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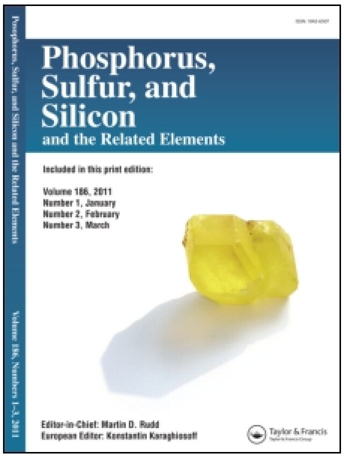

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Synthesis and Characterization of a New Chlorozincophosphate $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$

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Synthesis and Characterization of a New Chlorozincophosphate $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$

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A new zincophosphate $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$, was obtained at room temperature from a starting mixture of $ZnCl_2$, H_3PO_4, H_2O, and ethylene-diamine. Its unit cell is tricline P-1 (No. 2) with parameters $a = 7.709(2)$ Å, $b = 8.479(2)$ Å, $c = 5.175(2)$ Å, $\alpha = 104.99(3)$, $\beta = 107.41(4)$, $\gamma = 87.34(2)^\circ$, $Z = 2$, and $V = 311.6(2)$ Å^3. Its structure is resolved to $R = 0.024$, $Rw = 0.037$. The backbone of the title compound is a linear heteroanion built by PO_4 and ZnO_3Cl tetrahedra assembled to form four member rings themselves interconnected by sharing common oxygen atoms. Hydrogen bonds O—H···O established between these chains connect them as to build infinite planes. The organic entities, located between these planes form the 3D cohesion through N—H···O or N—H···Cl hydrogen bonds.

Keywords NMR spectroscopy; organic template; X-ray diffraction; zincophosphate

1. INTRODUCTION

Open-framework metal phosphates are an important class of materials. Their studies exhibit a particular interest due to their great potential applications in catalysis,[1] molecular sieving,[2] electronic area,[3] and photochemical and photophysical processes.[4] Several of them include heteroanions, built from MO_n ($n = 4, 5, 6$, and M: Al, Ga, Fe, Co, Zn ···) polyhedra and PO_4 tetrahedra in the presence of organic amine as structure directing agent have been reported.[5–12] The use of the reactional mixture ZnO, P_2O_5, amine, H_2O, with different molar composition enabled Wallau et al.[13] to prepare five new compounds at room temperature. The addition of chloride to this latter mixture (ZnO($ZnCl_2$), P_2O_5 (H_3PO_4), amine, HCl, H_2O) under the same conditions allow us new synthesis in

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acidic medium. Using this method, chloride ions are also involved in the structure of the framework and lead to a new serie of chlorozincophosphate with new geometries. Up to now, the literature reports only two organically metal-phosphate containing the Cl^- ion in the framework structure, $[C_6NH_{14}]Zn(HPO_4)Cl$[14] and $[C_5H_{10}NH_2]Zn(HPO_4)Cl$.[15] This work reports synthesis and crystal structure determination of a new 1-D chlorozincophosphate $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$, obtained in aqueous medium. The characterization by ^{31}P and ^{13}C solid state NMR spectroscopy is also reported.

2. RESULTS AND DISCUSSION

2.1. Description of the Structure

Final atomic coordinates and thermal parameters for $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$ are listed in Table I, with selected bond distances and angle data in Table II.

The structure of the title compound consists of infinite zincophosphate chains of formula $[Zn(HPO_4)Cl]_n^{n-}$. These chains are built up from edge-sharing PO_4 and ZnO_3Cl tetrahedra to form four member rings, with strictly alternating Zn and P nodes. Charge balance is achieved by the diprotonated 1,2-diaminoethane cations (Figure 1).

