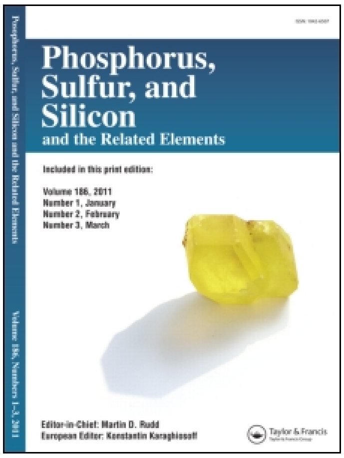

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Hydrothermal Synthesis, Crystal Structure, and Characterization of a Two-Dimensional Open-Framework Zinc Phosphate Templated by Hexylamine: $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$

A. Dakhlaoui[a]; L. S. Smiri[a]; A. Driss[b]
[a] Faculté des Sciences de Bizerte, Département de Chimie, Jarzouna, Tunisie [b] Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie

To cite this Article Dakhlaoui, A. , Smiri, L. S. and Driss, A.(2005) 'Hydrothermal Synthesis, Crystal Structure, and Characterization of a Two-Dimensional Open-Framework Zinc Phosphate Templated by Hexylamine: $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 8, 1967 — 1976
To link to this Article: DOI: 10.1080/104265090902732
URL: http://dx.doi.org/10.1080/104265090902732

Phosphorus, Sulfur, and Silicon, 180:1967–1976, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090902732

Hydrothermal Synthesis, Crystal Structure, and Characterization of a Two-Dimensional Open-Framework Zinc Phosphate Templated by Hexylamine: $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$

A. Dakhlaoui
L. S. Smiri
Faculté des Sciences de Bizerte, Département de Chimie, Jarzouna, Tunisie

A. Driss
Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie

The title compound has been synthesized under mild hydrothermal conditions (autogenous pressure, 368 K, 24 h). It crystallizes in the $P2_1/c$ *(N° 14) space group with* $a = 15.9323(4)$ Å; $b = 9.6203(1)$ Å; $c = 8.8024(2)$ Å; $\beta = 103.828(2)°$; $V = 1310{,}07(5)$ $Å^3$; *and* $Z = 4$. *Its structure, determined from X-ray single-crystal data (1266 reflexions with* $I > 2\sigma(I)$, $R = 7.4\%$, $Rw = 20.6\%$*), consists of inorganic* $[Zn(HPO_4)Cl]^-$ *sheets lying parallel to the (100) plane between which are located the protonated organic molecules. The infrared spectroscopy and the thermogravimetric analysis are reported.*

Keywords Crystal structure; hydrothermal synthesis; infrared spectroscopy; organic zinc phosphate; thermal behavior

INTRODUCTION

The interest in open framework zinc phosphates has increased in the early 1980s[1] and this has become more evident since Stucky et al. synthesized, in 1991, a series of microporous compounds of this family with the Zeolite topology.[2–4] Since then, a large number of organically templated zincophosphates (ZnPOs) with 1-D, 2-D, and 3-D structures have been prepared. These compounds are typically synthesized under hydrothermal or solvothermal conditions. Their crystal structures are strongly dependent on the identity of the organic species used.[5,6]

Received August 5, 2004; accepted September 14, 2004.

Address correspondence to L. S. Smiri, Faculté des Sciences de Bizerte, Unité de recherche 99/UR12-30, Jarzouna, Tunisie. E-mail: leila.smiri@fsb.rnu.tn

In this article, we report the hydrothermal synthesis, the crystal structure, and the characterization of a new 2-D framework zinc phosphate, $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$.

RESULTS AND DISCUSSION

Description of the Structure and Discussion

The lamellar structure of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ is built up from inorganic $[Zn(HPO_4)Cl]^-$ sheets lying parallel to the (100) plane between which the organic cations are arranged in double layers (Figure 1). The (ZnO_3Cl) and (HPO_4) tetrahedra are connected together via P—O—Zn linkages to give four- and eight-membered rings with approximate dimensions of $(4.5 \times 3.9\ Å^2)$ and $(9.7 \times 3.4\ Å^2)$, respectively. These rings share (ZnO_3Cl) and (HPO_4) tetrahedra to generate a (2-D) network designed 488 according to the topological classification of Smith[7] (Figure 2).

