



ACADEMIC  
PRESS

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Journal of Solid State Chemistry 177 (2004) 80–88

JOURNAL OF  
SOLID STATE  
CHEMISTRY

<http://elsevier.com/locate/jssc>

# Hydrothermal synthesis and structural characterization of two organically templated zincophosphites with three-dimensional frameworks, $(C_6H_{14}N_2) \cdot [Zn_3(HPO_3)_4]$ and $(C_4H_{12}N_2) \cdot [Zn_3(HPO_3)_4]$

Lei Wang, Zhan Shi, Wensheng Fu, Guanghua Li, Dong Zhang, Wenjun Dong, Zhimin Dai, Xiaobo Chen, and Shouhua Feng\*

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

Received 12 March 2003; received in revised form 9 May 2003; accepted 30 May 2003

## Abstract

Two organically templated zincophosphites,  $(C_6H_{14}N_2) \cdot [Zn_3(HPO_3)_4]$  and  $(C_4H_{12}N_2) \cdot [Zn_3(HPO_3)_4]$  have been prepared under hydrothermal conditions and characterized by single-crystal X-ray diffraction.  $(C_6H_{14}N_2) \cdot [Zn_3(HPO_3)_4]$  crystallizes in the triclinic space group  $P\bar{1}$ , with cell parameters,  $a = 9.363(4) \text{ \AA}$ ,  $b = 10.051(4) \text{ \AA}$ ,  $c = 10.051(4) \text{ \AA}$ ,  $\alpha = 85.777(13)^\circ$ ,  $\beta = 82.091(9)^\circ$ , and  $\gamma = 79.783(9)^\circ$ .  $(C_4H_{12}N_2) \cdot [Zn_3(HPO_3)_4]$  crystallizes in the monoclinic space group  $P2_1/c$ , with cell parameters,  $a = 9.9512(3) \text{ \AA}$ ,  $b = 10.1508(3) \text{ \AA}$ ,  $c = 17.8105(5) \text{ \AA}$ , and  $\beta = 95.6510(10)^\circ$ . Although the two structures are different, they have the same anionic framework compositions of  $[Zn_3(HPO_3)_4]^{2-}$ . Their frameworks are built up from strictly alternating  $ZnO_4$  tetrahedra and  $HPO_3$  pseudo pyramids by sharing vertexes. There exist channels with an eight-membered ring window along the  $a$ - and  $c$ -axis. Powder X-ray diffraction, IR spectroscopy,  $^{31}P$  MAS solid-state NMR, thermogravimetric and differential thermal analyses were also carried out.

© 2003 Elsevier Inc. All rights reserved.

**Keywords:** Hydrothermal synthesis; Organically templated; Zincophosphites; Structural characterization

## 1. Introduction

Since the discovery of microporous aluminophosphates  $AlPO_4-n$  [1] in 1982, studies on the synthesis of open-framework metal phosphates have been significantly developed, for their intensive applications in the fields of catalysis, adsorbent, ion exchange, and gas separation [2–5]. Most synthetic studies were focused on the substitution of metals for metals for years and most recently, the replacement of phosphate by phosphite was initiated in a different way [6–8]. Some of the organically templated and inorganic–organic hybrid phosphites have been synthesized [9–13], but with respect to the large numbers of metal phosphates, the synthetic studies on

the organically templated metal phosphites were less reported. The known synthesized compounds, such as  $(C_2H_{10}N_2) \cdot [Cr_3(HPO_3)_3F_3]$  [8],  $(C_2H_{10}N_2) \cdot [Mn_3(HPO_3)_4]$  [9],  $(CN_3H_6)_2 \cdot Zn(HPO_3)_2$  [10],  $(C_2H_{10}N_2)_{0.5} \cdot [V(HPO_3)_2]$  and  $(C_2H_{10}N_2)_{0.5} \cdot [Fe(HPO_3)_2]$  [11], showed novel structures. Based on our previous work on the syntheses of inorganic–organic hybrid phosphates [14–16] and organically templated phosphites [17–19], we extended our research into the investigation of the role of templates in a hydrothermal system. In this paper, we report the synthesis and structural characterization of two novel organically templated zincophosphites  $(C_6H_{14}N_2) \cdot [Zn_3(HPO_3)_4]$  1 and  $(C_4H_{12}N_2) \cdot [Zn_3(HPO_3)_4]$  2. Although the two compounds have different crystal structures due to the utility of different templates, they showed similar inorganic framework compositions of  $[Zn_3(HPO_3)_4]^{2-}$  and framework structures.

\*Corresponding author. Fax: +86-431-5671974.

E-mail address: [shfeng@mail.jlu.edu.cn](mailto:shfeng@mail.jlu.edu.cn) (S. Feng).

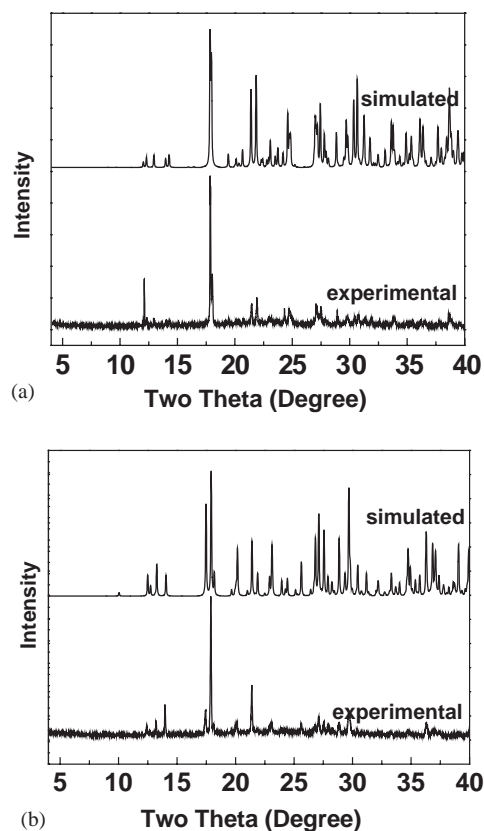


Fig. 1. Simulated and experimental powder X-ray diffraction patterns of compounds 1 (a) and 2 (b).