TABLE I Final Atomic Coordinates and Thermal Parameters in $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$

Atom	x(σ)	y(σ)	z(σ)	B_{eq}
Zn	0.803375(12)	0.372100(11)	0.65146(2)	1.075(2)
Cl	0.66565(3)	0.12950(3)	0.40040(5)	1.682(4)
P	1.23479(3)	0.41761(3)	0.78545(4)	0.945(3)
O(1)	1.06193(9)	0.33404(9)	0.7710(2)	1.692(11)
O(2)	1.38341(9)	0.28993(9)	0.8650(2)	1.643(11)
O(3)	1.27979(9)	0.57861(9)	1.0123(1)	1.407(10)
O(4)	1.23848(11)	0.44093(9)	0.5050(1)	1.656(11)
N	0.77154(12)	0.88879(11)	0.8332(2)	1.749(13)
C	0.96773(13)	0.92337(12)	0.8838(2)	1.63(1)
H(1)	0.7478	0.7918	0.7252	0.650
H(2)	0.7242	0.9202	0.9710	0.650
H(3)	0.7004	0.9615	0.7442	0.650
H(4)	0.9827	0.9326	0.6955	0.650
H(5)	1.0388	0.8219	0.9335	0.650
H(6)	1.4913	0.3254	0.9146	0.650

$B_{eq.} = 4/3\ \Sigma_i \Sigma_j \beta_{ij}\ a_i b_j$; Esd are given in parentheses.

TABLE II Interatomic Bond Distances (Å) and Angles (Å) in $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$

The HPO_4 Tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.5113(10)	2.409(2)	2.532(2)	2.540(2)
O(2)	102.52(6)	1.5771(11)	2.493(2)	2.535(2)
O(3)	112.83(6)	109.48(6)	1.5276(11)	2.511(2)
O(4)	113.63(7)	107.03(6)	110.80(6)	1.5234(12)
O(2)—H(O2) = 0.84			P—O(2)—H(2) = 114.9	
The ZnO_3Cl tetrahedron				
Zn	O(1)	O(3)	O(4)	Cl
O(1)	1.9404(11)	3.1472(2)	3.172(2)	3.359(2)
O(3)	107.17(6)	1.9696(12)	3.166(2)	3.314(2)
O(4)	110.01(5)	108.47(5)	1.9319(11)	3.6280(12)
Cl	106.52(4)	103.46(4)	112.82(3)	2.2454(9)
Zn—O(1)—P 136.32(7)	Zn—O(3)—P 123.50(6)	Zn—O(4)—P 132.32(6)		

Esd are given in parentheses.

Both zinc and phosphorus atoms are tetrahedrally coordinated. The single distinct zinc atom makes three connections via oxygen to phosphorus atoms and has one terminal Zn—Cl vertex. On the other hand, the only distinct P atom is surrounded by four oxygen atoms, among them, three are involved in Zn—O—P bridges, the other one is part of P—OH groups.

Bond lengths and angles are in good agreement with those found in other zincophosphates containing similar polyhedra ($Zn—O_{av} = 1.947(1)$ Å, Zn—Cl = 2.2460(5) Å, and $P—O_{av}$ = 1.533(1) Å. For example, in $[C_5H_{12}N]Zn(HPO_4)Cl$ [15] [$Zn—O_{av}$ = 1.940(2) Å, Zn—Cl = 2.249(1) Å and $P—O_{av}$ = 1.534(2) Å)]. Three oxygens of the $PO_3(OH)$ unit are involved in bridging to ZnO_3Cl units while the other one has a significantly longer bond length (P—O(2) = 1.576(1) Å) suggesting that oxygen O(2) is protonated.

The anionic part $[Zn(HPO_4)Cl]^-$ appears as an infinite ribbon whose repeating unit is a centrosymmetrical ring built by two PO_4 tetrahedra and two ZnO_3Cl tetrahedra connected by common oxygen atoms. These rings are themselves connected by sharing oxygen atoms to build infinite ribbons spreading parallel to the c axis. The period of such a ribbon is $[Zn_2P_2O_8Cl_2H_2]^{2-}$. These ribbons developed around (0, $^1/_2$, z) axis are connected by hydrogen bonds O(2)—H$\cdots$O(3) in the a direction (Figure 2).