The P-OH group of the $(HPO_4)^{2-}$ anion, easily identified by examination of the P—O distances, is involved in intra-layer H bonding $(O(4)\cdots O(2) = 2.674(9)$ Å). These intra-layer hydrogen bonds added to the weak H bonds established between the organic cations and the inorganic framework $(N\cdots O(1) = 2.99(1)$ Å, $N\cdots O(3) = 3.11(1)$ Å, and $N\cdots Cl = 3.33(1)$ Å) enhance the structural stability of this compound. Characteristics of hydrogen bonds are listed in Table I.

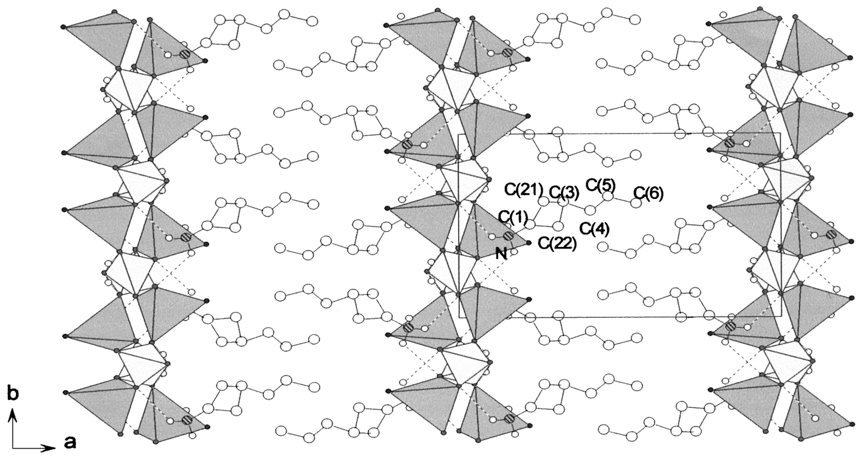

FIGURE 1 Projection of the structure of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ along the [001] direction.

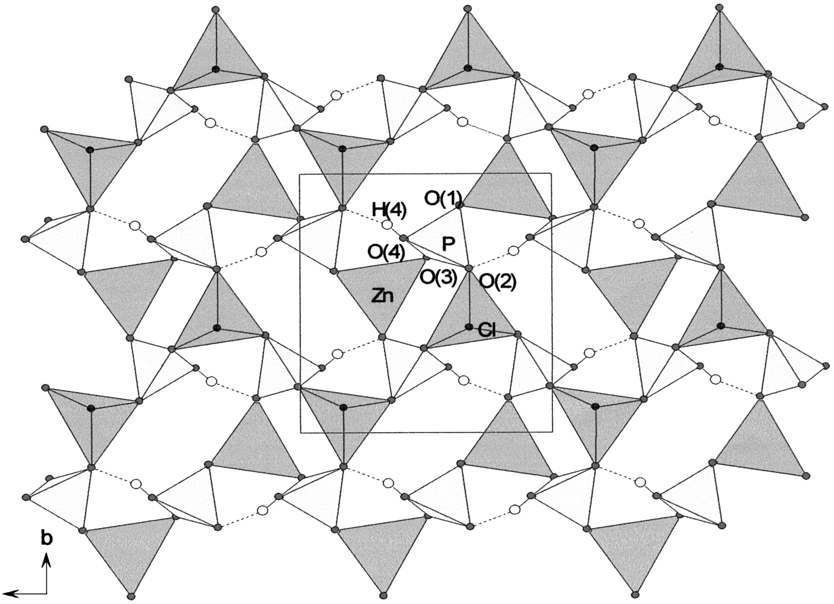

FIGURE 2 Polyhedral view of part of 488 tetrahedral sheet in $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ showing the connectivity between the (ZnO_3Cl) and (HPO_4) units. The minimum and maximum dimensions of the 4- and 8-rings are noted in the text.

