0.664 and -0.490 e $Å^{-3}$

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$

Atom	x	y	z	U(eq)[a]
Zn(1)	981(1)	−1067(1)	5960(1)	21(1)
Zn(2)	−1218(1)	−2065(1)	5889(1)	19(1)
Zn(3)	222(1)	−966(1)	4508(1)	19(1)
Zn(4)	735(1)	4004(1)	5976(1)	19(1)
Zn(5)	−74(1)	3988(1)	4574(1)	19(1)
Zn(6)	2110(1)	2924(1)	4643(1)	19(1)
P(1)	28(1)	−3234(3)	6775(1)	20(1)
P(2)	−277(1)	1130(3)	5517(1)	17(1)
P(3)	2116(1)	1726(3)	5985(1)	18(1)
P(4)	872(1)	1826(3)	3707(1)	18(1)
P(5)	1224(1)	6155(3)	4989(1)	17(1)
P(6)	3794(1)	3154(3)	4538(1)	17(1)
O(1)	386(4)	−1543(8)	6662(3)	29(2)
O(2)	316(3)	−148(8)	5342(3)	24(2)
O(3)	1719(3)	298(8)	6278(3)	30(2)
O(4)	1434(3)	−2925(7)	5542(3)	23(2)
O(5)	−166(4)	−3333(8)	7433(3)	34(2)
O(6)	−629(4)	−3463(8)	6396(3)	31(2)
O(7)	−938(3)	234(7)	5758(3)	22(2)
O(8)	−2139(3)	−1853(7)	6288(3)	22(2)
O(9)	7(3)	2290(7)	5998(3)	24(2)
O(10)	−483(3)	2079(8)	4944(3)	24(2)
O(11)	936(3)	−2728(7)	4506(3)	24(2)
O(12)	408(3)	262(8)	3791(3)	25(2)
O(13)	612(3)	4911(8)	5159(3)	23(2)
O(14)	1721(4)	3371(8)	6100(3)	30(2)
O(15)	566(3)	5400(8)	6662(3)	24(2)
O(16)	456(4)	3376(8)	3861(3)	25(2)
O(17)	−814(3)	5390(8)	4254(3)	24(2)
O(18)	1563(4)	1692(8)	4067(3)	29(2)
O(19)	1067(4)	1931(8)	3040(3)	28(2)
O(20)	2185(4)	1439(8)	5320(3)	28(2)
O(21)	1870(3)	5224(7)	4757(3)	23(2)
O(22)	3059(3)	2908(7)	4226(3)	21(1)
O(23)	3677(4)	3504(7)	5201(3)	28(2)
O(24)	4206(3)	1551(7)	4445(3)	23(2)
O(1W)	3036(4)	6407(8)	5595(3)	34(2)
O(2W)	2482(5)	4798(12)	3265(4)	66(3)
O(3W)	2281(5)	1160(12)	2473(4)	67(3)
O(4W)	1130(5)	−3892(9)	3378(3)	52(2)
O(5W)	971(4)	5401(12)	8045(3)	59(2)
N(1)	6913(4)	10,990(10)	9745(3)	28(2)
N(2)	6918(4)	9787(10)	8415(3)	28(2)
N(3)	5145(4)	9352(10)	7650(3)	28(2)
N(4)	3785(5)	7097(12)	6694(4)	41(2)
N(5)	2003(5)	5248(11)	7124(4)	43(2)
C(1)	7019(5)	12,078(13)	9195(5)	32(2)
C(2)	7357(5)	11,162(12)	8690(4)	28(2)
C(3)	6222(5)	10,298(12)	8197(5)	31(3)
C(4)	5893(6)	8886(13)	7851(5)	36(3)
C(5)	4773(6)	7891(13)	7363(4)	35(3)
C(6)	4069(6)	8438(13)	7100(5)	36(3)
C(7)	3277(6)	5875(13)	6958(5)	37(3)
C(8)	2510(6)	6626(11)	6992(5)	37(3)

[a] U(eq) is defined as one−third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$

