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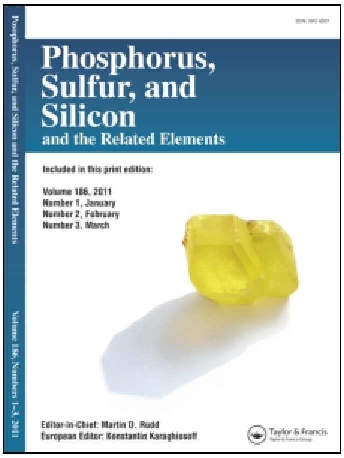

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The Synthesis and Characterization of a New Layered Chlorozincophosphate $Zn(HPO_4)Cl[C_4H_{10}N]$

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The Synthesis and Characterization of a New Layered Chlorozincophosphate $Zn(HPO_4)Cl[C_4H_{10}N]$

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Along a systematic study of open-framework materials aiming at producing new molecular sieves, we characterized a new zincophosphate $Zn(HPO_4)Cl[C_4H_{10}N]$*. It was synthesized under mild conditions (r.t.) in the presence of pyrrolidinium as an organic-structure directing agent. The structure of this compound, determinated by single crystal X-ray diffraction, consists of anionic parallel* $[Zn(HPO_4)Cl]^-$ *sheets alternating with thick slabs of organic molecules* $(C_4H_{10}N)^+$*. These latters are linked to the anionic sheets through hydrogen bonds.* $Zn(HPO_4)Cl[C_4H_{10}N]$ *crystallizes in the monoclinic system and the space group C2/c (No. 9) with cell parameters* $a = 24{,}83(9)$, $b = 9{,}258(5)$, $c = 8.778(3)$, $\beta = 110{,}45(4)$, $Z = 8$, $V = 1891.0(14)$ Å^3, $R = 0.045$, *and* $R_w = 0.07$*. Solid state* ^{31}P *and* ^{13}C *MAS NMR spectroscopies are in agreement with the X-ray structure.*

Keywords Layered compounds; NMR spectroscopy; pyrrolidine (organic template); X-ray diffraction

INTRODUCTION

Organically templated metallophosphates materials have been of great interest over recent years from both academic and industrial points of

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Address correspondence to C. Ben Nasr, Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisie. E-mail: cherif.bennasr@fsb.rnu.tn view.[1] Their anionic framework are usually built from vertex-sharing MO_n (n = 4, 5, 6 and M = Al, Ga, Fe, Co, Zn…) polyhedra and PO_4 tetrahedra, which delimit interconnected pores in which protonated organic molecules are inserted. The elimination of the organic molecule moieties in these compounds, if possible, could lead to new inorganic microporous materials, which could not be obtained by any other synthetic way. These microporous compounds have a great potential in catalysis,[2] photochemical, and photophysical[3] processes and could be used as molecular sieves.[4] Among these materials, zincophosphates display a large variety of new microporous compounds with one-, two- or three-dimensional structures. For example, the ND-1 zincophosphate, synthesized by Yang and Sevov in 1999, is one of the 5 microporous solids with the largest ring (24 T, T = P, Zn).[5] In our search for new framework structures, we observed that the addition of chloride to the mixture $ZnO(ZnCl_2)$, $P_2O_5(H_3PO_4)$, amine, and H_2O under mild conditions (r.t.) allowed the peparation of new materials in an acidic medium. Using this procedure, chloride ions were also involved in the structure of the framework and lead to a new series of chlorozincophosphates with various geometries.[6–8] This article reports the synthesis and structure determination of a new 2-D chlorozincophosphate $Zn(HPO_4)Cl[C_4H_{10}N]$ obtained in an aqueous medium using pyrrolidinium as an organic template.

RESULTS AND DISCUSSION

Structure Description

Final atomic coordinates and thermal parameters for $Zn(HPO_4)$-$Cl[C_4H_{10}N]$ are given in Table I. Main geometrical features entities are reported in Table II.

The structure of $Zn(HPO_4)Cl[C_4H_{10}N]$ consists of the anionic sheets of the formula $[Zn(HPO_4)Cl]_n^{n-}$ parallel to the (b, a) plane. Charge neutrality is achieved by the presence of protonated pyrrolidine template cations located in the inter-layer spacing (Figure 1).

An ORTEP drawing of the asymmetric unit of this zincophosphate is shown in Figure 2. Both zinc and phosphorus atoms are tetrahedrally coordinated. The zinc atom has three connections via oxygen to phosphorus atoms and has one terminal Zn—Cl vertex. The terminal chlorine atoms, hanging from the zinc center, project in a direction perpendicular to the layer. On the other hand, the P atom is surrounded by four distinct oxygen atoms; among them, three are involved in Zn—O—P bridges, and the forth one is part of P—OH groups.