The organic molecules located around the symmetrical center (0, 0, 0) participate in the network cohesion through N—H$\cdots$O and N—H$\cdots$Cl hydrogen bonds. Distances H$\cdots$Cl vary between 2.5 and 2.6 Å. These

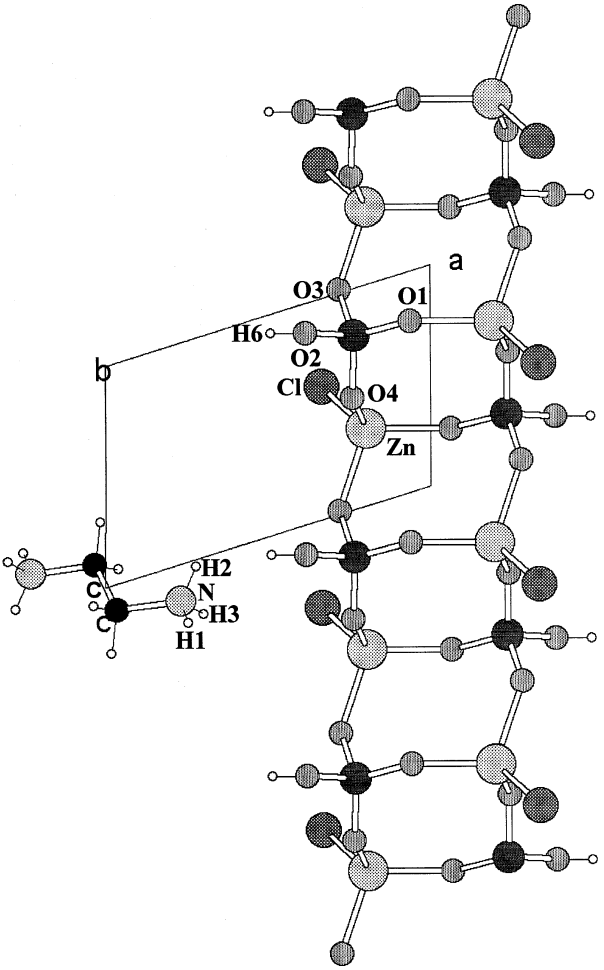

FIGURE 1 View of the $[Zn(HPO_4)Cl^-]_n$ unit along the a axis showing the one-dimensional chains for the title compound.

values are smaller than the sum of the radii of Van Der Waals of the chlorine and of hydrogen atoms ($r_{Cl} + r_H \leq 2.81$ Å); consequently these values correspond well to strong hydrogen bonds. The hydrogen bond scheme is described in Table III.

2.2. NMR Results

The ^{31}P MAS NMR spectrum reported in Figure 3 displays only one peak at 3.8 ppm corresponding to the only one crystallographic phosphorus site. Such a chemical shift value agrees with those corresponding