As a whole, the structure of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ templated by the hexylamine (hereafter designed (**I**)) is closely related to that of $[C_6H_{14}N]_2\cdot[(Zn_2(HPO_4)_2Cl_2]$ templated by the cyclohexylamine (hereafter designed (**II**)) (monoclinic, space group $P2_1/a$ (N°14), a = 8.830(3) Å; b = 9.278(3) Å; c = 26.950(9) Å; β = 90.74(3)°; and Z = 2) reported in reference 8 (Figure 3). Both compounds exhibit parallel inorganic sheets between which lie the organic cations in double layers. Moreover, the connectivity between the (ZnO_3Cl) and (HPO_4) tetrahedra leads to a layered topology based on a 488 network in two compounds. This common feature of a tetrahedral units connectivity can explain the comparative parameters ($a_{II} \approx c_I$; $b_{II} \approx b_I$). However, slight structural differences appear between the two compounds: there is only one distinct zincophosphate layer in the structure of (**I**), while two distinct layers, occurring at z = 0 and z = 0.5, are present in the structure of (**II**). As a consequence, the lattice parameter along the c axis is approximately doubled in (**II**) compared to its homologue in (**I**) ($c_{II} \approx 2a_I$). We note that the inorganic layer at z = 0.5 is closely related to that present in the structure of (**I**). The layer at z = 0 exhibits different morphology of the eight-membered rings and different orientation

TABLE I Selected Interatomic Distances (Å) and Angles (°) in $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$

The $[ZnO_4]$ tetrahedron				
Zn	O(1)	$O(2)^{i}$	$O(3)^{ii}$	Cl
O(1)	1.989(7)	2.980(9)	3.216(9)	3.501(8)
$O(2)^{i}$	98.0(3)	1.960(7)	3.355(9)	3.487(8)
$O(3)^{ii}$	109.3(3)	118.0(3)	1.954(7)	3.387(7)
Cl	111.7(2)	112.1(3)	107.5(3)	2.240(4)
The $[P(1)O_4]$ tetrahedron	$\langle P\text{-}O\rangle = 1.547(8)$			
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.535(7)	2.520(9)	2.534(9)	2.512(9)
O(2)	109.8(4)	1.545(7)	2.553(9)	2.491(9)
O(3)	111.9(5)	112.6(4)	1.523(9)	2.537(9)
O(4)	107.3(4)	105.5(4)	109.4(4)	1.585(7)
$[C_6NH_{16}]^+$ group				
N(1)–C(1)	1.54(3)	N–C(1)–C(21)	127(3)	
C(1)–C(21)	1.40(5)	N–C(1)–C(22)	138(3)	
C(1)–C(22)	1.39(4)	C(4)–C(3)–C(22)	90(3)	
C(21)–C(3)	1.64(6)	C(4)–C(3)–C(21)	133(3)	
C(22)–C(3)	1.60(6)	C(3)–C(4)–C(5)	119(3)	
C(3)–C(4)	1.39(5)	C(4)–C(5)–C(6)	112(3)	
C(4)–C(5)	1.48(5)	C(1)–C(21)–C(3)	101(3)	
C(5)–C(6)	1.40(5)	C(1)–C(22)–C(3)	103(3)	

Hydrogen-Bond Scheme in $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$. Symmetry codes: i = $-x, -1/2 + y, 1/2 - z$; ii = $x, -y + 3/2, z - 1/2$.

N(O)—H···O	H···O(Å)	N(O)···O	N(O)HO
O(4)–H(4)···O(2)	1.88	2.674(9)	161.7
N–H(1)···O(1)	2.43	2.990(13)	121.2
N–H(3)···O(3)	2.58	3.106(13)	118.9
N–H(2)···Cl	2.76	3.328(13)	122.6

of the tetrahedral units. This is closely related to the organic cations that adopt two distinct orientations with regard to the inorganic layers so they interact differently with oxygen of the (HPO_4) and Cl of the (ZnO_3Cl) tetrahedra to modify their orientations.