TABLE I Final Atomic Coordinates and Thermal Parameters in Zn(HPO$_4$)Cl[C$_4$H$_{10}$N]. Esd Are Given in Parentheses

atoms	x	y	z	B (eq)
Zn(1)	0.184303(11)	0.22352(3)	0.63762(3)	1.844(11)
Cl(1)	0.09868(3)	0.33251(8)	0.58721(10)	3.56(2)
P(1)	0.27207(3)	0.45473(6)	0.60459(6)	1.77(1)
O(1)	0.22155(8)	0.4892(2)	0.4405(2)	2.70(4)
O(2)	0.24327(8)	0.3749(2)	0.7084(2)	2.30(4)
O(3)	0.30020(10)	0.5907(2)	0.6856(2)	3.11(4)
O(4)	0.31534(8)	0.3586(2)	0.5662(2)	2.45(4)
N(1)	0.37971(11)	0.1716(3)	0.8279(3)	3.43(5)
C(1)	0.3696(2)	0.2351(4)	0.9729(5)	4.37(8)
C(2)	0.4122(3)	0.3485(6)	1.0290(7)	7.1(1)
C(3)	0.4512(2)	0.3427(6)	0.9335(9)	7.7(2)
C(4)	0.4399(2)	0.2050(5)	0.8478(5)	4.85(9)
H(1)	0.2322	0.5594	0.3747	2.156
H(2)	0.3498	0.2030	0.7406	2.156
H(3)	0.3638	0.0650	0.8049	2.156
H(4)	0.3312	0.2690	0.9410	5.126
H(5)	0.3752	0.1613	1.0535	5.126
H(6)	0.4340	0.3401	1.1411	8.390
H(7)	0.3932	0.4429	1.0124	8.390
H(8)	0.4901	0.3480	0.9975	9.493
H(9)	0.4426	0.4190	0.8516	9.493
H(10)	0.4658	0.1357	0.9094	5.765
H(11)	0.4442	0.2152	0.7433	5.765

Beq = 4/3 Σi Σj βij aibj.

The asymmetric unit is built by ZnO$_3$Cl and PO$_4$ entities bonded with bond-length values close to those observed in other zincophosphates containing similar polyhedra Zn—O$_{\rm av}$ = 1.940 (2) Å, Zn—Cl = 2.253 (1), and P—O$_{\rm av}$ = 1.530 (2). For example, in [Zn(HPO$_4$)ClC$_5$H$_{12}$N][5], Zn—O$_{\rm av}$ = 1.940 (2) Å, Zn—Cl = 2.249 (1) Å, and P—O$_{\rm av}$ = 1.534 (2) Å); [Zn$_2$(HPO$_4$)$_2$Cl$_2$2NC$_6$H$_{14}$][9], (Zn (1)–O$_{\rm av}$ = 1.946 (5) Å, Zn (2)–O$_{\rm av}$ = 1.936 (5) Å, Zn (1)–Cl = 2.220 (2) Å, Zn (2)–Cl = 2.255 (2) Å, and P(1)–O$_{\rm av}$ = .523 (6) Å, P(2)–O$_{\rm av}$ = 1.531 (6) Å. Among the 4 distinct oxygen atoms of the PO$_3$(OH) unit, three are bonded with Zn atoms, while the other one has a significantly longer bond length (P—O(1) = 1.577 (3) Å), suggesting that oxygen O(1) forms a hydroxyl group.

The topology of the zincophosphate connectivity pattern is shown in Figure 3. The ZnO$_3$Cl and PO$_4$ groups in Zn(HPO$_4$)Cl[C$_4$H$_{10}$N] link together via Zn—O—P bridges, leading to a bidimentional network. The resulting infinite anionic $[\mathrm{Zn(HPO_4)Cl}]_n^{n-}$ layers parallel to (b ,c) plane

TABLE II Main Interatomic Distances (Å) and Angles (°) in the $Zn(HPO_4)Cl[C_4H_{10}N]$ Atomic Arrangement

The HPO_4^{2-}				
P	O(1)[a]	O(2)	O(3)	O(4)
O(1)[a]	1,577(3)	2,460(3)	2,529(4)	2,511(4)
O(2)	104,6(2)	1,531(1)	2,497(4)	2,520(4)
O(3)	110,8(2)	111,2(1)	1,521(3)	2,477(4)
O(4)	108,3(1)	111,3(1)	110,4(2)	1,494(3)
O(1)-H(1) = 0.97			H(1)-O(1)-P = 112,6	
The ZnO_3Cl Tetrahedron				
Zn	O(2)	O(3)	O(4)	Cl
O(2)	1,965(3)	3,107(4)	3,187(4)	3,393(3)
O(3)	106,60(12)	1,910(3)	3,263(3)	3,433(3)
O(4)	109,11(11)	115,52(11)	1,947(2)	3,392(3)
Cl	106,92(9)	110,83(10)	107,54(9)	2,253(1)
Zn-O(2)-P = 127,4(1)		Zn-O(3)-P = 149,0(2)	Zn-O(2)-P = 131,5(2)	
The Organic Group				
N(1)-C(1)	1,500(7)	C(4)-N(1)-C(1)	106,3(4)	
C(1)-C(2)	1,450(10)	C(2)-C(1)-N(1)	104,7(5)	
C(2)-C(3)	1,488(13)	C(1)-C(2)-C(3)	108,9(5)	
C(3)-C(4)	1,457(10)	C(4)-C(3)-C(2)	106,0(6)	
C(4)-N(1)	1,477(7)	C(3)-C(4)-N(1)	104,5(5)	
Hydrogen bonds				
O(N)-H···O(Cl)	O(N)-H	H···O(Cl)	O(N)···O(Cl)	O(N)- H···O(Cl)
O(1)-H(1)···O(2)	0.97	1.69	2.607(4)	156(9)
N(1)-H(2)···O(4)	0.91	2.06	2.874(4)	148(9)
N(1)-H(3)···Cl	1.06	2.40	3.227(4)	133(9)