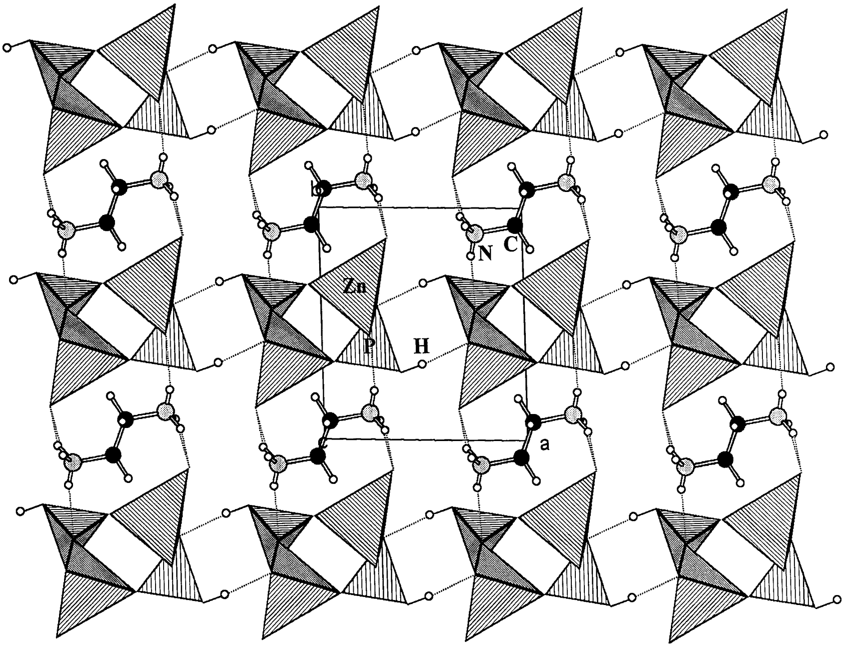

FIGURE 2 View of the $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$ unit along the a axis showing the symmetrical inter-chain hydrogen bonds to form a two-dimensional zincophosphate structure and the location of the template molecules (hydrogen atoms and chain-diamine H-bonds not shown).

to monophosphates (between −10 and +5 ppm).[16–22] The experiment with the high-power proton decoupling (Figure 4) induces a decrease of the width for the signal ($\Delta\nu_{1/2} = 110$ Hz versus $\Delta\nu_{1/2} = 700$ Hz). This proves that phosphorus atoms are close to protons.

The spectrum recorded by use of cross polarization from protons (Figure 5) induces an important increasing of the signal intensity due to the polarization transfer of protons to phosphorus atoms. This proves the presence of hydrogen near these atoms and confirms the existence of HPO_4^{2-} entities in the structure of this compound.

TABLE III Hydrogen Bond Scheme in $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$

D—H···A	D—H (Å)	H···A (Å)	A···D (Å)	DHA (°)
O(2)—H(6)···O(3)	0.84	1.87	2.702(2)	171.9
N—H(1)···O(4)	0.86	2.04	2.880(2)	165.4
N—H(2)···Cl	0.87	2.60	3.410(2)	154.2
N—H(3)···Cl	0.93	2.50	3.311(2)	146.2

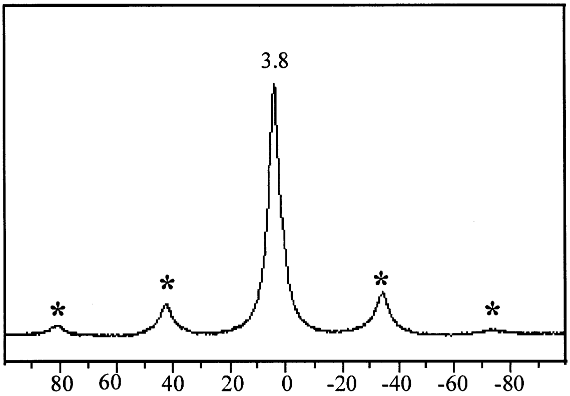

FIGURE 3 ^{31}P MAS–NMR spectrum of $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$. *Spinning side bands.

The ^{13}C CP-MAS NMR spectrum (Figure 6) of this compound is in good agreement with the X-ray structure. Indeed it exhibits a single resonance peak at 38.1 ppm corresponding to the only one crystallographic site.

2.3. Thermal Analysis

$[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$ is transformed by heating into diphosphate according to the following reaction:

$$2[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl \rightarrow Zn_2P_2O_7 + H_2O + ClH_3N(CH_2)_2NH_3Cl$$

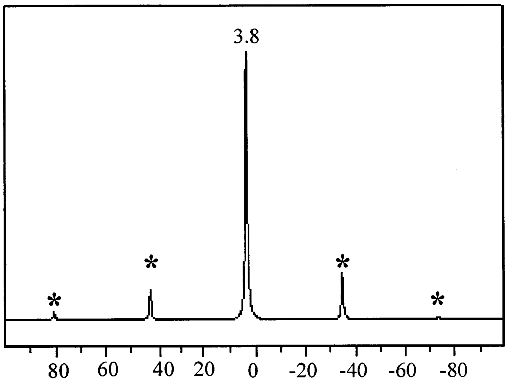

FIGURE 4 ^{31}P MAS with high decoupling NMR spectrum of $[H_3N(CH_2)_2$-$NH_3]_{0.5}Zn(HPO_4)Cl$. *Spinning side bands.