Table 1  
Crystal data and structure refinement parameters for 1 and 2

	1	2
Empirical formula	$C_6H_{18}N_2O_{12}P_4Zn_3$	$C_4H_{16}N_2O_{12}P_4Zn_3$
Formula weight	630.21	604.18
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	$a = 9.363(4)$ Å $b = 10.051(4)$ Å $c = 10.051(4)$ Å $\alpha = 85.777(13)^\circ$ $\beta = 82.091(9)^\circ$ $\gamma = 79.783(9)^\circ$	$a = 9.9512(3)$ Å $b = 10.1508(3)$ Å $c = 17.8105(5)$ Å $\beta = 95.6510(10)^\circ$
Volume	$920.8(6)$ Å <sup>3</sup>	$1790.34(9)$ Å <sup>3</sup>
Z	2	4
Density (calculated)	$2.273$ mg/m <sup>3</sup>	$2.241$ mg/m <sup>3</sup>
Absorption coefficient	$4.285$ mm <sup>-1</sup>	$4.403$ mm <sup>-1</sup>
$F(000)$	628	1200
Crystal size	$0.35 \times 0.27 \times 0.23$ mm	$0.50 \times 0.30 \times 0.25$ mm
$\theta$ range for data collection	$2.05$ – $23.59^\circ$	$2.06$ – $23.26^\circ$
Limiting indices	$-10 \leq h \leq 9$ , $-11 \leq k \leq 9$ , $-11 \leq l \leq 10$	$-11 \leq h \leq 11$ , $-5 \leq k \leq 11$ , $-19 \leq l \leq 19$
Reflections collected/unique	4455/2647 [ $R(\text{int}) = 0.0404$ ]	8411/2558 [ $R(\text{int}) = 0.0530$ ]
Completeness to $\theta = 23.27^\circ$	95.5%	99.7%
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	2647/0/316	2558/0/247
Goodness-of-fit on $F^2$	1.051	1.051
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0287$ , $wR_2 = 0.0752$	$R_1 = 0.0249$ , $wR_2 = 0.0643$
$R$ indices (all data)	$R_1 = 0.0338$ , $wR_2 = 0.0770$	$R_1 = 0.0298$ , $wR_2 = 0.0661$
Largest diff. peak and hole	$0.592$ and $-0.445$ e Å <sup>-3</sup>	$0.474$ and $-0.496$ e Å <sup>-3</sup>

Note:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^2 \}^{1/2}$ .

## 2. Experimental

### 2.1. Synthesis and characterization

Compounds 1 and 2 were hydrothermally synthesized from reaction mixtures of  $Zn(AC)_2 \cdot 2H_2O$ ,  $H_3PO_3$ , and triethylenediamine hexahydrate ( $C_6H_{12}N_2 \cdot 6H_2O$ ) for 1 and piperazine hexahydrate ( $C_4H_{10}N_2 \cdot 6H_2O$ ) for 2, and distilled water in the molar ratios 1:5:4:222 and 1:5:3:222, respectively. A typical synthetic procedure began with mixing  $Zn(AC)_2 \cdot 2H_2O$  (0.219 g),  $H_3PO_3$  (0.410 g),  $C_6H_{12}N_2 \cdot 6H_2O$  (0.881 g) or  $C_4H_{10}N_2 \cdot 6H_2O$  (0.582 g), and 2 mL distilled water to form a reaction mixture. The mixture was sealed in a 23 mL capacity of Teflon-lined stainless-steel autoclave under autogenous pressure, and heated at  $160^\circ C$  for 120 h. The products were washed with distilled water and dried at room temperature.

The powder X-ray diffraction (XRD) patterns were recorded (Bragg–Brentano) on a Siemens D5005 diffractometer by using  $CuK\alpha$  radiation ( $\lambda = 1.5418$  Å) with a graphite monochromator. The step size was  $0.02^\circ$  and the count time was 4 s. The powder X-ray diffraction pattern of the two compounds are in good agreement with the simulated ones based on the data of the single-crystal structures (Fig. 1), suggesting the purity of synthesized samples.

The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The inductively couple plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The ICP analysis and elemental analyses were also consistent with the theoretical values. Calcd for 1: Zn, 31.12; P, 19.65; C, 11.42; H, 2.87; N, 4.44%. Found: Zn, 31.07; P, 19.70; C, 11.48; H, 2.83; N, 4.42%. Calcd for 2: Zn, 32.46; P, 20.50; C, 7.95; H, 2.67; N, 4.64%. Found: Zn, 32.40; P, 20.53; C, 7.99; H, 2.71; N, 4.60%.

The infrared (IR) spectrum was recorded within the 400–4000  $\text{cm}^{-1}$  region on a Nicolet Impact 410FTIR spectrometer using KBr pellets. IR spectra of the compounds showed the characteristic bands of the organic amine cations at 1619, 1463, and 1385  $\text{cm}^{-1}$  for 1; and at 1481, 1448, and 1392  $\text{cm}^{-1}$  for 2. The intense bands in the range 1158–992  $\text{cm}^{-1}$  for 1 and 1104–979  $\text{cm}^{-1}$  for 2 were attributed to the asymmetric and symmetric stretching vibrations of the  $\text{PO}_3$  groups. The symmetric and asymmetric  $\text{PO}_3$  deformation can also be observed at approximately 615, 590, 473, and 433  $\text{cm}^{-1}$  for 1, and 605, 528, 464 and 441  $\text{cm}^{-1}$  for 2. A weak band at around 2487  $\text{cm}^{-1}$  for 1 and 2465  $\text{cm}^{-1}$  for 2, indicated the presence of the H–P bond of the phosphite group.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on a Perkin-Elmer DTA 1700 differential thermal analyzer and a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10  $^\circ\text{C min}^{-1}$ . The  $^{31}\text{P}$  MAS-NMR spectra of the compounds were collected on a Varian Unity-400 NMR spectrometer.