IR Spectroscopy

The IR spectrum of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ (Figure 4) shows bands corresponding to the vibration modes of the organic cations and the phosphate anions. Attribution of different bands has been done with regard to other hydrogen phosphates.[9–11] The stretching and bending modes of the (PO_4) units are respectively observed in the (1200–800 cm^{-1}) and

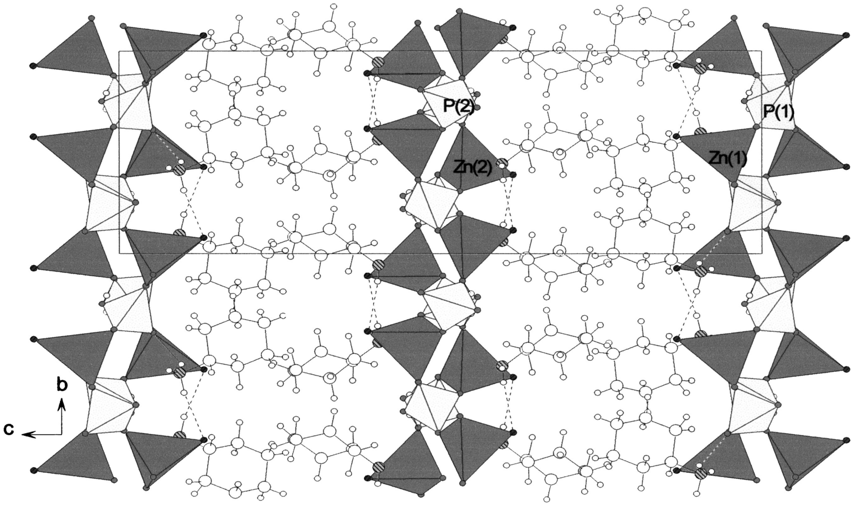

FIGURE 3 [100] projection of the structure of $[C_6H_{14}N]_2 \cdot [(Zn_2(HPO_4)_2Cl_2]$ showing the two alternative orientations of the cyclohexylammonium cations between the inorganic layers.

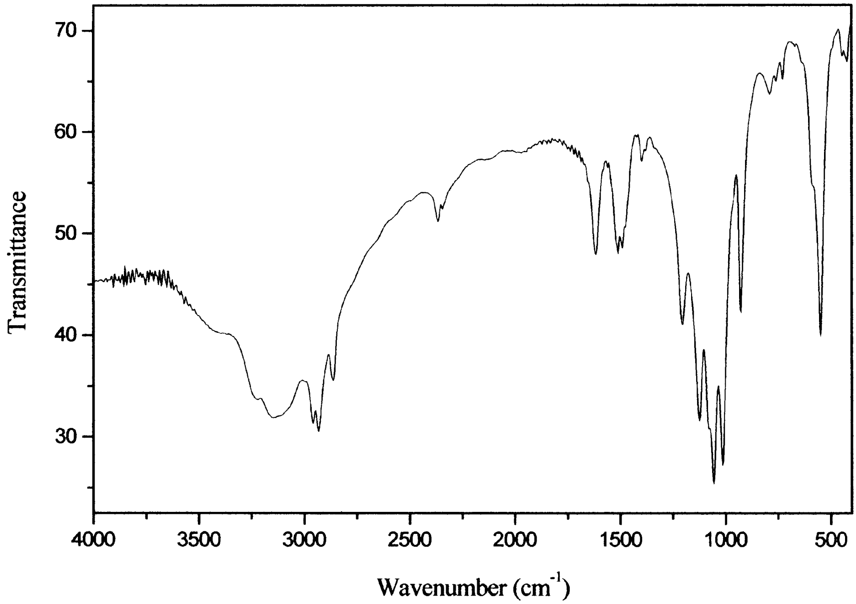

FIGURE 4 Infrared spectrum of $[C_6H_{16}N] \cdot [(Zn(HPO_4)Cl]$.

(600–400 cm^{-1}) regions with asymmetric modes at higher frequencies and symmetric ones at lower frequencies. Thus, bands appearing at (1204, 1124, 1080, 1056, and 1013 cm^{-1}) correspond to the asymmetric stretching mode, and those appearing at (929, 861, and 791 cm^{-1}) correspond to the symmetric stretching one. Bands at (582 and 548 cm^{-1}) are attributed to the asymmetric bending mode and those at (444, 425, and 408 cm^{-1}) are assigned to symmetric bending mode of this group. The band at 1385 cm^{-1} and that at 763 cm^{-1} should correspond to the δ_{P-O-H} in plane bending mode and υ_{P-O-H} out of plane bending mode, respectively. Remaining bands in (1200–3500 cm^{-1}) region correspond to the combination and overlapping of (N(O,C)-H) bending and stretching modes. We note that the ABC type bands characteristic of the OH modes in the (HPO$_4$) groups are barely perceived at around 1963, 2100, and 2365 cm^{-1}.