Zn(1)–O(3)	1.903(6)	Zn(2)–O(6)	1.945(7)
Zn(1)–O(4)	1.964(6)	Zn(2)–O(8)	1.945(6)
Zn(1)–O(1)	1.968(6)	Zn(2)–O(23)#1	1.946(7)
Zn(1)–O(2)	2.005(6)	Zn(2)–O(7)	1.952(6)
Zn(3)–O(12)	1.925(7)	Zn(4)–O(14)	1.928(7)
Zn(3)–O(11)	1.948(6)	Zn(4)–O(15)	1.937(6)
Zn(3)–O(24)#1	1.956(6)	Zn(4)–O(9)	1.939(6)
Zn(3)–O(2)	1.998(6)	Zn(4)–O(13)	1.992(6)
Zn(5)–O(10)	1.911(6)	Zn(6)–O(18)	1.925(6)
Zn(5)–O(17)	1.924(6)	Zn(6)–O(21)	1.929(6)
Zn(5)–O(16)	1.947(6)	Zn(6)–O(20)	1.944(7)
Zn(5)–O(13)	1.980(6)	Zn(6)–O(22)	2.003(6)
P(1)–O(6)	1.503(7)	P(2)–O(9)	1.527(7)
P(1)–O(15)#2	1.513(7)	P(2)–O(7)	1.529(6)
P(1)–O(5)	1.525(7)	P(2)–O(10)	1.548(7)
P(1)–O(1)	1.542(7)	P(2)–O(2)	1.561(7)
P(3)–O(20)	1.520(7)	P(4)–O(16)	1.513(7)
P(3)–O(3)	1.522(7)	P(4)–O(18)	1.525(7)
P(3)–O(14)	1.540(7)	P(4)–O(12)	1.543(7)
P(3)–O(8)#3	1.549(6)	P(4)–O(19)	1.547(7)
P(5)–O(4)#4	1.502(6)	P(6)–O(24)	1.520(6)
P(5)–O(11)#4	1.511(7)	P(6)–O(17)#5	1.525(6)
P(5)–O(21)	1.512(6)	P(6)–O(23)	1.534(7)
P(5)–O(13)	1.568(7)	P(6)–O(22)	1.550(6)
O(3)–Zn(1)–O(4)	108.2(3)	O(6)–Zn(2)–O(8)	106.1(3)
O(3)–Zn(1)–O(1)	102.6(3)	O(6)–Zn(2)–O(23)#1	100.2(3)
O(4)–Zn(1)–O(1)	118.5(3)	O(8)–Zn(2)–O(23)#1	109.4(3)
O(3)–Zn(1)–O(2)	119.5(3)	O(6)–Zn(2)–O(7)	119.4(3)
O(4)–Zn(1)–O(2)	102.5(3)	O(8)–Zn(2)–O(7)	102.8(3)
O(1)–Zn(1)–O(2)	106.3(3)	O(23)#1–Zn(2)–O(7)	118.4(3)
O(12)–Zn(3)–O(11)	104.6(3)	O(14)–Zn(4)–O(15)	101.2(3)
O(12)–Zn(3)–O(24)#1	103.8(3)	O(14)–Zn(4)–O(9)	118.2(3)
O(11)–Zn(3)–O(24)#1	118.9(2)	O(15)–Zn(4)–O(9)	106.4(3)
O(12)–Zn(3)–O(2)	126.9(3)	O(14)–Zn(4)–O(13)	109.9(3)
O(11)–Zn(3)–O(2)	100.7(3)	O(15)–Zn(4)–O(13)	120.2(3)
O(24)#1–Zn(3)–O(2)	103.4(3)	O(9)–Zn(4)–O(13)	101.9(3)
O(10)–Zn(5)–O(17)	110.6(3)	O(18)–Zn(6)–O(21)	117.7(3)
O(10)–Zn(5)–O(16)	110.9(3)	O(18)–Zn(6)–O(20)	104.2(3)
O(17)–Zn(5)–O(16)	101.8(3)	O(21)–Zn(6)–O(20)	120.5(3)
O(10)–Zn(5)–O(13)	105.8(3)	O(18)–Zn(6)–O(22)	98.6(3)
O(17)–Zn(5)–O(13)	119.3(3)	O(21)–Zn(6)–O(22)	105.9(3)
O(16)–Zn(5)–O(13)	108.4(3)	O(20)–Zn(6)–O(22)	107.4(3)
O(6)–P(1)–O(15)#2	110.7(4)	O(9)–P(2)–O(7)	108.5(4)
O(6)–P(1)–O(5)	110.6(4)	O(9)–P(2)–O(10)	111.9(4)
O(15)#2–P(1)–O(5)	106.4(4)	O(7)–P(2)–O(10)	109.3(4)
O(6)–P(1)–O(1)	111.5(4)	O(9)–P(2)–O(2)	109.9(4)
O(15)#2–P(1)–O(1)	109.4(4)	O(7)–P(2)–O(2)	110.2(4)
O(5)–P(1)–O(1)	108.0(4)	O(10)–P(2)–O(2)	107.1(4)
O(20)–P(3)–O(3)	110.7(4)	O(16)–P(4)–O(18)	111.7(4)
O(20)–P(3)–O(14)	109.7(4)	O(16)–P(4)–O(12)	111.3(4)
O(3)–P(3)–O(14)	110.4(4)	O(18)–P(4)–O(12)	110.5(4)
O(20)–P(3)–O(8)#3	111.6(4)	O(16)–P(4)–O(19)	107.3(4)
O(3)–P(3)–O(8)#3	107.1(4)	O(18)–P(4)–O(19)	108.8(4)
O(14)–P(3)–O(8)#3	107.2(4)	O(12)–P(4)–O(19)	107.2(4)
O(4)#4–P(5)–O(11)#4	113.1(4)	O(24)–P(6)–O(17)#5	111.0(4)
O(4)#4–P(5)–O(21)	108.9(4)	O(24)–P(6)–O(23)	111.2(4)
O(11)#4–P(5)–O(21)	109.4(4)	O(17)#5–P(6)–O(23)	109.5(4)
O(4)#4–P(5)–O(13)	107.7(4)	O(24)–P(6)–O(22)	105.9(3)
O(11)#4–P(5)–O(13)	107.5(4)	O(17)#5–P(6)–O(22)	109.4(4)
O(21)–P(5)–O(13)	110.1(4)	O(23)–P(6)–O(22)	109.8(4)

