

# $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$ clusters and $\infty[\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2]^{4-}$ layers in two new zinc phosphates templated by $[\text{H}_2(4\text{-amino-2.2.6.6-tetramethylpiperidine})]^{2+}$ cations

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## Abstract

Two zinc phosphates (ZnPO),  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**) and  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**), are synthesized under hydrothermal conditions using 4-amino-2.2.6.6-tetramethylpiperidine as organic template. **I** crystallizes in  $P\bar{1}$  space group with  $a = 8.7398(3) \text{ \AA}$ ,  $b = 9.0417(3) \text{ \AA}$ ,  $c = 15.3822(1) \text{ \AA}$ ,  $\alpha = 92.57(1)^\circ$ ,  $\beta = 89.76(1)^\circ$ ,  $\gamma = 102.16(2)^\circ$ ,  $V = 1187.1(1) \text{ \AA}^3$  and  $Z = 2$ . Its structure, refined to  $R = 0.029$  and  $R_w = 0.076$  for 4279 independent reflections, consists of  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  clusters held together through strong hydrogen bonds to form pseudo-layers between which the doubly protonated amine molecules are inserted. **II** is monoclinic,  $C2$ , with  $a = 27.57(2) \text{ \AA}$ ,  $b = 9.745(5) \text{ \AA}$ ,  $c = 14.08(1) \text{ \AA}$ ,  $\beta = 103.72(5)^\circ$ ,  $V = 3675(4) \text{ \AA}^3$  and  $Z = 4$  ( $R = 0.079$ ,  $R_w = 0.268$ , 2477 independent reflections). The structure of **II** consists of  $\infty[\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2]^{4-}$  inorganic (2D) layers built up from vertex-sharing  $[\text{ZnO}_4]$  and  $[(\text{H}_2/\text{H})\text{PO}_4]$  tetrahedra. Organic cations and water molecules ensure the connection between these layers via hydrogen bonds. It is shown that numerous (1D), (2D), e.g.,  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ , and (3D) (ZnPO) result from the condensation of the  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  clusters.

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**Keywords:** Hydrothermal synthesis; Amine; Zinc phosphates; Crystal structure

## 1. Introduction

During the past decade, the interest in the field of open-framework metal phosphates, in particular those of zinc, has considerably increased, as a reason of their potential catalytic activities and their rich structural chemistry [1–4]. Thus, more than 80 phases of organically templated zinc phosphates (ZnPO) have been prepared and characterized [5]. Their structures are based on various zero-, one-, two- or three-dimensional inorganic networks. The 3D channel architectures are

frequent while isolated clusters are rare. Until now, only four (ZnPO) clusters are reported in  $[\text{N}(\text{CH}_3)_4] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_3]$  [1],  $[(\text{NC}_5\text{H}_5)(\text{N}_2\text{C}_4\text{H}_{10})] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$  [2],  $[\text{N}_2\text{C}_6\text{H}_{18}] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$  [6] and  $[\text{N}_4\text{C}_6\text{H}_{21}] \cdot [\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$  [7]. The frameworks are built up from similar isolated  $[\text{Zn}_2(\text{H}_2/\text{HPO}_4)_6]^{4-}$  octamers, formed of  $[\text{Zn}_2(\text{H}_2/\text{HPO}_4)_2]$  four membered-ring (S4R) with terminal  $[(\text{H}_2/\text{H})\text{PO}_4]$  moieties hanging from the  $[\text{ZnO}_4]$  tetrahedra. In the present work, we report on the synthesis, the characterization and the crystal structures of two new organically templated ZnPO:  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**) and  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**) with 0D and 2D inorganic networks, respectively.

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## 2. Experimental

### 2.1. Synthesis

$[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**) and  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**) were synthesized by hydrothermal synthesis from  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}/\text{H}_3\text{PO}_4/4$ -amino-2.2.6.6-tetramethylpiperidine/water(or ethanol) in the molar ratio (1/7/2.5/~200) and (1/4.33/4/~34), respectively. **I** is prepared as good-quality crystal in an aqueous medium after 36 h of reaction at 393 K in 11 mL

Teflon-lined autoclave (filling factor 45%). The XRD pattern of this compound is entirely consistent with the pattern simulated from the coordinates of the single-crystal study (Fig. 1).