## 2.2. Determination of crystal structure

Crystals with dimensions of 0.35  $\times$  0.27  $\times$  0.23 mm for 1 and 0.50  $\times$  0.30  $\times$  0.25 mm for 2 were selected for X-ray diffraction analyses, respectively. The intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at a temperature of  $298 \pm 2 \text{ K}$ . A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30  $^\circ$  in  $\omega$  and an exposure time of 30 s/frame. Datum processing was accomplished with the SAINT processing program [20]. The structures were solved by Direct Methods using the SHELXTL crystallographic software package [21]. The zinc and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the difference Fourier maps. The hydrogen atoms residing on the amine molecules were placed geometrically. The hydrogen atoms residing on the phosphorus were located by Fourier maps. The total number of measured reflections and observed unique reflections were 4455 and 2647 for 1, for 2 were 8411 and 2558, respectively. For compound 1, intensity data of 2647

independent reflections ( $-10 \leq h \leq 9$ ,  $-11 \leq k \leq 9$ ,  $-11 \leq l \leq 10$ ) were collected. For compound 2, intensity data of 2558 independent reflections ( $-11 \leq h \leq 11$ ,  $-5 \leq k \leq 11$ ,  $-19 \leq l \leq 19$ ) were collected in the  $\omega$  scan mode. Crystallographic data for two compounds are listed in Table 1.

## 3. Results and discussion

### 3.1. Crystal structure of $(\text{C}_6\text{H}_{14}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot 1$

The asymmetric unit of 1 is shown in Fig. 2(a). It contains 27 unique non-hydrogen atoms, 19 of which belong to the framework and 8 to the amine. There are three crystallographically distinct Zn atoms and four crystallographically distinct P atoms in the asymmetric unit (Table 2). Selected bond lengths and angles of 1 are listed in Table 3. All Zn atoms adopt tetrahedral

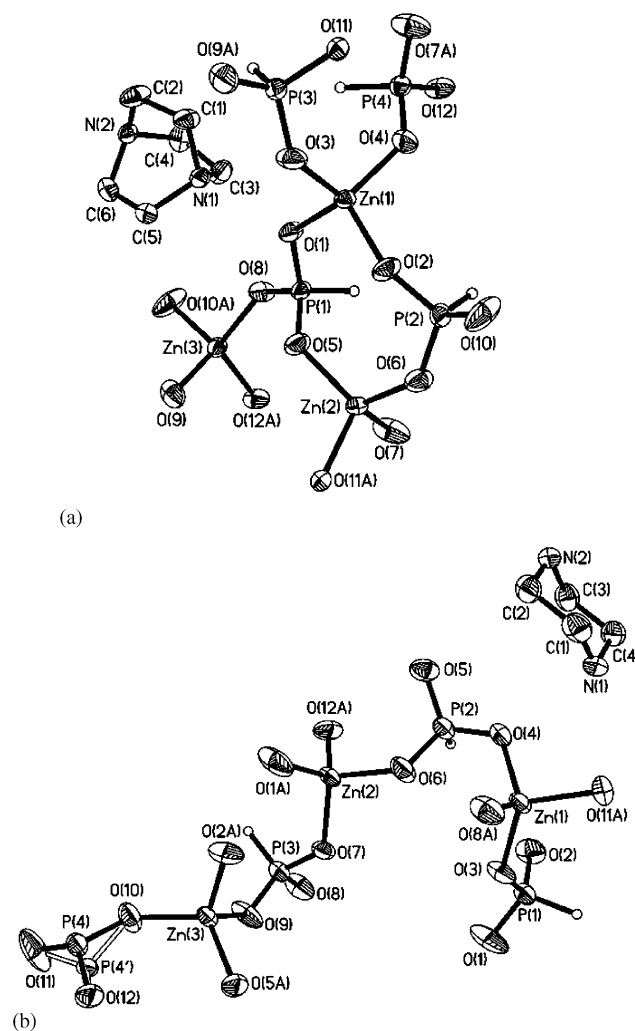


Fig. 2. ORTEP drawing of the asymmetric unit of 1 (a) and 2 (b) (50% thermal ellipsoids).

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 1 and 2

Atom	<i>x</i>	<i>y</i>	<i>Z</i>	<i>U</i> (eq) <sup>a</sup>
<i>Compound 1</i>				
Zn(1)	3819(1)	2772(1)	2461(1)	21(1)
Zn(2)	8834(1)	2324(1)	2658(1)	22(1)
Zn(3)	7621(1)	7135(1)	2729(1)	26(1)
P(1)	6048(1)	4547(1)	2995(1)	23(1)
P(2)	6551(1)	331(1)	3038(1)	26(1)
P(3)	1380(1)	3112(1)	494(1)	23(1)
P(4)	976(1)	3089(1)	4577(1)	25(1)
O(1)	4578(3)	4472(3)	2511(3)	30(1)
O(2)	5480(3)	1340(3)	2323(3)	35(1)
O(3)	2931(3)	2886(4)	811(3)	38(1)
O(4)	2409(3)	2319(3)	3918(3)	34(1)
O(5)	7352(3)	3796(3)	2142(3)	34(1)
O(6)	8101(3)	630(3)	2766(4)	44(1)
O(7)	9633(3)	2585(4)	4251(3)	52(1)
O(8)	6119(3)	6017(3)	3139(3)	32(1)
O(9)	8741(3)	6804(4)	972(3)	44(1)
O(10)	6469(4)	−1070(3)	2684(5)	61(1)
O(11)	522(3)	2053(3)	1240(3)	25(1)
O(12)	905(3)	3122(3)	6083(3)	36(1)
N(1)	3168(4)	7111(4)	2000(4)	25(1)
N(2)	1925(4)	9498(4)	1711(4)	24(1)
C(1)	1727(5)	7111(5)	1519(6)	35(1)
C(2)	1073(6)	8575(5)	1160(6)	39(1)
C(3)	2946(6)	7761(5)	3296(5)	35(1)
C(4)	1992(7)	9154(5)	3165(5)	36(1)
C(5)	4085(5)	7846(5)	946(5)	30(1)
C(6)	3437(5)	9341(5)	969(5)	34(1)
<i>Compound 2</i>				
Zn(1)	7803(1)	2090(1)	6372(1)	32(1)
Zn(2)	2990(1)	1979(1)	6866(1)	29(1)
Zn(3)	2446(1)	2395(1)	9391(1)	27(1)
P(1)	7930(1)	−729(1)	7075(1)	29(1)
P(2)	4916(1)	1849(1)	5637(1)	32(1)
P(3)	2154(1)	172(1)	8161(1)	29(1)
P(4)	563(2)	3595(3)	10528(1)	31(1)
P(4')	601(2)	2780(2)	10702(1)	27(1)
O(1)	7486(4)	−1322(3)	7782(2)	65(1)
O(2)	7253(3)	−1303(3)	6361(1)	49(1)
O(3)	7725(3)	746(2)	7139(1)	39(1)
O(4)	6407(3)	2000(3)	5519(1)	44(1)
O(5)	4055(3)	2694(3)	5086(2)	43(1)
O(6)	4707(3)	2119(3)	6455(1)	46(1)
O(7)	3256(2)	748(2)	7714(1)	33(1)
O(8)	2073(3)	−1291(2)	8077(1)	51(1)
O(9)	2297(3)	620(2)	8972(1)	51(1)
O(10)	787(3)	2703(3)	9842(2)	53(1)
O(11)	−692(3)	3181(4)	10807(2)	80(1)
O(12)	1757(3)	3743(3)	11074(1)	44(1)
N(1)	7922(3)	2702(3)	4347(2)	41(1)
N(2)	5902(3)	3714(3)	3255(2)	36(1)
C(1)	7680(4)	4145(4)	4281(2)	45(1)
C(2)	6225(4)	4399(4)	3990(2)	41(1)
C(3)	6125(4)	2267(4)	3331(2)	41(1)
C(4)	7572(4)	2007(4)	3618(2)	41(1)