Thermal Analysis

Thermogravimetric analysis of [$C_6H_{16}N$]·[(Zn(HPO$_4$)Cl] (Figure 5) shows two weight losses of 5.8% and 37.6% in the ranges (495–545 K) and (547–730 K), respectively. The first mass loss should correspond to the departure of a water molecule after the condensation of the —OH

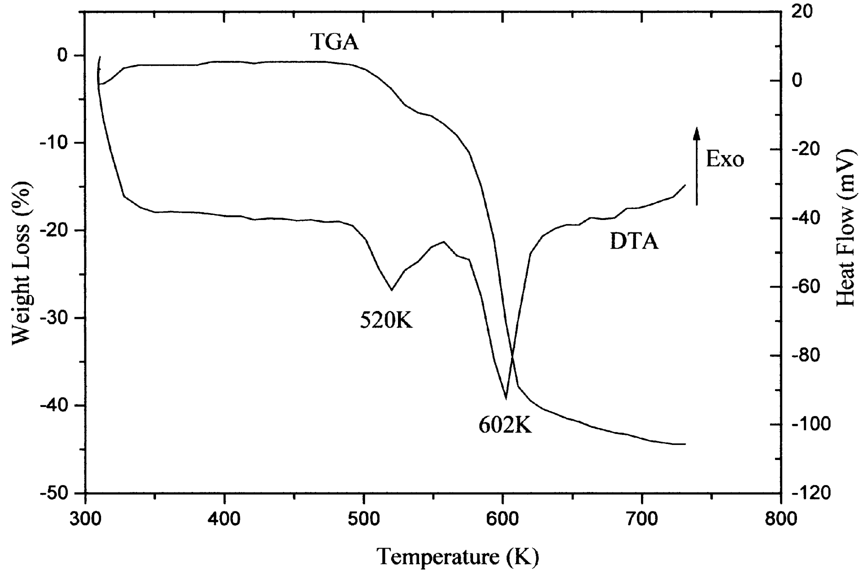

FIGURE 5 TG-DTA curves showing thermal behavior of [$C_6H_{16}N$]·[(Zn(HPO$_4$)Cl].

groups (cal. 6.01%). The IR spectrum of this compound, calcined at 530 K, exhibits bands corresponding to the ν_{O-P-O}. The second mass loss should correspond to the departure of HCl gas as well as the beginning of decomposition of the amine molecule. However, the observed weight loss (37.6%) was much lower than the expected value (cal. 46.7%). The lower reduction in this stage can be due to the retention of carbon in the solid residue (black color). After calcinations at 773 K, $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ is converted to an amorphous phase that recrystallizes giving the β-$Zn_2P_2O_7$ (JCPDS: 34-1275).

EXPERIMENTAL

Chemical Preparation

The title compound was synthesized under hydrothermal conditions. The reagents $ZnCl_2$ (0.11 g), H_3PO_4 (0.054 mL; 85%), hexylamine (0.08 mL), and ethanol (5 mL) were placed without stirring in a Teflon-lined stainless steel autoclave and heated at 368 K for 24 h. After cooling to room temperature, fine plates of medium quality corresponding to $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ were obtained. The X-ray powder pattern showing intense Bragg peaks at a low angle ($d_1 = 14.926$ Å; $d_2 = 11.69$ Å, Figure 6) is typical of a lamellar solid.