**II** is obtained as colourless crystal which grows with an unidentified powder after 2 h of microwave heating at 463 K in ethanol. Whatever the synthesis conditions, **II** appears as a minor part of the mixture and therefore prevents from any quantitative analysis and TGA experiments. Furthermore, the crystals are small and systematically twinned. Numerous tests in Teflon-lined

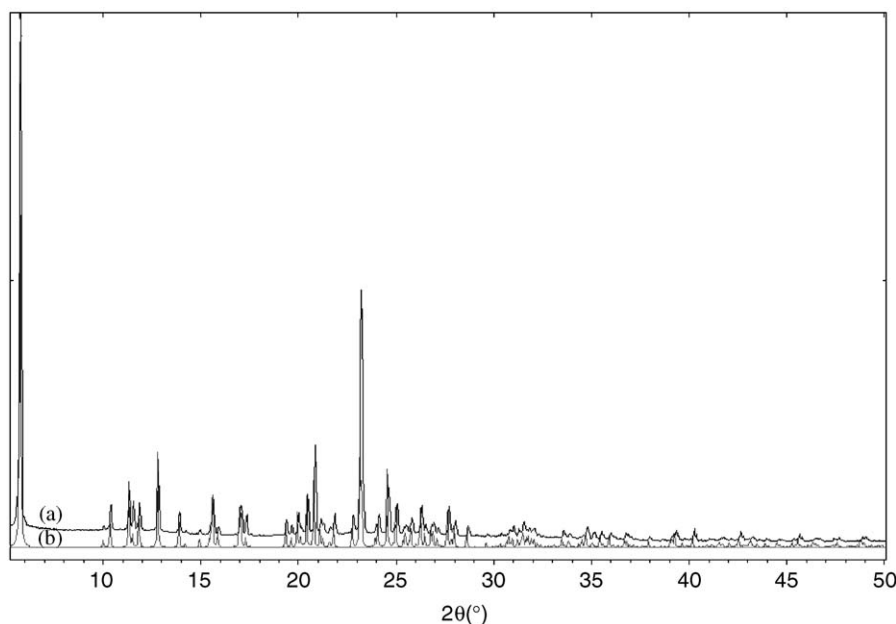


Fig. 1. X-ray powder diffraction pattern of  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$ : (a) experimental; and (b) simulated.

Table 1

Crystal data, intensity measurements and refinement parameters for **I** and **II**

	<b>I</b>	<b>II</b>
Formula	$[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$	$[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$
Molecular weight ( $\text{g} \cdot \text{mol}^{-1}$ )	611.62	947.23
Space group	$\bar{1}$ (No. 2)	C2 (No. 5)
$a$ (Å), $b$ (Å), $c$ (Å)	8.7398(3), 9.0417(3), 15.3822(1)	27.57(2), 9.745(5), 14.08(1)
$\alpha$ (°), $\beta$ (°), $\gamma$ (°)	92.57(1), 89.76(1), 102.16(2)	103.72(5)
Volume (Å <sup>3</sup> ), $Z$	1187.1(1), 2	3675(4), 4
$\rho_{\text{calc}}$ ( $\text{g} \cdot \text{cm}^{-3}$ )	1.711	1.61
Diffractometer, $T$ (K)	Enraf–Nonius CAD4	Siemens AED2, 293 (2)
Radiation (graphite monochromated)	$\text{MoK}\alpha$ 0.71073 Å	
Scan mode	$\omega-2\theta$	
$hkl$ min–max	$0 \leq h \leq 11$ , $-11 \leq k \leq 11$ , $-19 \leq l \leq 19$	$-32 \leq h \leq 32$ , $-11 \leq k \leq 11$ , $-16 \leq l \leq 16$
Absorption correction ( $A_{\text{min}}$ , $A_{\text{max}}$ )	$\psi$ scan (0.724, 0.874)	Gauss (0.856, 0.984)
$2\theta$ limit (°)	54	50
Number of independent reflections	4279 ( $I > 2\sigma(I)$ )	2477 ( $I > 4\sigma(I)$ )
Number of refined parameters	299	303
Flack parameter		0.01(5)
Final $R/R_w$ indices	0.029/0.076	0.079/0.268
Goodness of fit on $F^2$	1.069	1.372

autoclaves in different preparation conditions (time of reaction, temperature, etc.) did not improve their quality.