[a] An oxygen atom of the OH group.

are located at $x = 1/4$ and $x = 3/4$ leading to an interplane period of 12.421 Å. These layers are arranged in such a way as to create 2 kinds of pores. The first one is built up from 4 membered (Zn—P) ×2 rings, while the second one is built up from (Zn—P) × 4 rings. However, the second pore system is not fully accessible due to the presence of P—OH groups extending into them, thereby blocking their entry (Figure 3).

Hydrogen bonding plays an important role in stabilizing the $Zn(HPO_4)Cl[C_4H_{10}N]$ structure. Both inter- and intra layer hydrogen bond interactions are observed. The pyrrolidinium cations occupy the interlayer sites and interact with zincophosphate layers via N—H—O(Cl) hydrogen bonds as N—H(2)···O(4) [$d_{H\cdots O} = 2.06$ Å], and via the chloride atom N—H(3)—Cl [$d_{H\cdots Cl} = 2.40$ Å]. The P—OH groups participate in the sheets by H-bonds: O(1)-H(O1)···O(2) [$d_{H\cdots O} = 1.69$ Å].

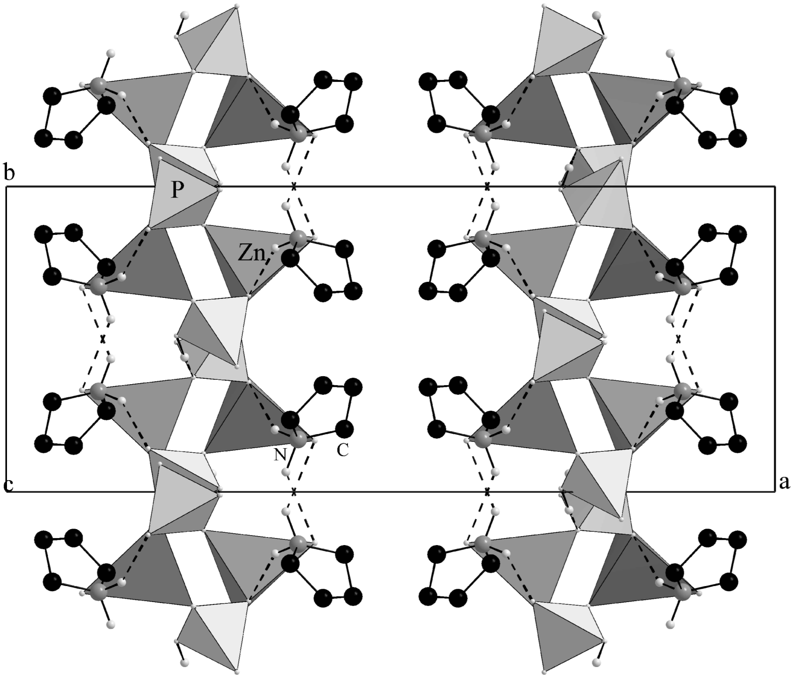

FIGURE 1 ORTEP representation of the asymmetric unit of the $Zn(HPO_4)Cl[C_4H_{10}N]$.

The main geometrical features in the hydrogen bonds are reported in Table II.

NMR Results

The ^{31}P MAS NMR spectrum of the crystalline monophosphate $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ is shown in Figure 4 and is in good agreement with the X-ray structure. Indeed, it exhibits a single resonance peak corresponding to only one crystallographic site. The chemical shift value (−3 ppm) agrees with those corresponding to monophosphates (between −10 and +5 ppm).[10–16] By the use of cross-polarization, the signal is greatly enhanced, showing (1) the presence of hydrogen atoms near the phosphorous ones and (2) that the P—H vectors are not mobile at all.