Note. Symmetry transformations used to generate equivalent atoms: #1: $x-\frac{1}{2}, -y, z$; #2: $x, y-1, z$; #3: $x+\frac{1}{2}, -y, z$; #4: $x, y+1, z$; #5: $x+\frac{1}{2}, y+1, z$.

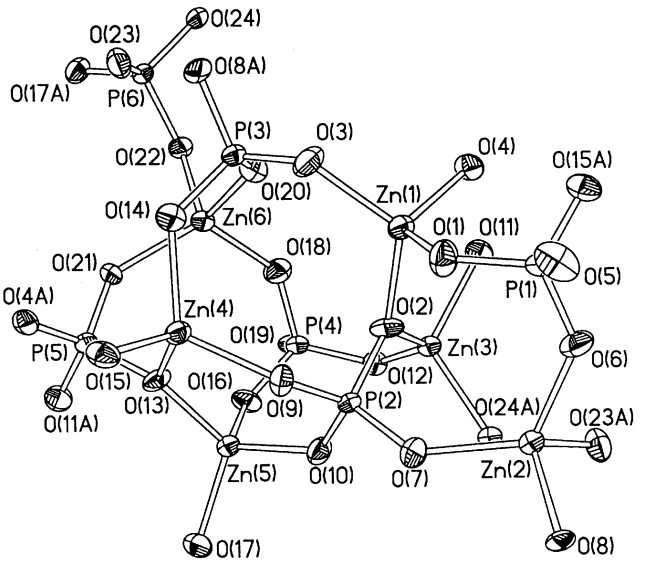

FIG. 1. ORTEP view of the structure of $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$ showing the atom-labeling scheme (50% thermal ellipsoids).

atoms of the amine molecule were placed geometrically and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. Crystal data, and