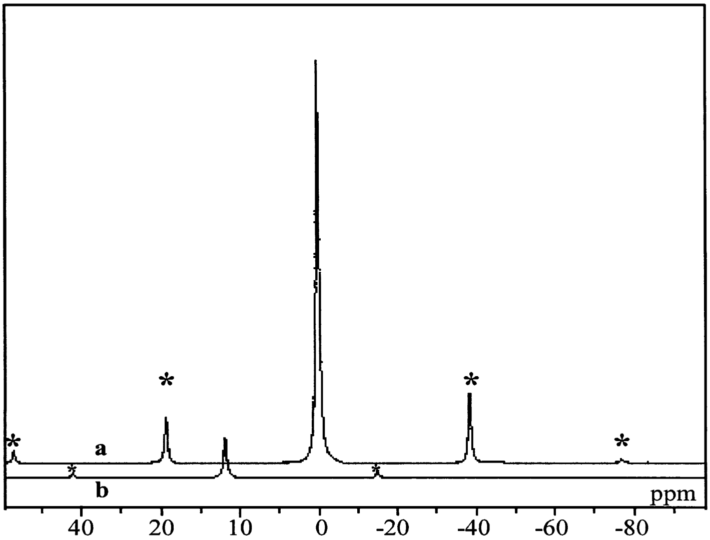

FIGURE 5 ^{31}P MAS–NMR spectrum of $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$. (a) with cross polarization; (b) without cross polarization of proton. Contact time = 5 ms and number of scans = 200. *Spinning side bands.

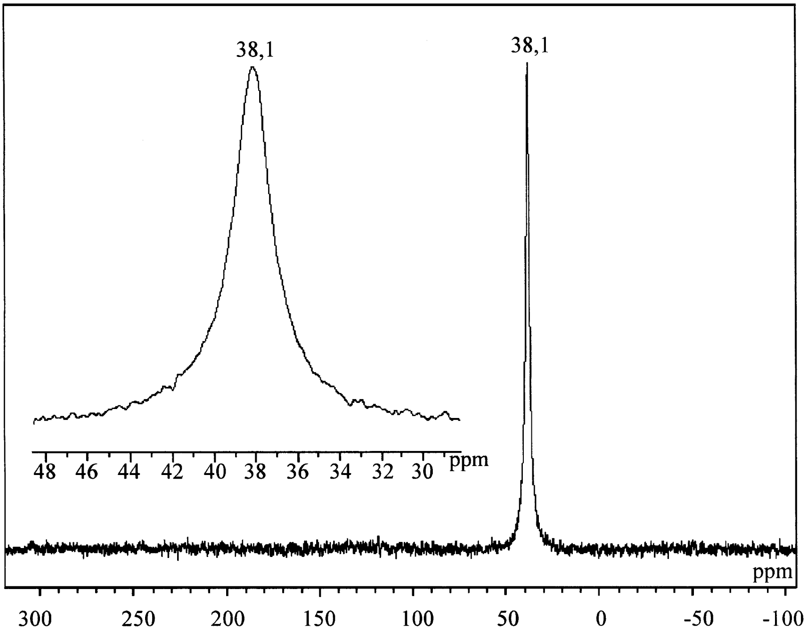

FIGURE 6 ^{13}C CP MAS–NMR spectrum of $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$.