The ^{13}C HPDEC MAS NMR spectrum of the so-synthesized zincophosphate is given in Figure 5. This spectrum consists of only 2 relatively broad signals at 26.7 and 50.0 ppm, while four peaks are expected from the crystallographic experiments, all carbon atoms in the pyrrolidinium ion being unequivalent. Ab initio calculations (at the

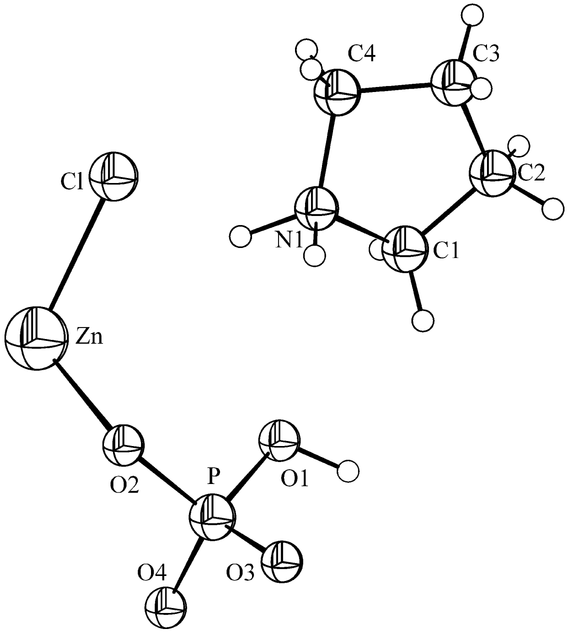

FIGURE 2 The projection of the $Zn(HPO_4)Cl[C_4H_{10}N]$ structure in the plane (b, a) (hydrogen atoms and layer-diamine H-bonds are not shown).

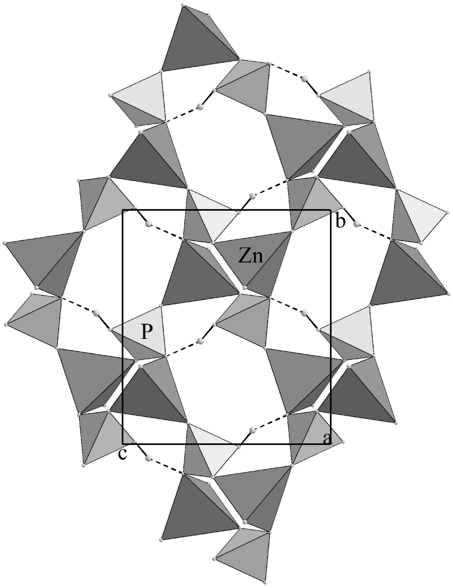

FIGURE 3 The polyhedral representation of the framework $Zn(HPO_4)$-$Cl[C_4H_{10}N]$ viewed down the a direction.

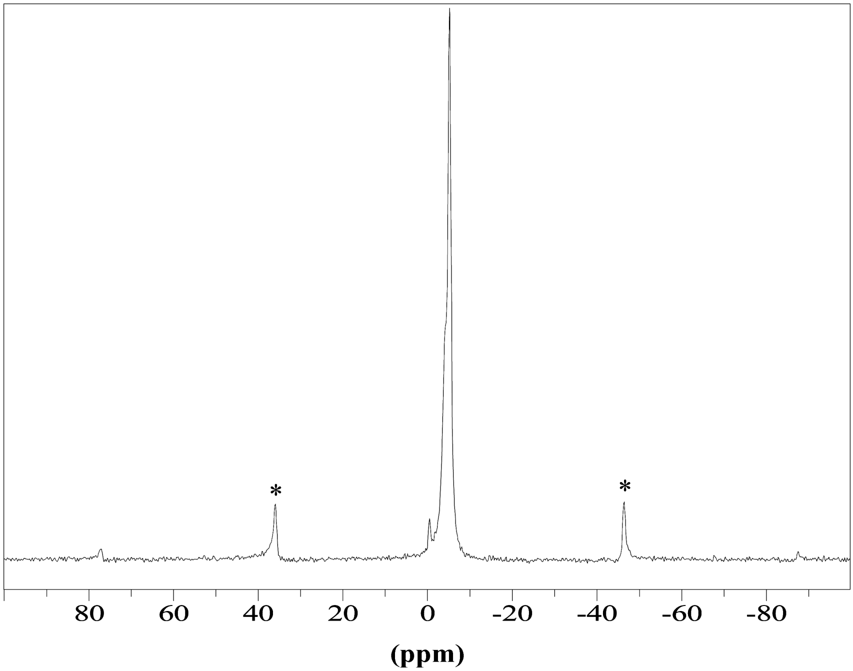

FIGURE 4 The ^{31}P MAS NMR spectrum of $Zn(HPO_4)Cl[C_4H_{10}N]$. *Spinning sidebands.

B3LYP/6-31+G* level) show that for the two carbons linked to nitrogen, a difference of a chemical shift of 2 ppm should be expected (Table III), which could be in agreement with the observed linewidth. However, the 2 other carbon atoms should be separated by at least 6 ppm, which is a value that cannot explain the experimental data. In order to determine if this was due to a bad positioning of the hydrogen atoms in the X-ray solution, a new calculation was made allowing them to move freely to their equilibrium position. The resulting chemical shifts differences were quite the same as the ones obtained by taking the crystallographic data even if the chemical shifts were in better agreement with the experimental values (Table III). A more detailed approach consists to combine Ab initio calculations, solid-state NMR, and X-ray diffraction data for the location of protons will be published elsewhere.