TABLE 4
Hydrogen Bonds for $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	Angle (D–H···A) (deg)
O(19)–H(19)···O(5)#7	0.82	1.75	2.442(9)	141.6
O(19)–H(19)···N(3)#8	0.82	2.67	3.196(10)	123.7
N(1)–H(1A)···O(1W)#9	0.89	2.11	2.844(10)	139.0
N(1)–H(1A)···O(10)#10	0.89	2.33	2.840(10)	116.6
N(1)–H(1A)···O(7)#10	0.89	2.43	2.979(10)	119.9
N(1)–H(1B)···O(20)#11	0.89	2.14	2.890(10)	141.4
N(1)–H(1C)···O(24)#11	0.89	2.12	3.002(10)	168.9
N(2)–H(2A)···O(3W)#11	0.90	1.81	2.702(11)	169.9
N(2)–H(2B)···O(22)#11	0.90	1.96	2.842(10)	166.8
N(2)–H(2B)···O(24)#11	0.90	2.65	3.306(10)	130.9
N(3)–H(3A)···O(1)#5	0.90	2.01	2.878(10)	162.6
N(3)–H(3A)···O(5)#5	0.90	2.62	3.305(10)	134.0
N(3)–H(3B)···O(12)#10	0.90	1.99	2.862(10)	162.4
N(3)–H(3B)···O(19)#10	0.90	2.54	3.196(10)	130.2
N(4)–H(4A)···O(1W)	0.90	2.25	2.894(11)	128.6
N(4)–H(4A)···O(7)#5	0.90	2.44	3.058(11)	126.2
N(4)–H(4B)···O(9)#5	0.90	2.21	2.808(10)	123.1
N(4)–H(4B)···O(6)#3	0.90	2.54	3.204(11)	131.4
N(5)–H(5A)···O(15)	0.89	2.15	2.875(11)	138.5
N(5)–H(5A)···O(5W)	0.89	2.32	2.830(12)	116.5
N(5)–H(5B)···O(2W)#12	0.89	1.94	2.766(13)	154.4
N(5)–H(5C)···O(14)	0.89	1.98	2.808(11)	154.6

Note. Symmetry transformations used to generate equivalent atoms: #1: $x-\frac{1}{2}, -y, z$; #2: $x, y-1, z$; #3: $x+\frac{1}{2}, -y, z$; #4: $x, y+1, z$; #5: $x+\frac{1}{2}, -y+1, z$; #6: $x-\frac{1}{2}, -y+1, z$; #7: $-x, -y, z-\frac{1}{2}$; #8: $-x+\frac{1}{2}, y-1, z-\frac{1}{2}$; #9: $-x+1, -y+2, z+\frac{1}{2}$; #10: $-x+\frac{1}{2}, y+1, z+\frac{1}{2}$; #11: $-x+1, -y+1, z+\frac{1}{2}$; #12: $-x+\frac{1}{2}, y, z+\frac{1}{2}$.

details of data collection and refinement are given in Table 1.

RESULTS AND DISCUSSION

Characterization

The powder X-ray diffraction pattern for $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$ is entirely consistent with that simulated on the basis of the single-crystal structure. The diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample. The ICP analysis shows that the compound contains 30.8% Zn and 14.4% P, suggesting that the molar ratio of Zn:P = 1:1. The elemental analysis indicates the contents of C, H, and N are 7.78, 3.20, and 5.75% respectively, in good agreement with the values (7.70, 3.13, and 5.61%) based on the single-crystal structure formula $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$.

The thermogravimetic analysis shows that the weight loss of the compound is ca. 28% from 200 to 460°C corresponding to the loss of the guest water molecules (calcd. 11.5%) and the decomposition of the TEPA template (calcd. 15.2%). The structure collapses and converts into an amorphous phase after calcination at 500°C for 2 h. At 700°C, the resulting solid is the β-$Zn_2P_2O_7$ phase (JCPDS: 34-1275) as indicated by powder X-ray diffraction.

Description of the Structure

The final atomic coordinates, selected bond lengths, and bond angles are listed in Tables 2 and 3, respectively.

The asymmetric unit consists of 54 nonhydrogen atoms, 36 of which belong to the framework (6 Zn, 6 P, and 24 O atoms) and 18 to the guest (5Ow, 5N and 8C atoms). Figure 1 shows the connectivity between the Zn–O and P–O tetrahedra. O(2) and O(13) of the framework are three-coordinated with two Zn and one P atoms, and give rise to Zn(1)–O(2)–Zn(3) and Zn(4)–O(13)–Zn(5) linkage in the structure, which has been reported in several zincophosphates. The remaining framework oxygens have normal Zn–O–P links.