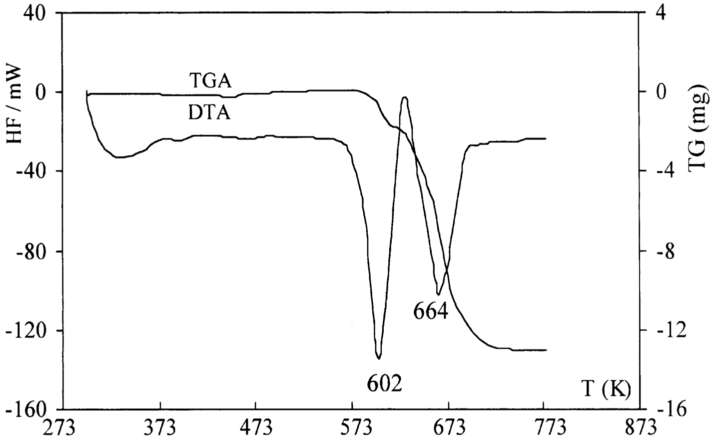

FIGURE 7 DTA and TGA curves of $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$ at rising temperature.

Two curves corresponding to DTA and TGA analysis, under argon atmospheric, are reported in (Figure 7). The DTA curve shows two significant endothermic peaks about 602 K and 664 K. The TGA curve shows an important weight loss corresponding to these peaks. The first phenomenon produced at 602 K probably corresponds to the removal of one H_2O molecule arising from dehydroxylation reaction due to the presence of terminal P—OH groups (weight loss calculated 4%, experimental 3.94%). The second weight loss produced at 664 K could be assigned to a sublimation[23] and a decomposition of ethan-diammonium chloride. The remaining substance is viscous and contains a carbon black residue. This latter can be eliminated by calcination of the sample at 1100 K in air. The calcination product has a X-ray diffractogram in good agreement with that of $Zn_2P_2O_7$.[24]

2.4. IR Absorption Spectroscopy

Infrared absorption spectrum (Figure 8) of the title compound shows the bands corresponding to vibrations of ethane-diammonium cation and HPO_4^{2-} anion. The stretching vibrations of the $-CH_2-$ groups appear in the 2950–2860 cm^{-1} region and the bending modes are observed in the 1565–1454 cm^{-1} range. The stretching and bending modes of NH_3^+ groups appear at ca. 3158 cm^{-1} and 1607 cm^{-1} respectively. They are indicative of the presence of the ethane-diammonium molecule in its protonated form.[25,26] The absorption bands in the range 1220–1020 cm^{-1} correspond to the stretching vibrations modes of C—C and C—N. In this case, these bands are difficultly assigned because of their

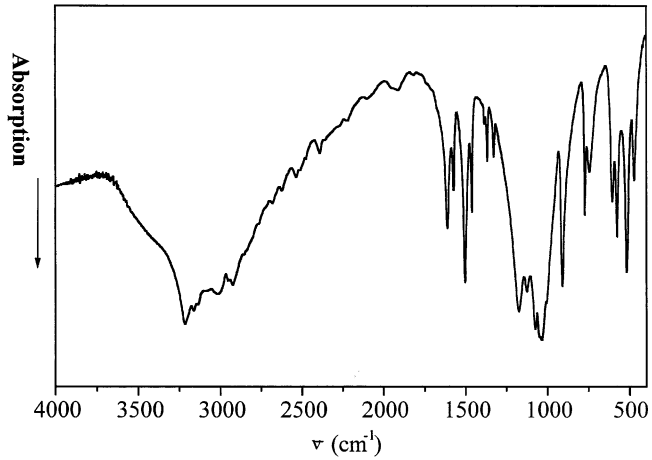

FIGURE 8 IR spectra of $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$.

possible overlapping with asymmetric $\nu_3(F_2)$ stretching vibrations of PO_4^{3-} group. Various valence and bending vibration bands whose number and positions, between 1200 and 300 cm^{-1}, are both characteristic of a PO_4 tetrahedral.[27] In this case, the stretching vibrations bands originate from both symmetric $\nu_1(A_1)$ and asymmetric $\nu_3(F_2)$ modes are respectively observed in the ranges (1000–800) and (1200–1000) cm^{-1}. On the other hand, the bending vibration bands originates from both symmetric $\nu_4(F_2)$ and asymmetric $\nu_2(E)$ modes appear respectively in the (650–500) and (500–300) cm^{-1} regions.