Another surprising feature of the ^{13}C NMR spectrum is that cross-polarization is not efficient, in contrast to what is observed with phosphorus. As all carbon atoms are linked to protons, the only explanation is that the pyrrolidinium ions are “mobile” in the inorganic channels. This mobility can be seen as jumps between the two non-equivalent

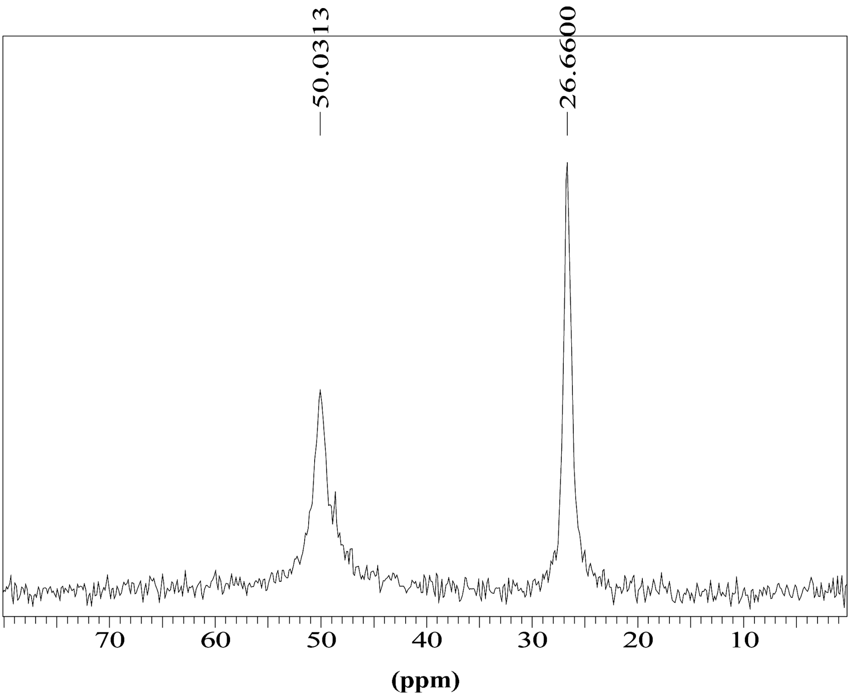

FIGURE 5 The ^{13}C CP-MAS-NMR spectrum of $Zn(HPO_4)Cl[C_4H_{10}N]$.

crystallographic positions, the rate being large compared to the NMR measure time and short compared to that of the X-ray measure. In addition to this explanation, the experimental chemical shifts are close to the mean value of the theoretical ones and very different from those of the isolated pyrrolidinium ion as they can be determined by the optimization of all atoms.

TABLE III Experimental and Calculated (at the B3LYP/6-31+G* Level) Chemical Shifts of the Pyrrolidinium Cation

Chemical shifts (ppm)	CH_2-N		CH_2-CH_2-N	
Experimental	50.0		26.6	
Calculated from the C and H crystallographic positions	41.2	39.5	9.8	3.7
Calculated with optimization of H positions	53.8	51.8	25.8	20.1
Calculated with optimization of all C, N, and H positions	60.6		35.0	

Thermal Analysis

Transformation without Weight Loss

The DTA analysis of a sample of $Zn(HPO_4)Cl[C_4H_{10}N]$ was carried out between 325 and 473 K. The sample was heated under an argon flow at a heating rate of 1°C/mn. The resulting curve exhibited an important endothermic peak at about 447 K (Figure 6), without a sample weight variation when raising the temperature and an important exothermic peak at 415 K when cooling.

With the aim to examine the nature of this transformation, the initial sample was heated at 460 K for some minutes. The resulting product had a crystalline sight. An investigation by powder X-Ray diffraction (Figure 7) and IR absorption (Figure 8) showed that there was no difference with the initial compound $Zn(HPO_4)Cl[C_4H_{10}N]$. These results indicate a reversible phase transition due to a structure rearrangement.

Transformation with Weight Loss

Crystals of $Zn(HPO_4)Cl[C_4H_{10}N]$ were transformed by heating into diphosphates according to Eq. (1)

$$2[Zn(HPO_4)Cl[C_4H_{10}N] \rightarrow Zn_2P_2O_7 + H_2O + 2HCl + 2C_4H_9N \qquad (1)$$