Table 2  
Atomic coordinates and equivalent isotropic displacement parameters in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**)

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{eq.}}(\sigma)(\text{\AA}^2)$
Zn	0.09833(3)	0.27773(3)	0.35540(2)	1.446(8)
P(1)	0.24206(7)	0.01929(6)	0.42466(4)	1.48(2)
P(2)	-0.24790(7)	0.35374(6)	0.38883(4)	1.58(2)
P(3)	0.36051(7)	0.57288(6)	0.34066(4)	1.70(2)
P(4)	0.21756(8)	0.18138(8)	0.16152(4)	2.13(2)
O(1)	0.1552(2)	-0.1284(2)	0.3854(1)	2.21(4)
O(2)	0.1507(2)	0.1414(2)	0.4391(1)	2.38(4)
O(3)	0.3140(2)	0.0042(2)	0.5169(1)	2.00(4)
O(4)	0.3865(2)	0.0749(2)	0.3631(1)	2.30(4)
O(5)	-0.1189(2)	0.2724(2)	0.3723(1)	2.87(5)
O(6)	-0.3042(2)	0.3950(2)	0.2994(1)	2.64(6)
O(7)	-0.3810(2)	0.2606(2)	0.4401(1)	1.87(4)
O(8)	-0.1881(3)	0.5101(2)	0.4397(1)	2.93(5)
O(9)	0.2277(2)	0.4760(2)	0.3899(1)	2.45(4)
O(10)	0.4873(2)	0.6543(3)	0.4079(1)	3.59(5)
O(11)	0.2978(3)	0.6945(2)	0.2918(1)	3.62(5)
O(12)	0.4414(2)	0.4884(2)	0.2749(1)	2.23(4)
O(13)	0.1306(2)	0.1023(2)	0.0836(1)	2.71(4)
O(14)	0.1186(2)	0.2004(2)	0.2394(1)	2.79(5)
O(15)	0.3105(3)	0.3389(3)	0.1323(1)	4.76(6)
O(16)	0.3431(3)	0.0907(4)	0.1875(1)	5.24(7)
N(1)	0.8569(2)	0.8638(2)	0.0925(1)	1.94(5)
N(2)	0.8269(2)	0.8001(2)	0.3636(1)	1.96(5)
C(1)	0.9000(3)	0.7184(3)	0.1215(1)	2.20(6)
C(2)	0.9245(3)	0.7367(3)	0.2200(1)	2.05(6)
C(3)	0.7874(3)	0.7811(3)	0.2684(1)	1.74(5)
C(4)	0.7551(3)	0.9288(3)	0.2362(1)	2.02(6)
C(5)	0.7237(3)	0.9222(3)	0.1377(2)	2.19(5)
C(6)	0.5633(3)	0.8235(4)	0.1115(2)	3.33(7)
C(7)	0.7336(4)	1.0829(3)	0.1071(2)	3.33(8)
C(8)	0.7760(4)	0.5776(3)	0.0937(2)	3.43(8)
C(9)	0.0555(4)	0.7103(3)	0.0769(2)	3.29(7)

Table 3  
Selected inter-atomic distances ( $\text{\AA}$ ) in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**)