3. EXPERIMENTAL

3.1. Chemical Preparation

The title compound was prepared at room temperature by adding 11.2 g of H_3PO_4 to a solution of 6.2 g of ethylene-diamine in 80 ml of water. To this solution is added dropwise an aqueous solution of 13.6 g of zinc chlorine in 80 ml of water under continuous stirring. A white precipitate is formed and then we added a phosphoric acid until it disappears. Schematically the reaction can be written as follows.

$$H_3PO_4 + 0.5NH_2(CH_2)_2NH_2 + (Zn^{2+}, 2Cl^-)$$
$$\rightarrow [H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl + HCl$$

The obtained solution is slowly evaporated at room temperature until the formation of large prismatic-shaped crystals of the title compound.

3.2. Investigation Techniques

3.2.1. X-Ray-Diffraction

A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. Intensity data were collected on an Enraf-Nonius MACH3 automated four-circle diffractometer using graphite monochromated $AgK_{\bar{\alpha}}$ radiation,_ = 0.5608 Å. The structure was solved by direct methods.[28] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms position were located by difference-Fourier synthesis and not refined. All calculations were performed using the teXsan[28] crystallographic software package. Crystal data and experimental parameters used for the intensity data collection are summarized in Table IV.

Crystallographic Data (CIF) for the structure reported in this paper has been deposited in to the Cambridge Crystallographic Data Center as supplementary publication No. 197399. Copies of the data can be

TABLE IV Crystal Data and Experimental Parameters Used for the Intensity Data Collection

Empirical formula	$[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$
Formula Weight	227.87
Crystal system	Triclinic
Space group	P-1
a	7.709(2) Å
b	8.479(2) Å
c	5.175 (2)Å
α	104.99(3)°
β	107.41(4)°
δ	87.34(2)°
Z	2
V	311.6(2) Å^3
$\rho_{cal.}$	2.429 g.cm^{-3}
F(000)	226
$\mu(AgK_{\bar{\alpha}})$	2.377 (cm^{-1})
Crystal size [mm]	0.24 ↔ 0.20 ↔ 0.18
Index ranges: ±h, ±k, 1	$h_{max} = 11$, $k_{max} = 12$, $I_{max} = 7$
Collected reflexions	2437
Independent reflexions	2225
Unique reflections included	1904 [$I > 3\sigma(I)$]
R_{int}	0.0068
Refined parameters	82
R ($I > 3\sigma(I)$)	0.024
R_w	0.037
Goodness of fit	1.666

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^2$.

obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK (Fax: +44(1233)336-033; E-mail: deposit@ ccdc.cam.ac.uk).

3.2.2. Physical Measurements

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 and equipped with a classical 4 mm probehead allowing spinning rates up to 10 KHz. ^{13}C NMR chemical shifts are given relative to tetramethylsilane and ^{31}P ones relative to 85% H_3PO_4 (external references, precision 0.5 ppm).

Thermal Analysis. Thermal analysis was performed using the multimodule 92 Setaram analyzer operating from room temperature up to 500°C at average heating rate of 5°C/min under argon.

Infrared Spectroscopy. Spectrum is recorded in the range 4000–200 cm^{-1} with a Perkin Elmer FT-IR spectrometer 1000 using a sample dispersed in spectroscopically pure KBr pellets.

CONCLUSION

The title compound $[H_3N(CH_2)_2NH_3]_{0.5}Zn(HPO_4)Cl$ was prepared under normal conditions of pressure and temperature, whereas the known zincophosphates are generally prepared by hydrothermal methods. On the structural level, this compound is different from the known zincophosphates by its anionic framework, where one oxygen atom of ZnO_4 tetrahedron is substituted by a chlorine atom, which led to strong hydrogen bonds and consequently to a heat-resisting material until to 569 K.

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