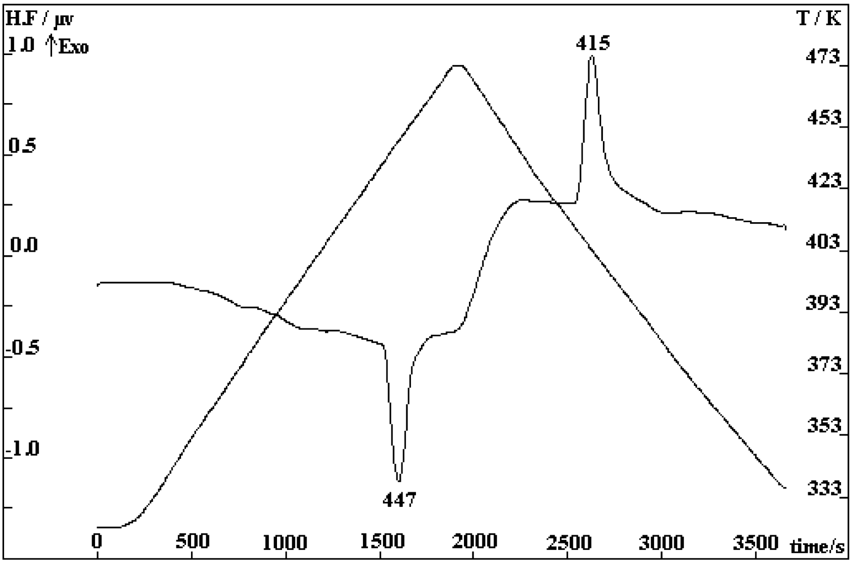

FIGURE 6 The DTA curve of $Zn(HPO_4)Cl[C_4H_{10}N]$ during two heating and cooling runs.

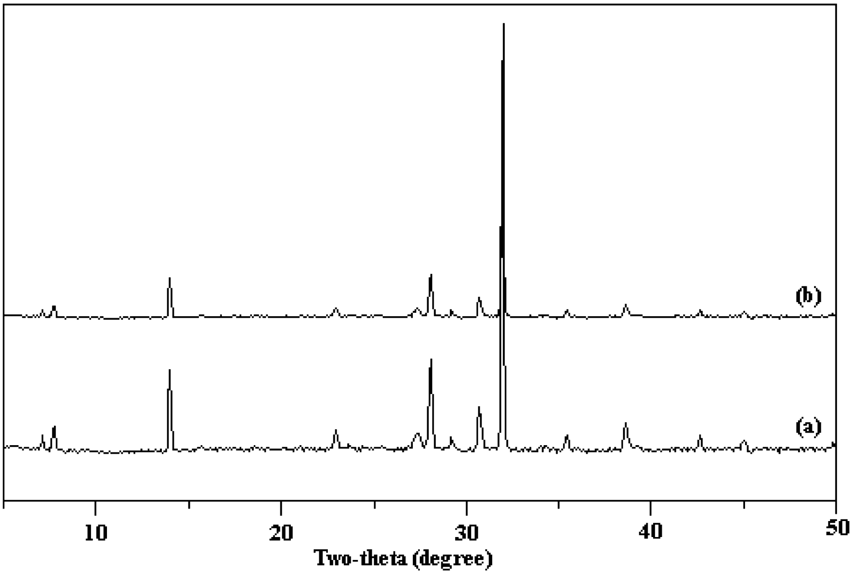

FIGURE 7 X-ray powder patterns of Zn(HPO$_4$)Cl[C$_4$H$_{10}$NO]: (a) not heated; (b) after heating and cooling at r.t.

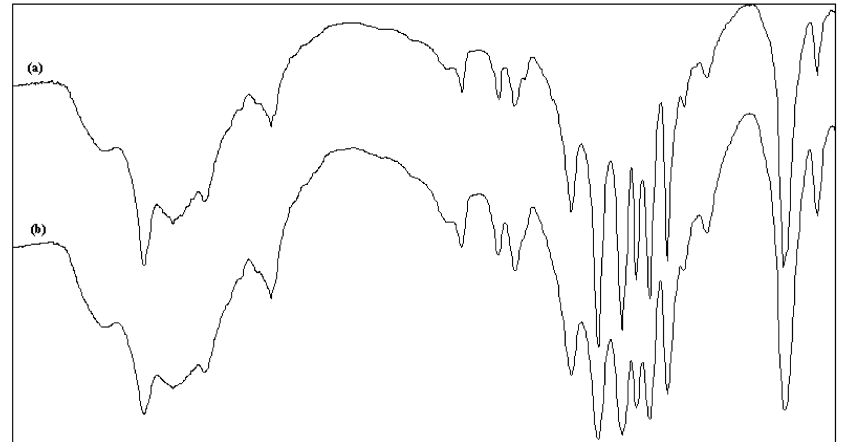

FIGURE 8 IR spectra of Zn(HPO$_4$)Cl[C$_4$H$_{10}$N]: (a) not heated; (b) after heating and cooling at r.t.