[ZnO <sub>4</sub> ] tetrahedron		[P(1)O <sub>4</sub> ] tetrahedron		[P(2)O <sub>4</sub> ] tetrahedron	
Zn–O(2)	1.942(2)	P(1)–O(1)	1.493(2)	P(2)–O(5)	1.486(2)
Zn–O(5)	1.906(2)	P(1)–O(2)	1.501(2)	P(2)–O(6)	1.551(2)
Zn–O(9)	1.960(2)	P(1)–O(3)	1.578(2)	P(2)–O(7)	1.524(2)
Zn–O(14)	1.909(2)	P(1)–O(4)	1.583(2)	P(2)–O(8)	1.574(2)
[P(3)O <sub>4</sub> ] tetrahedron		[P(4)O <sub>4</sub> ] tetrahedron			
P(3)–O(9)	1.520(2)	P(4)–O(13)	1.492(2)		
P(3)–O(10)	1.561(2)	P(4)–O(14)	1.499(2)		
P(3)–O(11)	1.551(2)	P(4)–O(15)	1.567(3)		
P(3)–O(12)	1.503(2)	P(4)–O(16)	1.565(3)		
[N <sub>2</sub> C <sub>9</sub> H <sub>22</sub> ] <sup>2+</sup> cation					
N(1)–C(1)	1.527(3)	C(1)–C(2)	1.526(3)	C(5)–C(4)	1.538(3)
N(1)–C(5)	1.529(3)	C(1)–C(8)	1.534(4)	C(5)–C(6)	1.539(4)
N(2)–C(3)	1.500(3)	C(1)–C(9)	1.534(4)	C(5)–C(7)	1.532(4)
C(3)–C(2)	1.523(4)				
C(3)–C(4)	1.526(4)				

## 2.2. Thermal analysis

TGA measurements were performed on a “Multi-module 92 Setaram Analyser” under argon flow with a heating rate of  $5 \text{ K} \cdot \text{min}^{-1}$  between room temperature and 773 K.

## 2.3. Structure determination

The structures of **I** and **II** were determined by single-crystal X-ray diffraction. Intensity data were respectively collected on an Enraf–Nonius CAD4 and a Siemens AED2 four-circle diffractometer. Lorentz and polarization effects were taken into account and absorption was corrected by the  $\psi$ -scan method [8] for **I** and by the Gauss Method for **II** (SHELX-76 program [9]). Crystallographic data and some details of the refinements are summarized in Table 1.

The structure refinement of **I** was carried out in the centrosymmetric  $P\bar{1}$  space group. The heavy Zn and P atoms were first located by direct methods (SHELXS-97 program [10]). The O, C and N atoms were then deduced from Fourier difference maps (SHELXL-97 program [11]) and distance considerations. All the hydrogen atoms were located in the difference Fourier maps, but during the refinement, the hydrogen atoms were placed geometrically and an overall  $U_{\text{iso}}$  was fixed to  $0.05 \text{ \AA}^2$ . All non-hydrogen atoms were refined anisotropically and the reliability factors converged to  $R = 0.029$ ,  $R_w = 0.076$  for 4279 independent reflections ( $I > 2\sigma(I)$ ) and 299 refined parameters.

The crystal cell of **II** was first found to be monoclinic with no systematic extinctions and all attempts of structure determination in the  $P2/m$ ,  $Pm$  and  $P2$  space groups failed. Then, the presence of poorly centred reflections indicated that the crystal was twinned. Using the  $(\bar{2}01)$  plane, twin resolution permitted to conclude

Table 4  
Hydrogen bond scheme in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**)

N(O)–H...O	H...O (Å)	N(O)...O (Å)	N(O)HO (°)
O(11)–H(11)...O(1) <sup>i</sup>	1.80	2.610(3)	169.5
O(10)–H(10)...O(7) <sup>ii</sup>	1.85	2.655(2)	167.4
O(3)–H(3)...O(7) <sup>iii</sup>	1.89	2.692(2)	164.8
O(4)–H(4)...O(7) <sup>iv</sup>	1.78	2.598(2)	172.3
O(6)–H(6)...O(12) <sup>v</sup>	1.80	2.574(2)	157.8
O(8)–H(8)...O(9) <sup>ii</sup>	1.84	2.643(3)	167.0
O(16)–H(16)...O(4)	1.94	2.744(3)	168.5
O(15)–H(15)...O(12)	1.84	2.655(3)	173.8
N(2)–H(2A)...O(3) <sup>viii</sup>	2.18	2.939(3)	143.5
N(2)–H(1B)...O(1) <sup>vi</sup>	2.13	2.823(3)	133.9
N(2)–H(1C)...O(8) <sup>iv</sup>	2.04	2.897(3)	161.7
N(2)–H(2C)...O(13) <sup>vii</sup>	1.91	2.738(3)	152.6
N(2)–H(2D)...O(13) <sup>vi</sup>	1.98	2.871(3)	168.5