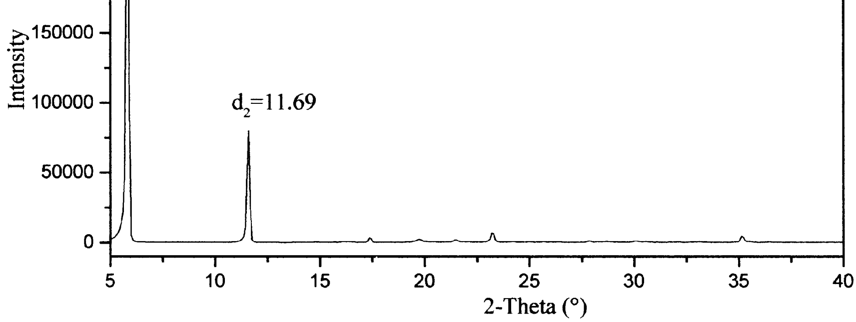

FIGURE 6 X-ray diffraction pattern of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ showing the most intense Bragg peaks (Å).

In order to improve the crystal quality, a large number of essays by modifying the preparative conditions (mass ratio of reactants, time of reaction, temperature of reaction . . .) have been carried out but they unfortunately failed.

Investigation Techniques

X-Ray Diffraction

Data collection on a colorless platelet-shaped single crystal of $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$ were recorded on an Enraf-Nonius CAD4 automated 4-circles diffractometer. A summary of crystal data and details of collection are presented in Table II and Figure 6.

The structure was solved in the space group $P2_1/c$ (N°14) by direct methods using the TREF option of the program SHELXS-97[12] and refined using the program SHELXL-97.[13] The Zn, P, and Cl atoms were first located and all the remaining nonhydrogen atoms (O, C, N) were found from the subsequent Fourier maps analysis. C(2) was disordered over two sites: C(21) and C(22) with occupancy of 0.6 and 0.4, respectively. Two distance constraints were applied during the refinement to

TABLE II Crystal Data, Intensity Measurements, and Refinement Parameters for $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$

Formula	$[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$
Molecular weight ($g \cdot mol^{-1}$)	279.94
Space group	$P2_1/c$ (N°14)
Cell parameters	a = 15.9323(4) Å b = 9.6203(1) Å c = 8.8024(2) Å $\beta = 103.828(2)°$
Volume; Z	1310,07(5) Å^3; 4
ρ_{calc} ($g \cdot cm^{-3}$)	1.419
Absorption coefficient (mm^{-1})	2.187
T(K) of data collection	298
Diffractometer	Enraf-Nonius CAD4
Radiation (graphite monochromated)	MoKα 0.71073 Å
Scan mode	$\omega - 2\theta$
Limiting indices	$-18 \leq h \leq 18$, $-11 \leq k \leq 0$, $-6 \leq l \leq 10$
Absorption correction	Ψ-scan
2θ limit	$4° < 2\theta < 50$
Number of independent reflections ($\lvert Fo\rvert > 4\sigma\lvert Fo\rvert$)	1266
Number of refinement parameters	129
Final R indices [$I > 2\sigma(I)$]	R = 0.074; Rw = 20.6%
Goodness-of-fit on F^2	1.043

keep the C(1)-C(21) and C(1)-C(22) distances quite correct. The H atoms of the hydroxyl and ammonium groups were geometrically placed using the HFIX option of the SHELXL-97 program. The thermal factors of carbon atoms are quite high, so it was not possible to locate their hydrogen atoms. The refinement with anisotropic thermal parameters for Zn, P, O, N, and C atoms, except for C(21) and C(22) (isotropically refined), and isotropic for H atoms give R = 7.4% and Rw = 20.6% for 1266 reflexions ($I > 2\sigma(I)$). The magnitude of the reliability factors can be explained by the borderline quality of the crystal used in the data collection and also by the disorder of the organic molecule. The final atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Centre (CCDC 243786). The atomic coordinates with equivalent isotropic ADPs, main interatomic distances, and angles are reported in Table III and I, respectively.

Physical Measurements

Thermal Analysis. TGA measurements were performed on a "multimodule 92 Setaram Analyzer" under Argon flow, with a heating rate of 2 K/min between room temperature and 723 K.