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

Table 3  
Selected bond lengths (Å) and angles (deg) for 1

Zn(1)–O(1)	1.970(3)	P(1)–O(8)	1.509(3)
Zn(1)–O(2)	1.920(3)	P(1)–H(1)	1.32(4)
Zn(1)–O(3)	1.942(3)	P(2)–O(2)	1.510(3)
Zn(1)–O(4)	1.918(3)	P(2)–O(6)	1.518(3)
Zn(2)–O(5)	1.934(3)	P(2)–O(10)	1.495(4)
Zn(2)–O(6)	1.936(3)	P(2)–H(2)	1.33(5)
Zn(2)–O(7)	1.911(3)	P(3)–O(3)	1.504(3)
Zn(2)–O(11)#1	1.972(3)	P(3)–O(9)#4	1.489(3)
Zn(3)–O(8)	1.935(3)	P(3)–O(11)	1.536(3)
Zn(3)–O(9)	1.945(3)	P(3)–H(3)	1.30(4)
Zn(3)–O(10)#3	1.931(3)	P(4)–O(4)	1.517(3)
Zn(3)–O(12)#2	1.918(3)	P(4)–O(7)#5	1.520(3)
P(1)–O(1)	1.537(3)	P(4)–O(12)	1.508(3)
P(1)–O(5)	1.509(3)	P(4)–H(4)	1.43(5)
O(4)–Zn(1)–O(2)	109.02(13)	O(5)–P(1)–H(1)	104.5(18)
O(4)–Zn(1)–O(3)	107.80(13)	O(8)–P(1)–H(1)	107.7(19)
O(2)–Zn(1)–O(3)	107.93(14)	O(1)–P(1)–H(1)	108.6(17)
O(4)–Zn(1)–O(1)	118.18(14)	O(10)–P(2)–O(2)	109.54(19)
O(2)–Zn(1)–O(1)	106.90(12)	O(10)–P(2)–O(6)	112.1(2)
O(3)–Zn(1)–O(1)	106.61(14)	O(2)–P(2)–O(6)	112.79(18)
O(7)–Zn(2)–O(5)	114.68(16)	O(10)–P(2)–H(2)	109.8(19)
O(7)–Zn(2)–O(6)	111.94(16)	O(2)–P(2)–H(2)	103.9(18)
O(5)–Zn(2)–O(6)	109.95(13)	O(6)–P(2)–H(2)	108.4(18)
O(7)–Zn(2)–O(11)#1	105.28(13)	O(9)#4–P(3)–O(3)	113.69(19)
O(5)–Zn(2)–O(11)#1	110.89(12)	O(9)#4–P(3)–O(11)	111.08(18)
O(6)–Zn(2)–O(11)#1	103.42(14)	O(3)–P(3)–O(11)	111.59(17)
O(12)#2–Zn(3)–O(10)#3	114.64(15)	O(9)#4–P(3)–H(3)	106.2(18)
O(12)#2–Zn(3)–O(8)	116.02(13)	O(3)–P(3)–H(3)	106.1(17)
O(10)#3–Zn(3)–O(8)	101.70(14)	O(11)–P(3)–H(3)	107.7(17)
O(12)#2–Zn(3)–O(9)	103.38(13)	O(12)–P(4)–O(4)	113.25(18)
O(10)#3–Zn(3)–O(9)	109.11(18)	O(12)–P(4)–O(7)#5	109.00(18)
O(8)–Zn(3)–O(9)	112.14(14)	O(4)–P(4)–O(7)#5	113.7(2)
O(5)–P(1)–O(8)	114.16(18)	O(12)–P(4)–H(4)	111(2)
O(5)–P(1)–O(1)	113.54(19)	O(4)–P(4)–H(4)	102(2)
O(8)–P(1)–O(1)	108.09(16)	O(7)#5–P(4)–H(4)	107(2)
P(1)–O(1)–Zn(1)	123.60(16)	P(4)#1–O(7)–Zn(2)	136.3(2)
P(2)–O(2)–Zn(1)	147.8(2)	P(1)–O(8)–Zn(3)	135.07(19)
P(3)–O(3)–Zn(1)	134.2(2)	P(3)#4–O(9)–Zn(3)	143.2(2)
P(4)–O(4)–Zn(1)	133.06(19)	P(2)–O(10)–Zn(3)#6	139.2(2)
P(1)–O(5)–Zn(2)	129.3(2)	P(3)–O(11)–Zn(2)#5	128.62(18)
P(2)–O(6)–Zn(2)	131.04(19)	P(4)–O(12)–Zn(3)#2	132.90(19)

Symmetry transformations used to generate equivalent atoms: #1  $x+1, y, z$ ; #2  $-x+1, -y+1, -z+1$ ; #3  $x, y+1, z$ ; #4  $-x+1, -y+1, -z$ ; #5  $x-1, y, z$ ; #6  $x, y-1, z$ .