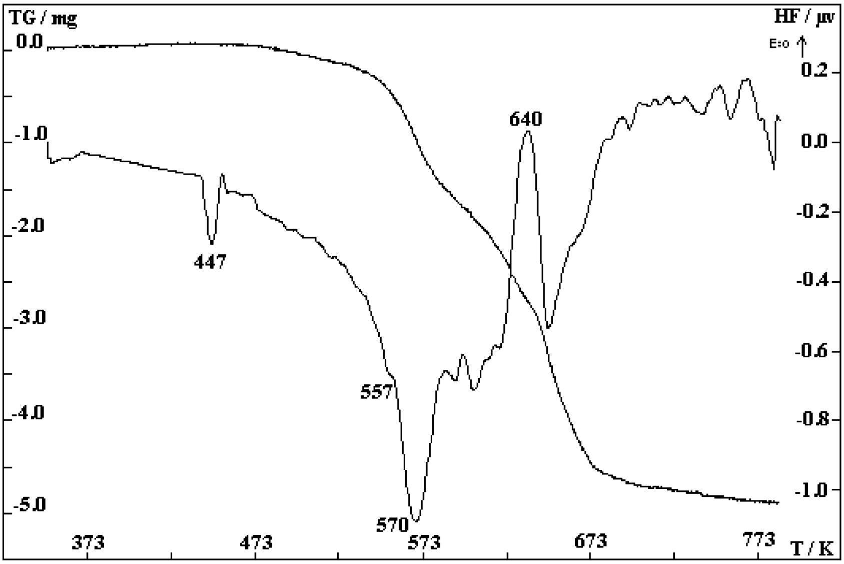

FIGURE 9 The thermal analysis (DTA and TG) under the argon of $Zn(HPO_4)Cl[C_4H_{10}N]$.

Two curves corresponding to DTA and TGA analysis in open air are reported in Figure 9. The DTA curve shows at first the phase transition peak at 447 K and a significant endothermic peak at about 570 K, followed by a series of endothermic peaks in a wide temperature range (560–770 K). The TGA curve shows an important weight loss corresponding to those peaks. The first phenomenon produced at 557 K corresponds to the loss of an H_2O molecule from the condensation of two molecules of $Zn(HPO_4)Cl[C_4H_{10}N]$ as previously indicated by the reaction scheme (weight loss calculated at 3.34%, experimental at 3.18%). The second weight loss, between 557 K and 585 K, corresponds to the loss of HCl from the molecule $Zn(HPO_4)Cl[C_4H_{10}N]$ (weight loss calculated at 13.56%, experimental at 12.83%). Finally, the weight loss, between 585 K and 775 K, corresponds to the degradation of the template molecule (organic entities). The grey solid obtained after heating contains probably a residual organic carbon. This latter can be eliminated by calcination of the sample at 1,100 K in air. The remaining compound has an X-ray diffractogram in good agreement with that of $Zn_2P_2O_7$.

IR Spectroscopy Investigations

The infrared spectrum (Figure 9) of $[Zn(HPO_4)Cl[C_4H_{10}N]$ contains characteristic bands of the pyrrolidinium and HPO_4^- anions. The stretching and bending modes of the (NH_2^+) group appear as large and weak bands at 3168 and 1580 cm^{-1}, respectively. They are indicative of the presence of the pyrrolidinium molecule in its protonated form.[17,18] The stretching vibration (—CH_2—) groups appear in the 2990–2800 cm^{-1} range, and the bending modes are observed in the 1480–1410 cm^{-1} region. The vibrational modes of the PO_4 tetrahedra anions show different groups of bands between 1200–300 cm^{-1}.[19] In this case, the stretching vibration bands originate from both symmetric $\nu_1(A_1)$ and asymmetric $\nu_3(F_2)$ modes and are observed respectively in the ranges 1000–800 cm^{-1} and 1200–1000 cm^{-1}. The bending modes symmetric $\nu_4(F_2)$ and asymmetric $\nu_2(E)$ appear respectively in the 650–500 cm^{-1} regions. As in other phosphate groups,[20,21] the IR bands in the range 2900–2300 $cm^{-1}$are assigned to ν(P—OH), whereas the bands observed in the IR spectrum in the 1240–1100 cm^{-1} regions are ascribed to the δ (P—O—H) in plane bending with the γ (P—O—H) out of plane bending modes appearing in the range 930–820 cm^{-1}.

EXPERIMENTAL

Chemical Preparation

The title compound was prepared according to Eq. (2)

$$C_4H_9N + H_3PO_4 + ZnCl_2 \rightarrow Zn(HPO_4)Cl[C_4H_{10}N] + HCl \qquad (2)$$

by adding dropwise, under continuous stirring, an aqueous solution containing 5 g (36 mmol) of zinc chloride (Prolabo) to a mixture of 3 mL (36 mmol) of pyrrolidine (Across, d = 0.86) dissolved in water and 2.4 mL (36 mmol) of phosphoric acid (Fluka, 85% weight H_3PO_4, d = 1.7). A white precipitate was obtained, which was fully soluble in phosphoric acid. The so-obtained solution was slowly evaporated at r.t. until a formation of single crystals of $Zn(HPO_4)Cl[C_4H_{10}N]$ (5.3 g, 55% yield) with suitable dimensions for crystallographic study. The crystals are stable for months under normal conditions of temperature and humidity. The compound chemical formula was determined when resolving the crystal structure by X-ray diffraction.

Investigation Techniques

The title compound has been studied by various physico-chemical methods: X-ray diffraction, solid state NMR spectroscopy, infrared spectroscopy, and thermal analysis.