TABLE III Atomic Coordinates and Equivalent Thermal Parameters in $[C_6H_{16}N]\cdot[Zn(HPO_4)Cl]$

Atoms	x (σ)	y (σ)	z (σ)	B_{eq} (Å^2)
Zn	0.08080(8)	0.4356(1)	0.3348(1)	3.35(3)
P	−0.0178(2)	0.2329(3)	0.0601(3)	3.21(7)
Cl	0.2191(2)	0.4047(5)	0.3273(4)	7.3(2)
O(1)	0.0002(5)	0.3768(7)	0.1361(7)	3.5(1)
O(2)	0.0490(5)	0.6328(7)	0.3276(7)	4.2(1)
O(3)	0.0598(5)	0.3234(8)	0.5070(8)	4.0(2)
O(4)	−0.0972(4)	0.2490(8)	−0.0867(7)	3.(2)
H(4)	−0.08382	0.30112	−0.15078	3.95*
N	0.1566(7)	0.442(1)	0.941(1)	6.4(4)
C(1)	0.221(2)	0.507(3)	0.857(3)	12.1(9)
C(21)	0.267(3)	0.631(4)	0.895(7)	7.1(1)*
C(22)	0.308(2)	0.493(5)	0.858(5)	4.6(3)*
C(3)	0.327(2)	0.629(4)	0.768(4)	16.9(1)
C(4)	0.410(2)	0.580(3)	0.774(4)	18.1(1)
C(5)	0.465(2)	0.658(4)	0.690(4)	18.1(1)
C(6)	0.552(2)	0.619(4)	0.740(5)	21.3(1)
H(1)	0.10462	0.43767	0.87523	3.95*
H(2)	0.15378	0.49310	1.02348	3.95*
H(3)	0.17388	0.35609	0.97225	3.95*

*B_{iso}

Infrared Spectroscopy. IR data were collected in the 4000–400 cm^{-1} range with a Perkin-Elmer FT-IR 1000 spectrophotometer using KBr pellet technique. Spectra resolution was 4 cm^{-1}.

CONCLUSION

A new layered organically-templated zincophosphate, $[C_6H_{16}N]\cdot[(Zn(HPO_4)Cl]$, has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction and IR spectroscopy. Its structure consists of (HPO_4) and (ZnO_3Cl) tetrahedral units linked through their vertex, forming layers with 488 net. A structural comparison of the as-synthesized compound and the $[C_6H_{14}N]_2\cdot[(Zn_2(HPO_4)_2Cl_2]$ shows the essential role of the organic entities in directing the structure of these compounds.

REFERENCES

[1] S. Natarajan, L. V. Wullen, and M. Jansen, *Inorg. Chem.*, **42,** 6265 (2003).

[2] W. T. A. Harrison, T. E. Gier, K. L. Moran, J. M. Nicol, H. Eckert, and G. D. Stucky, *Chem. Mater.*, **3,** 27 (1991).

[3] T. M. Nenoff, W. T. A. Harrison, T. E. Gier, and G. D. Stucky, *J. Am. Chem. Soc.*, **113,** 378 (1991).

[4] T. E. Gier and G. D. Stucky, *Nature,* **349,** 508 (1991).

[5] A. V. Chavez, T. M. Nenoff, L. Hannooman, and W. T. A. Harrison, *J. Solid State Chem.*, **147,** 584 (1999).

[6] W. T. A. Harrison, Z. Bricsak, L. Hannooman, and Z. Zhang, *J. Solid State Chem.*, **136,** 93 (1998).

[7] J. V. Smith, *Chem. Rev.*, **88,** 149 (1988).

[8] B. Trojette, A. A. Hajem, A. Driss, and T. Juini, *J. of Chem. Cryst.*, **28,** 339 (1998).

[9] L. B. Taher, L. S. Smiri, and A. Bulou, *J. Solid State Chem.*, **161,** 97 (2001).

[10] I. H. Joe, V. S. Jayakumar, and G. Aruldhas, *J. Solid State Chem.*, **120,** 343 (1995).

[11] L. B. Taher, S. Chabchoub, and L. Smiri-Dogguy, *Solid State Sciences*, **t.1,** 15 (1999).

[12] G. M. Sheldrick, SHELXS-97, A Program for Automatic Crystal Structure Solution, University of Göttingen, Germany, 1997.

[13] G. M. Sheldrick, SHELXL-97, Program for the Refinement of the Crystal Structure, University of Göttingen, Germany, 1997.