coordinations with typical geometrical parameters [ $d_{\text{av}}(\text{Zn1-O})=1.938(3)\text{\AA}$ ,  $d_{\text{av}}(\text{Zn2-O})=1.938(3)\text{\AA}$ ,  $d_{\text{av}}(\text{Zn3-O})=1.932(3)\text{\AA}$ . The O–Zn–O angles are in the range  $103.42^\circ$ – $118.18^\circ$ . Each Zn atom links four adjacent P atoms via bridging oxygen. Thus, there are no terminal Zn–O and Zn–O–Zn bonds. As expected, all P atoms form the centers of the pseudo pyramid with hydrogen phosphite groups  $d_{\text{av}}(\text{P1-O})=1.518(3)\text{\AA}$ ,  $d_{\text{av}}(\text{P2-O})=1.508(3)\text{\AA}$ ,  $d_{\text{av}}(\text{P3-O})=1.510(3)\text{\AA}$ , and  $d_{\text{av}}(\text{P4-O})=1.515(3)\text{\AA}$ . The O–P–O bond angles are in the range  $108.9^\circ$ – $114.16^\circ$ . Each of the four distinct P atoms makes three bonds to nearby Zn atoms via bridging oxygen. Thus, there are no terminal P–O bonds.

Structure of 1 is built from strictly alternating  $\text{ZnO}_4$  tetrahedra and  $\text{HPO}_3$  pseudo pyramids that are linked through their vertices giving rise to the three-dimensional architecture (Fig. 3(a)). There are four-membered ring chains along the  $a$ -axis (Fig. 3(b)). The four-membered ring chain is made of Zn(1), Zn(2), P(1), P(2), P(3), and P(4) which are connected to each other by sharing vertices as Zn–O–P. The oxygen neighbors of both Zn(1) and Zn(2) are all connected within the four-membered ring chains, but P(1), P(2), P(3), and P(4) only have two of the three possible connections within

the chains. The third connection of the four P atoms is linked with the neighboring Zn(3) atom by P–O–Zn bonds, leading to the three-dimensional architecture with the channels of eight-membered ring window along the  $a$ -axis. Thus, the three-dimensional structure can be viewed as constructed by  $\text{Zn(3)O}_4$  tetrahedra linking four infinite four-membered ring chains. There are four types of intersecting eight-membered channels built up from four  $\text{ZnO}_4$  and four  $\text{HPO}_3$  units along the  $a$ -axis. The eight-membered rings of the structure are actually the joining of two four-membered rings (e.g., Zn1–P3–

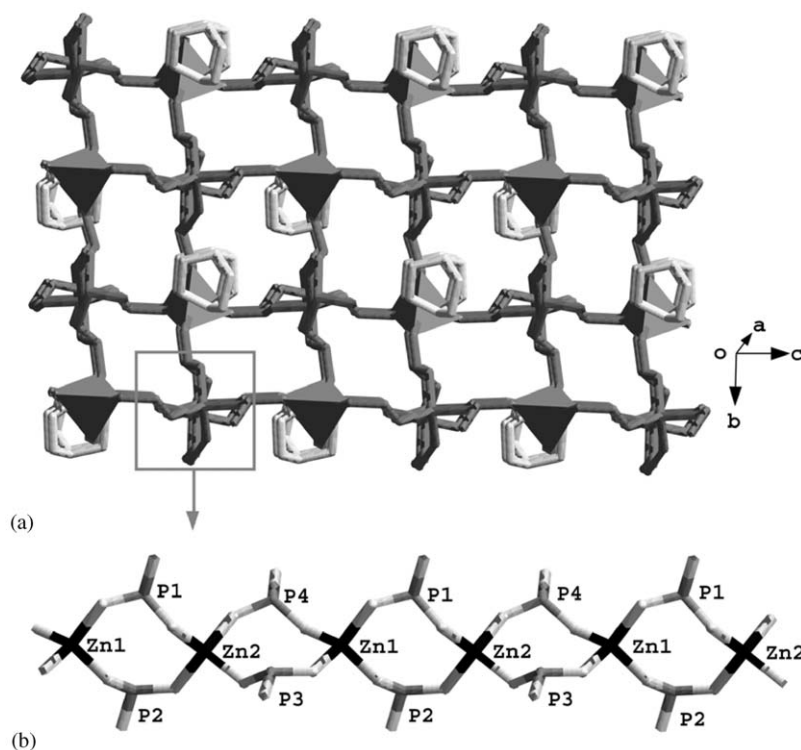


Fig. 3. (a) Framework structure of 1 viewed along the  $a$ -axis and (b) the infinite four-membered ring chains in the framework along the  $a$ -axis. All H atoms are omitted for clarity and these dark polyhedra represent the  $\text{Zn(3)O}_4$  tetrahedra.

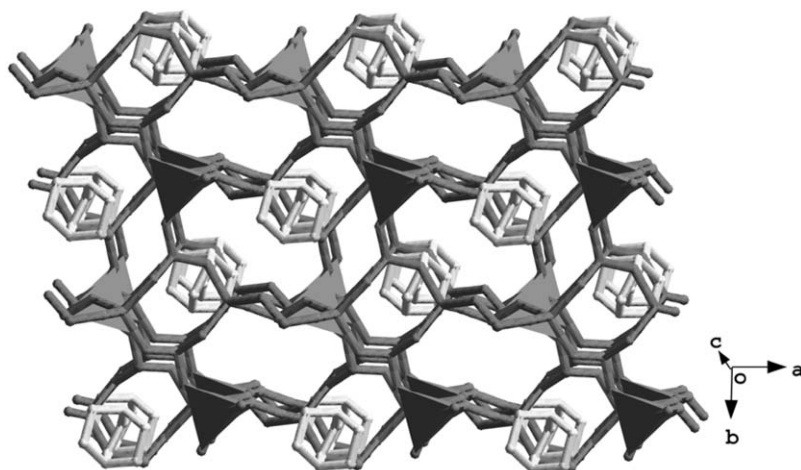


Fig. 4. Framework structure of 1 along the  $c$ -axis. All H atoms are omitted for clarity and these dark polyhedra represent the  $\text{Zn(3)O}_4$  tetrahedra.