X-Ray Diffraction

The intensity data collection was performed using a $MACH_3$ Enraf Nonius diffractometer. The experimental conditions of data collection, the strategy followed for the structure determination, and final results are given in Table IV. The structure was solved by direct methods using the SIR92 program[22] and refined by full matrix least-squares techniques based on F, using teXsan.[23] The structure factors were obtained after a Lorentz-polarization correction. The positions of the heavier atoms, including the Zn atom, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps

TABLE IV Crystal Data and Experimental Parameters Used for the Intensity Data Collection Strategy and Final Results of the Structure Determination

I. Crystal data	
Formula: $Zn(HPO_4)Cl[C_4H_{10}N]$	$F_w = 267{,}93$
Crystal system: monoclinic $a = 24{,}83(9)$, $b = 9, 258(5)$, $c = 8{,}778(3)$ Å, $\beta = 110{,}45(4)^\circ$ $V = 1891{,}0(14)$ Å^3, $Z = 8$	Space group: C2/c
Refinement of unit-cell parameters with	25 reflection ($8, 22^\circ < \theta < 9, 77^\circ$)
$\rho_{cal.} = 1{,}882\ g \cdot cm^{-3}$	$F(000) = 1080{,}00$
Linear absorption factor: μ (MoK_α) = 3.025 cm^{-1}	Morphology: losangic prism
Crystal size (mm): $0, 11 \times 0, 03 \times 0, 015$	Color: transparent
II. Intensity Measurements	
Temperature: 296,2 K	Wavelength: MoK_α (0.7107 Å)
Diffractometer: Enraf-Nonius MACH 3	Scan mode: $\omega - 2\theta$
Monochromator: graphite plate	Theta range: 2,37–25,97°
Measurement area: $(\pm h, k, l)$	$h_{max} = 29; k_{max} = 10; l_{max} = 10$
Nb of scanned reflections	2625 ($R_{int} = 0{,}025$)
Nb of independent reflections	1570
Orientation and control reflections	1204 and 025
III. Structure determination	
Lorentz and polarization corrections	No absorption correction
Program used: TeXsan[23]	Determination : direct methods[22]
All the hydrogen atoms were located from difference Fourier maps.	
They are not refined.	
Unique reflections included: (1570 ($I > 3\sigma$))	Refined parameters: 140
Weighting scheme: σ	$R = 0{,}045$; $R_w = 0, 070$
Residual Fourier density: $-0{,}66$ Å^3 $< \rho < 0, 44$ Å^3	Esd(S): 1,83
Drawings made with Diamont[26]	Largest shift/error = 0.01

and least-square refinements. The positions of the hydrogen atoms were located directly from the difference Fourier maps. The drawings were made with Diamond.[24]

Crystallographic Data (CIF) for the structure reported in this article have been deposited in the Cambridge Crystallographic Data Center as supplementary publication No. 286851. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK (Fax: +44(1223)336-033; E-mail: deposit@ ccdc.cam.ac. uk).

NMR Spectroscopy

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 121.51 MHz for ^{31}P with a classical 4 mm probehead allowing spinning rates up to 10 KHz. ^{1}H and ^{13}C NMR chemical shifts are given relative to tetramethylsiline and ^{31}P ones relative to 85% H_3PO_4 (external references, precision 0.5 ppm). Both phosphorous and carbon spectra were recorded by the use of cross-polarization (contact time 5 ms) and with a one-pulse sequence and high power proton decoupling. ^{1}H NMR spectra were also recorded under static and MAS conditions.

Thermal Behavior

Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operating from r.t. up to 450°C at an average heating rate of $5^{\circ}C\,min^{-1}$.

IR Spectroscopy

Spectra were recorded in the range 4000–200 cm^{-1} with a Perkin-Elmer FTIR spectrophotometer 1000 using a sample dispersed in a spectroscopically pure KBr pellet.

CONCLUSION

The use of pyrrolidine as organic-structure directing agent leads to the 2-D zincophosphate of chemical formula $Zn(HPO_4)Cl[C_4H_{10}N]$. Its framework topology is similar to that of $Zn(HPO_4)Cl[C_5H_{12}N]$ synthesized in the presence of piperidinium as a structure-directing agent. The anionic part is built up from a two-dimensional network of vertex-linked HPO_4^- and ZnO_3Cl building units. The template molecule (pyrrolidine) occupies the space between the anionic layers and participates in strong hydrogen bonding with the inorganic framework. The existence of terminal Cl atoms and —OH groups leads to porous sheets containing four- and eight-membered rings within $[Zn(HPO_4)Cl]^-$ layers. Compared to other metalphosphates, these layers can be related to the structure type 488, which was previously seen in many zincophosphates,[5,25,26] aluminophosphates (AlPO-12),[27] and gallophosphates ($GaPO_4$-14).[28] Solid state ^{31}P and ^{13}C MAS NMR spectroscopies are in agreement with the X-ray structure. Upon heating, this new zincophosphate is stable until 566 K. It undergoes a reversible phase at 445 K and the loss of H_2O molecule from 540 K, and the loss of HCl and pyrrolidine molecules occurs between 560 K and 775 K. After heating at 775 K, the amorphous material gives $Zn_2P_2O_7$ characterized elsewhere.

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