Symmetry codes: i =  $x, y + 1, z$ ; ii =  $-x, -y + 1, -z + 1$ ; iii =  $-x, -y, -z + 1$ ; iv =  $x + 1, y, z$ ; v =  $x - 1, y, z$ ; vi =  $x + 1, y + 1, z$ ; vii =  $-x + 1, -y + 1, z$ ; viii =  $-x + 1, -y + 1, -z + 1$

that the Bravais network is C centred. Owing to the very small size of the crystal, numerous reflections were very weak and the reflections with  $I > 4\sigma(I)$  were only used. A convenient structure solution with correct distances and angles was then obtained in  $C2$  space group ( $R = 0.079$ ,  $R_w = 0.268$  for 2477 for independent reflections and 302 refined parameters); however, the reliability factors remained high.

The atomic coordinates, selected interatomic distances, and hydrogen bond scheme are reported in Table 2, Table 3 and Table 4 for **I** and Table 5, Table 6 and Table 7 for **II**, respectively. These final atomic coordinates and thermal parameters are deposited at the Cambridge Crystallographic Centre (CCDC 244071 **I**; CCDC 261201 **II**).

### 3. Results and discussion

#### 3.1. Description of the structures and discussion

In **I** and **II**, the 4-amino-2.2.6.6-tetramethylpiperidine molecules are doubly protonated and adopt a chair-like geometry (Fig. 2). The C–C and C–N distances have similar values in both compounds (Tables 3 and 6); they are in good agreement with those observed in other cyclic amine cations.

The Zn–O distances and the O–Zn–O bond angles are in the range [1.906(2)–1.960(2) Å; 104.55(8)–117.86(8)°] and [1.86(2)–1.97(2) Å; 100.1(8)–117.2(9)°] for **I** and **II**, respectively which clearly indicate that zinc atoms are in regular tetrahedral environments. The  $[(\text{H}_2/\text{H})\text{PO}_4]$  entities have tetrahedral geometries with P–O and P–OH distances ranging from 1.486(2) to 1.524(2) Å and 1.551(2) to 1.583(2) Å in **I** and from 1.48(2) to

Table 5  
Atomic coordinates and equivalent isotropic displacement parameters in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**)