Zn2–P4) by two P1–Zn3–P2 links. Along the *c*-axis, the connectivity between ZnO<sub>4</sub> tetrahedra and HPO<sub>3</sub> pseudo pyramids result in other distorted eight-membered channels (Fig. 4). There is a spherical cage

formed by six Zn(3)O<sub>4</sub> tetrahedra and four four-membered ring chains. The protonated amine molecules sit in the middle of the cage and interact with the framework via hydrogen bonds, see Table 4,

Table 4  
Hydrogen bonds for 1 and 2

D–H···A	d(D–H) (Å)	d(H···A) (Å)	D(D···A) (Å)	Angle (D–H···A) (deg)
1				
N(1)–H(1C)···O(1)	0.93(5)	1.86(5)	2.790(4)	170(4)
2				
N(1)–H(1A)···O(4)	0.90	1.90	2.785(4)	168.8
N(1)–H(1B)···O(10)#1	0.90	2.03	2.929(4)	178.0
N(1)–H(1B)···O(11)#1	0.90	2.44	2.959(4)	116.6
N(2)–H(2A)···O(7)#2	0.90	1.87	2.768(3)	177.7
N(2)–H(2B)···O(3)#2	0.90	2.00	2.874(4)	164.6
N(2)–H(2B)···O(1)#2	0.90	2.57	3.235(4)	131.6

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

Table 5  
Selected bond lengths (Å) and angles (deg) for 2

Zn(1)–O(3)	1.937(2)	P(1)–O(3)	1.517(2)
Zn(1)–O(4)	1.958(3)	P(1)–H(1)	1.36(3)
Zn(1)–O(8)#2	1.905(3)	P(2)–O(5)	1.506(3)
Zn(1)–O(11)#1	1.905(3)	P(2)–O(6)	1.517(3)
Zn(2)–O(1)#2	1.910(3)	P(2)–O(4)	1.527(3)
Zn(2)–O(6)	1.929(3)	P(2)–H(2)	1.27(3)
Zn(2)–O(7)	1.957(2)	P(3)–O(7)	1.533(2)
Zn(2)–O(12)#3	1.922(2)	P(3)–O(8)	1.494(3)
Zn(3)–O(2)#2	1.926(2)	P(3)–O(9)	1.508(3)
Zn(3)–O(5)#4	1.927(3)	P(3)–H(3)	1.33(3)
Zn(3)–O(9)	1.950(2)	P(4)–O(10)	1.554(3)
Zn(3)–O(10)	1.931(3)	P(4)–O(11)	1.452(4)
P(1)–O(1)	1.501(3)	P(4)–O(12)	1.467(3)
P(1)–O(2)	1.498(3)		
O(11)#1–Zn(1)–O(3)	111.04(13)	O(10)–Zn(3)–O(9)	105.84(13)
O(8)#2–Zn(1)–O(3)	104.42(10)	O(2)–P(1)–O(3)	113.25(15)
O(11)#1–Zn(1)–O(4)	96.72(13)	O(1)–P(1)–O(3)	106.29(15)
O(11)#1–Zn(1)–O(8)#2	112.41(16)	O(2)–P(1)–H(1)	106.5(14)
O(8)#2–Zn(1)–O(4)	116.32(12)	O(1)–P(1)–H(1)	109.0(14)
O(3)–Zn(1)–O(4)	116.10(11)	O(3)–P(1)–H(1)	107.2(14)
O(1)#2–Zn(2)–O(12)#3	115.07(13)	O(5)–P(2)–O(6)	113.58(16)
O(1)#2–Zn(2)–O(6)	108.41(13)	O(5)–P(2)–O(4)	110.55(15)
O(12)#3–Zn(2)–O(6)	105.92(11)	O(6)–P(2)–O(4)	109.93(15)
O(1)#2–Zn(2)–O(7)	110.03(11)	O(5)–P(2)–H(2)	113.8(14)
O(12)#3–Zn(2)–O(7)	110.53(10)	O(6)–P(2)–H(2)	103.0(15)
O(6)–Zn(2)–O(7)	106.41(11)	O(4)–P(2)–H(2)	105.5(14)
O(2)#2–Zn(3)–O(5)#4	107.62(12)	O(7)–P(3)–H(3)	104.4(14)
O(2)#2–Zn(3)–O(10)	112.06(13)	O(11)–P(4)–O(10)	107.2(2)
O(5)#4–Zn(3)–O(10)	115.55(11)	O(12)–P(4)–O(10)	114.27(19)
O(2)#2–Zn(3)–O(9)	112.25(11)	O(11)–P(4)–O(12)	118.1(2)
O(5)#4–Zn(3)–O(9)	103.26(11)	P(3)–O(7)–Zn(2)	126.53(14)
P(1)–O(1)–Zn(2)#5	137.75(17)	P(3)–O(8)–Zn(1)#5	143.46(17)
P(1)–O(2)–Zn(3)#5	140.37(18)	P(3)–O(9)–Zn(3)	129.94(16)
P(1)–O(3)–Zn(1)	128.87(15)	P(4)–O(10)–Zn(3)	127.99(17)
P(2)–O(4)–Zn(1)	121.53(15)	P(4)–O(11)–Zn(1)#6	166.1(2)
P(2)–O(5)–Zn(3)#3	140.80(16)	P(4)–O(12)–Zn(2)#4	149.9(2)
P(2)–O(6)–Zn(2)	124.17(16)		

Symmetry transformations used to generate equivalent atoms: #1  $x+1, -y+1/2, z-1/2$ ; #2  $-x+1, y+1/2, -z+3/2$ ; #3  $x, -y+1/2, z-1/2$ ; #4  $x, -y+1/2, z+1/2$ ; #5  $-x+1, y-1/2, -z+3/2$ ; #6  $x-1, -y+1/2, z+1/2$ .



similar to those in other zincophosphites reported [22–25].