The title compound characterizes with a new layered structure based on sheets of ZnO_4, PO_4, and HPO_4 tetrahedra fused together via Zn–O–P and Zn–O–Zn bonds. The six distinct Zn atoms are all tetrahedrally coordinated by O atoms with the Zn–O bond distances in a range of 1.903–2.005 Å [d_{av}(Zn(1)–O) = 1.960 Å, d_{av}(Zn(2)–O) = 1.947 Å, d_{av}(Zn(3)–O) = 1.957 Å, d_{av}(Zn(4)–O) = 1.956 Å, d_{av}(Zn(5)–O) = 1.941 Å, d_{av}(Zn(6)–O) = 1.950 Å]. The O–Zn–O bond angles are in the range of 98.6–126.9° [(O–Zn(1)–O)$_{av}$ = 109.6°, (O–Zn(2)–O)$_{av}$ = 109.4°, (O–Zn(3)–O)$_{av}$ = 109.7°, (O–Zn(4)–O)$_{av}$ = 109.6°, (O–Zn(5)–O)$_{av}$ = 109.5°, (O–Zn(6)–O)$_{av}$ = 109.1°]. Of the six crystallographically distinct P atoms, P(3) and P(6) make four normal

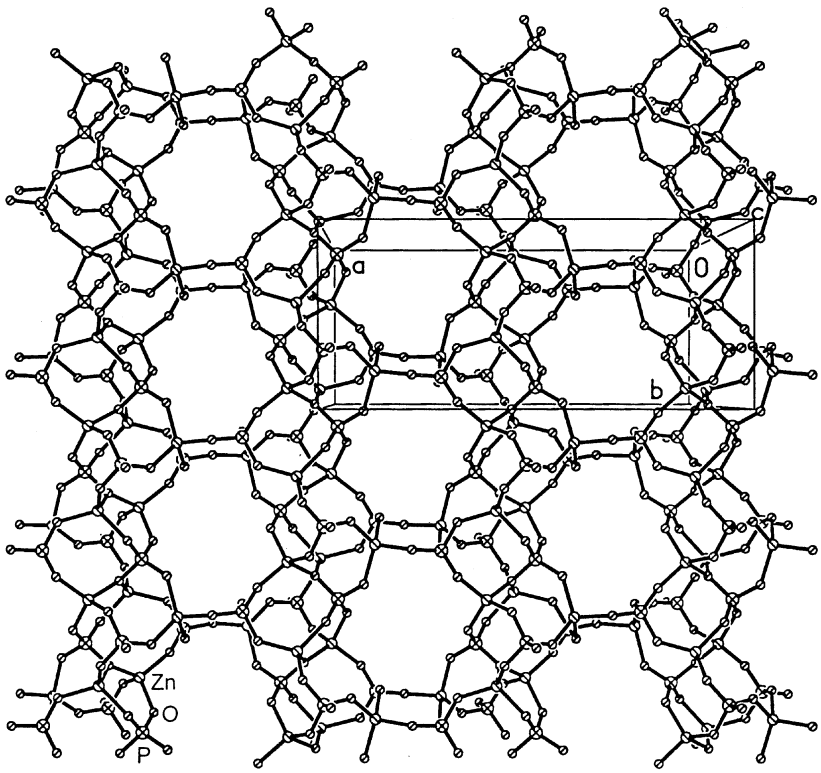

FIG. 2. The inorganic layer structure of $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$ viewed along the [001] direction, showing the eight-membered aperture. The organic cations are omitted for clarity.

P–O–Zn bonds via the bridging oxygen atoms. P(1) and P(4) form three P–O–Zn bonds and possess one terminal P–O bond [a terminal –OH group for P(4) with d(P(4)–O(19)) = 1.547(7) Å, for P(1) with d(P(1)–O(5)) = 1.525(7) Å implying an unsaturated = O]. P(2) and P(5) are bound to five Zn atoms [Zn(1), Zn(2), Zn(3), Zn(4), Zn(5) for P(2), and Zn(1), Zn(3), Zn(4), Zn(5), Zn(6) for P(5)] due to the two triply coordinated oxygen atoms O(2) and O(13). The longest P–O bond in $P(2)O_4$ and $P(5)O_4$ tetrahedra are also associated with three-coordinated oxygen atoms.