### 3.2. Crystal structure of $(C_6H_{14}N_2) \cdot [Zn_3(HPO_3)_4] 2$

The asymmetric unit of **2** is shown in Fig. 2(b). It contains 25 unique non-hydrogen atoms, 19 of which belong to the framework and 6 to the amine. There are three crystallographically distinct Zn atoms and four crystallographically distinct P atoms in the asymmetric unit. Selected bond lengths and angles of **2** are listed in Table 5. The three distinct zinc atoms form the centers of  $ZnO_4$  tetrahedra and make four Zn–O–P bonds with normal geometrical parameters [ $d_{av}(Zn1-O)=1.926$  (3) Å,  $d_{av}(Zn2-O)=1.930$  (3) Å,  $d_{av}(Zn3-O)=1.934$  (3) Å]. The O–Zn–O angles are in the range 96.72–116.32°. Each of the four distinct P atoms makes three links to Zn via O with  $d_{av}(P1-O)=1.505$  (3) Å,  $d_{av}(P2-O)=1.516$  (3) Å,  $d_{av}(P3-O)=1.512$  (3) Å, and  $d_{av}(P4-O)=1.491$  (3) Å, with the fourth vertex assumed to be a P–H bond. Thus, as seen for **1**, there are no terminal Zn–O or P–O bonds. The O–P–O bond angles are in the range 106.29–118.1°. The connectivity between  $ZnO_4$  tetrahedra and  $HPO_3$  pseudo pyramids result in a three-dimensional architecture similar to the structure of **1** (Fig. 5). Comparing Fig. 3 with Fig. 5 and Fig. 4 with Fig. 6, these two compounds show the same inorganic framework compositions of  $[Zn_3HPO_3]_4^{2-}$  and similar framework structures constructed by  $ZnO_4$  tetrahedra linking four infinite four-membered ring chains, but

different crystal structures due to the utility of different templates. In both anionic networks, the basic connectivity of the  $ZnO_4$  tetrahedral and pyramidal  $HPO_3$  units (O atoms shared) is the same. The outstanding structural motif are linear chains of Zn–O–P–O–Zn–O–P–O– rings, whereby the Zn atoms are shared between adjacent rings. The consecutive “vertical” and “horizontal” rings connect to adjacent chains via the third P–O– link to afford the grid-like three-dimensional arrays.

TGA study was carried out from room temperature to 1000°C. The TGA profile of **1** showed an obvious weight loss of 17.55% at 390–520°C, due to the decomposition of triethylenediamine (calcd 18.10 wt%). The DTA of **1** curve exhibited one exothermic peak at ca. 416°C corresponding to the decomposition of the template. The TGA profile of **2** showed a weight loss of 13.92% at 380–500°C, attributed to the decomposition of piperazine molecules (calcd 14.57 wt%) and the DTA of **2** curve exhibited one exothermic peak at ca. 435°C, corresponding to the decomposition of the template. As indicated by the TGA/DTA curves, both compounds were thermally stable up to ca. 300°C, above which structures of two compounds collapsed and converted to amorphous phases. At 800°C, the amorphous phase recrystallized mainly into a  $ZnP_2O_7$  phase (JCPDS: 34-0623) with some other phase, which was confirmed by powder X-ray diffraction analysis.

$^{31}P$  MAS Solid State NMR spectra (Fig. 7) showed four resonance peaks at 5.43, 2.74, 1.23, –0.51 ppm for

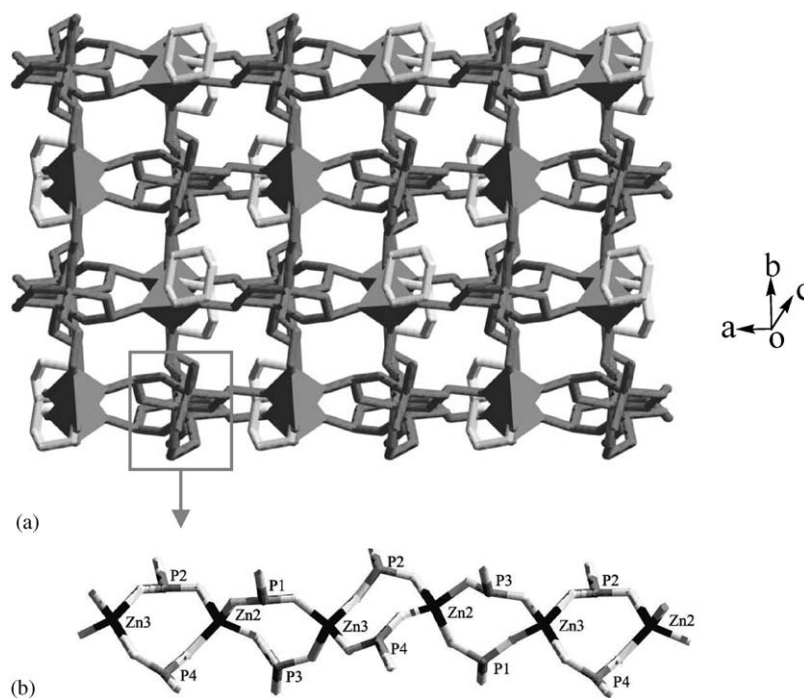


Fig. 5. (a) Framework structure of **2** viewed along the *c*-axis and (b) the infinite four-membered ring chains in the framework. All H atoms are omitted for clarity and these dark polyhedra represent the  $Zn(1)O_4$  tetrahedra.

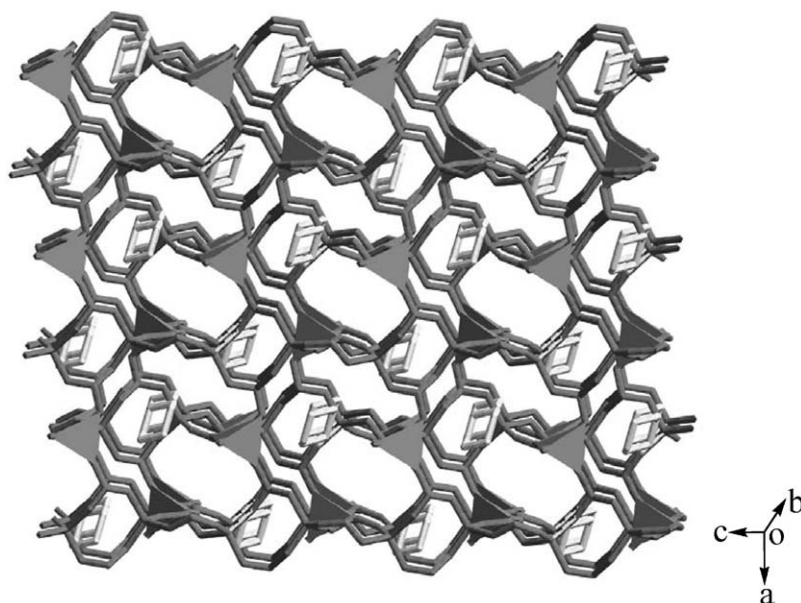


Fig. 6. Framework structure of 2 along the *b*-axis. All H atoms are omitted for clarity and these dark polyhedra represent the Zn(1)O<sub>4</sub> tetrahedra.