The macroanionic inorganic sheet viewed down the [001] direction is shown in Fig. 2. The sheet structure consists of three-, four-, and eight-membered rings that form a network of alternatively linked corner-sharing PO_4, HPO_4 and ZnO_4 tetrahedra. The network can be viewed as constructed from one-dimensional tubes. The basic building unit in the title compound is four-membered ring chains fused together by three-coordinated oxygen atom to form strips along the *b*-axis. The strips with capped $Zn(2)O_4$ and $Zn(6)O_4$ tetrahedra form a one-dimensional tube. These infinite tubes link together to form the layers. Such structural feature has been reported in two new layered zincophosphates (15, 16), $(C_6N_4H_{22})[Zn_6(PO_4)_4(HPO_4)_2]$ and $(C_{10}N_4H_{28})[Zn_6(HPO_4)_2(PO_4)_4]\cdot 2H_2O$. We note that the inorganic layers of $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$ are somewhat similar to those in $(C_6N_4H_{22})[Zn_6(PO_4)_4(HPO_4)_2]$. The latter crystallized in the monoclinic space group $P2_1/c$. The guest molecules are one TEPA and five water, and there are five PO_4 groups and one HPO_4 group in the asymmetric unit of $Zn_6(PO_4)_5(HPO_4)\cdot C_8N_5H_{28}\cdot 5H_2O$.

The inorganic sheets are anionic and the empirical formula of the layer is $[Zn_6(PO_4)_5(HPO_4)]^{5-}$, the negative charge is achieved by incorporation of quintuply protonated TEPA. The TEPA cations occupy the space between the layers, and one $H_3N(1)$ group of the organic cation inserts into the eight-membered ring aperture. Although the water molecule $H_2O(1w)$ is also located within the eight-membered ring aperture, the other four water molecules occupy the interlayer spaces. The inorganic–organic layers are shown in Fig. 3. The layered structure is stabilized by the strong hydrogen bonds between the P(4)–O(19)H and the terminal oxygen atom O(5) of the adjacent layer with the distance O(19)–H(19) $\cdots$ O(5) = 2.442(9) Å. The quintuply protonated molecule TEPA also participates in hydrogen bonding with the framework contributing to the additional structural stability of this compound. Detailed information about the hydrogen bonding is summarized in Table 4.

In conclusion, a new zinc phosphate with a layered structure has been synthesized and characterized. Its layered

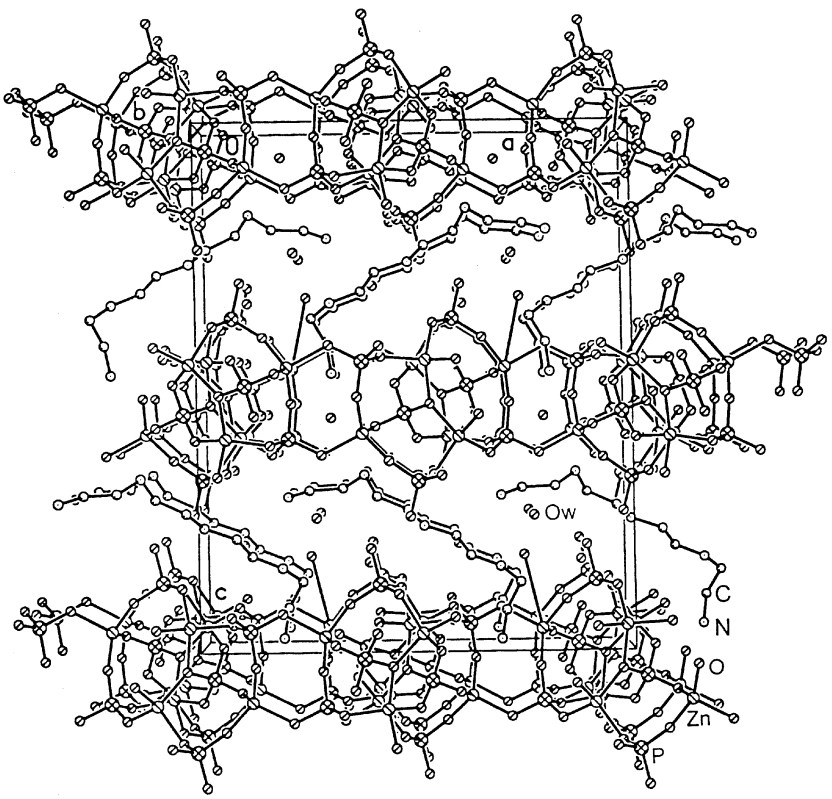

FIG. 3. The stacking of the layers with the intercalated organic cations and the water molecules viewed along the [010] direction, H atoms and H-bonds are not shown for clarity.