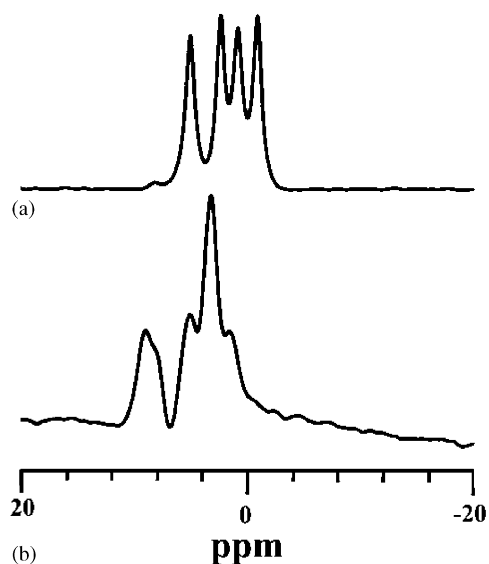


Fig. 7. <sup>31</sup>P MAS NMR spectra of 1 (a) and 2 (b).

1 and 6.97, 3.16, 1.47,  $-0.28$  ppm for 2, relative to a standard of 85% H<sub>3</sub>PO<sub>4</sub>. These values agreed well with those reported in literatures [10,12], and with four distinct phosphorus as indicated from X-ray structural analysis.

#### 4. Conclusions

Two novel three-dimensional open-framework zincophosphites (C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)·[Zn<sub>3</sub>(HPO<sub>3</sub>)<sub>4</sub>] 1 and (C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>)·[Zn<sub>3</sub>(HPO<sub>3</sub>)<sub>4</sub>] 2, have been obtained from hydrothermal systems. 1 and 2 have similar frameworks with the same compositions of [Zn<sub>3</sub>(HPO<sub>3</sub>)<sub>4</sub>]<sup>2-</sup>. Their structures are

built up from alternating ZnO<sub>4</sub> tetrahedra and HPO<sub>3</sub> pseudo pyramids by sharing vertexes. The four-membered ring chains in 1 and 2 are similar to those of H<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>·Zn(HPO<sub>3</sub>)<sub>2</sub> reported earlier by Harrison [24], where each P atom in the four-membered ring of H<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>·Zn(HPO<sub>3</sub>)<sub>2</sub> has one terminal P–O bond. In our structures, however, there are no terminal P–O bonds in the rings. Thus, the structure reported by Harrison's group is two-dimensional, whereas the structures of 1 and 2 are three-dimensional.

The formation of zincophosphite similar to zincophosphate has been shown to be sensitive to the organic templates. When organic templates such as ethylenediamine, 1,3-diaminopropane were used as the templates, several different open-framework zincophosphites were obtained. From our work, we concluded that similar frameworks could be formed by different template molecules, in this case, triethylenediamine and piperazine.

#### Acknowledgments

We thank the National Science Foundation of China (No. 20071013), the State Basic Research Project of China (G2000077507) and Foundation for "Chang-Jiang" scholarship by the Ministry of Education of China for support.

#### References

- [1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, *J. Am. Chem. Soc.* 104 (1982) 1146.
- [2] C.L. Bowes, G.A. Ozin, *Adv. Mater.* 8 (1996) 13.



- [3] S.R. Batrten, R. Robson, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 1460.
- [4] M.J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 1211.
- [5] T.E. Gier, G.D. Stucky, *Nature*. 349 (1991) 508.
- [6] G. Bonavia, J. Debord, R.C. Haushalter, J. Zubieta, *Chem. Mater.* 7 (1995) 1995.
- [7] S. Fernandez, J.L. Pizarro, J.L. Mesa, L. Lezama, M.I. Arriortua, T. Rojo, *Int. J. Inorg. Mater.* 3 (2001) 331.
- [8] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo, *Angew. Chem. Int. Ed.* 41 (2002) 3683–3685.
- [9] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, R. Olazcuag, T. Rojo, *Chem. Mater.* 12 (2000) 2092.
- [10] W.T.A. Harrison, M.L.F. Phillips, T.M. Nenoff, *J. Chem. Soc., Dalton Trans.* (2001) 2459.
- [11] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, R. Olazcuag, T. Rojo, *Chem. Mater.* 14 (2002) 2300.
- [12] J.A. Rodgers, W.T.A. Harrison, *Chem. Commun.* (2000) 2385.
- [13] M.L.F. Phillips, T.M. Nenoff, C.T. Thompson, W.T.A. Harrison, *J. Solid State Chem.* 167 (2002) 337.
- [14] Z. Shi, L. Zhang, G. Zhu, G. Yang, J. Hua, H. Ding, S. Feng, *Chem. Mater.* 11 (1999) 3565.
- [15] Z. Shi, S. Feng, S. Gao, L. Zhang, G. Yang, J. Hua, *Angew. Chem. Int. Ed.* 39 (2000) 2325.
- [16] Z. Shi, S. Feng, L. Zhang, G. Yang, J. Hua, *Chem. Mater.* 12 (2000) 2930.
- [17] Z. Shi, D. Zhang, S. Feng, *J. Solid State Chem.* 172 (2003) 464.
- [18] Z. Shi, G. Li, S. Feng, *Inorg. Chem.* 42 (2003) 2357.
- [19] W. Fu, Z. Shi, S. Feng, *J. Solid State Chem.* 174 (2003) 11.
- [20] SMART and SAINT; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996.
- [21] SHELXTL, Version 5.1; Siemens Industrial Automation, Inc., 1997.
- [22] W.T.A. Harrison, *Int. J. Inorg. Mater.* 3 (2001) 179.
- [23] W.T.A. Harrison, M.L.F. Phillips, J. Stanchfield, T.M. Nenoff, *Inorg. Chem.* 40 (2001) 895.
- [24] W.T.A. Harrison, *Int. J. Inorg. Mater.* 3 (2001) 187.
- [25] W.T.A. Harrison, *J. Solid State Chem.* 160 (2001) 4.