structure consists of interesting one-dimensional tubes. Further synthesis of new open-framework zincophosphates in the presence of a pentamine is in progress.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the State Basic Research Project of China (G200077507), the National Natural Science Foundation of China (20141004), and the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

REFERENCES

1. T. E. Gier and G. D. Stucky, *Nature* **349,** 508 (1991).
2. S. Neeraj, S. Natarajan, and C. N. R. Rao, *J. Solid State Chem.* **150,** 417 (2000).
3. C. N. R. Rao, S. Natarajan, and S. Neeraj, *J. Am. Chem. Soc.* **122,** 2810 (2000).
4. C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, and A. A. Ayi, *Acc. Chem. Res.* **34**(1), 80 (2001) and references therein.
5. W. Liu, Y. Liu, Z. Shi, and W. Pang, *J. Mater. Chem.* **10,** 1451 (2000) and references therein.
6. W. T. A. Harrison, J. T. Vaughey, L. L. Dussack, A. J. Jacobson, T. E. Martin, and G. D. Stucky, *J. Solid State Chem.* **114,** 151 (1995).
7. S. Neeraj, S. Natarajan, and C. N. R. Rao, *Chem. Commun.* 165 (1999).
8. G. Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.* **121,** 8389 (1999).
9. J. Zhu, X. H. Bu, P. Y. Feng, and G. D. Stucky, *J. Am. Chem. Soc.* **122,** 11 563 (2000).
10. J. A. Rodgers and W. T. A. Harrison, *J. Mater. Chem.* **10,** 2853 (2000).
11. A. Choudhury, S. Natarajan, and C. N. R. Rao, *Inorg. Chem.* **39,** 4295 (2000).
12. W. T. A. Harrison and M. L. F. Philips, *Chem. Mater.* **9,** 1837 (1997).
13. S. Neeraj, S. Natarajan, and C. N. R. Rao, *Chem. Mater.* **11,** 1390 (1999).
14. S. Neeraj, S. Natarajan, and C. N. R. Rao, *New J. Chem.* **23,** 303 (1999).
15. A. Choudhury, S. Natarajan, and C. N. R. Rao, *J. Solid State Chem.* **157,** 110 (2001).
16. Y. Chiang, H. Kao, and K. Lii, *J. Solid State Chem.* **162,** 168 (2001).
17. S. Neeraj and S. Natarajan, *J. Phys. Chem. Solids* **62,** 1499 (2001).
18. Y. Zhao, G. Zhu, W. Liu, Y. Zou, and W. Pang, *Chem. Commun.* 2219 (1999).
19. Y. Zhao, G. Zhu, X. Jiao, W. Liu, and W. Pang, *J. Mater. Chem.* **10,** 463 (2000).
20. Y. Liu, Z. Shi, L. Zhang, Y. Fu, J. Chen, B. Li, J. Hua, and W. Pang, *Chem. Mater.* **13,** 2017 (2001).
21. Y. Guo, Z. Shi, J. Yu, J. Wang, Y. Liu, N. Bai, and W. Pang, *Chem. Mater.* **13,** 203 (2001).
22. Y. Liu, L. Zhang, Z. Shi, H. Yuan, and W. Pang, *J. Solid State Chem.* **158,** 68 (2001).
23. P. Zhang, Y. Wang, G. Zhu, Z. Shi, Y. Liu, H. Yuan, and W. Pang, *J. Solid State Chem.* **154,** 368 (2000).
24. "Software packages SMART and SAINT." Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
25. G. M. Sheldrick, "SHELXTL-NT." Version 5.1, Bruker AXS Inc., Madison, WI, 1997.