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{eq}}$ (Å <sup>2</sup> )
Zn(1)	0.7095(1)	0.8868(3)	0.9112	2.4(1)
Zn(2)	0.7988(1)	0.6122(3)	0.6224(3)	2.39(9)
P(1)	0.7846(2)	1.1287(8)	0.9361(5)	1.6(1)
P(2)	0.5980(3)	0.8494(7)	0.8173(7)	2.8(2)
P(3)	0.7401(3)	0.3973(9)	0.4747(7)	4.7(3)
P(4)	0.9089(3)	0.7400(8)	0.6730(6)	2.3(2)
P(5)	0.7852(3)	0.7325(9)	0.8187(6)	2.9(5)
O(1)	0.8326(8)	1.050(2)	0.923(2)	3.5(5) <sup>a</sup>
O(2)	0.7572(9)	1.176(2)	0.836(2)	4.5(7)
O(3)	0.7517(7)	1.029(2)	0.981(1)	2.6(4) <sup>a</sup>
O(4)	0.8044(8)	1.242(2)	1.005(1)	4.5(5) <sup>a</sup>
O(5)	0.5503(6)	0.922(2)	0.788(1)	2.5(4) <sup>a</sup>
O(6)	0.601(1)	0.752(4)	0.731(2)	7.9(8) <sup>a</sup>
O(7)	0.5945(9)	0.754(3)	0.903(2)	7(1)
O(8)	0.6425(6)	0.942(2)	0.846(2)	4.5(7)
O(9)	0.7345(9)	0.243(2)	0.465(2)	6.0(8)
O(10)	0.7773(7)	0.428(2)	0.571(1)	3.2(5) <sup>a</sup>
O(11)	0.768(1)	0.450(3)	0.395(2)	7.1(7) <sup>a</sup>
O(12)	0.6877(8)	0.463(2)	0.457(2)	6.6(9) <sup>a</sup>
O(13)	0.8707(6)	0.621(2)	0.657(1)	2.4(3) <sup>a</sup>
O(14)	0.8973(7)	0.841(2)	0.584(1)	3.9(7)
O(15)	0.9065(7)	0.817(3)	0.769(1)	4.8(7)
O(16)	0.9608(8)	0.689(2)	0.687(2)	4.3(5) <sup>a</sup>
O(17)	0.7856(7)	0.613(3)	0.750(1)	4.1(5) <sup>a</sup>
O(18)	0.7342(8)	0.785(2)	0.814(2)	4.3(5) <sup>a</sup>
O(19)	0.8220(9)	0.843(2)	0.805(1)	5.3(8)
O(20)	0.8062(8)	0.670(3)	0.923(1)	6(1)
O(w)	0.671(1)	0.609(5)	0.642(2)	2.2(5) <sup>a</sup>
N(1A)	0.5603(8)	0.219(2)	0.760(1)	3.3(5) <sup>a</sup>
N(2A)	0.7016(9)	0.419(2)	0.819(2)	1.7(5) <sup>a</sup>
C(1A)	0.5776(9)	0.295(3)	0.857(2)	4.8(9) <sup>a</sup>
C(2A)	0.631(1)	0.323(4)	0.875(3)	2.5(9) <sup>a</sup>
C(3A)	0.6488(9)	0.388(3)	0.789(2)	3.0(5) <sup>a</sup>
C(4A)	0.636(1)	0.290(3)	0.704(2)	1.3(6) <sup>a</sup>
C(5A)	0.5793(8)	0.258(3)	0.672(2)	2.8(5) <sup>a</sup>
C(6A)	0.5522(9)	0.384(3)	0.621(1)	3.2(5) <sup>a</sup>
C(7A)	0.569(1)	0.146(3))	0.601(2)	3.1(6) <sup>a</sup>
C(8A)	0.544(1)	0.430(3)	0.851(2)	4.4(6) <sup>a</sup>
C(9A)	0.561(1)	0.208(4)	0.933(2)	1.3(8) <sup>a</sup>
N(1B)	0.9489(7)	0.383(2)	0.734(2)	2.2(4) <sup>a</sup>
N(2B)	0.8063(8)	0.194(2)	0.677(2)	3.3(5) <sup>a</sup>
C(1B)	0.929(1)	0.346(3)	0.821(2)	2.5(7) <sup>a</sup>
C(2B)	0.874(1)	0.313(3)	0.790(3)	1.1(5) <sup>a</sup>
C(3B)	0.8625(9)	0.208(2)	0.710(2)	1.8(5) <sup>a</sup>
C(4B)	0.8772(9)	0.256(3)	0.624(3)	3.0(5) <sup>a</sup>
C(5B)	0.935(1)	0.284(3)	0.641(2)	2.7(6) <sup>a</sup>
C(6B)	0.948(1)	0.369(3)	0.564(2)	4.6(5) <sup>a</sup>
C(7B)	0.968(1)	0.152(3)	0.657(2)	2.9(9) <sup>a</sup>
C(8B)	0.958(1)	0.217(3)	0.877(2)	3.6(6) <sup>a</sup>
C(9B)	0.941(1)	0.461(3)	0.889(2)	2.3(7) <sup>a</sup>

<sup>a</sup> $B_{\text{iso}}$ .

1.53(2) Å and 1.54(3) to 1.59(1) Å in **II**. The O–P–O angles range from 104.18(9) to 116.7(1)° in **I** and from 102.7(14) to 117.9(14)° in **II**. These distances and angles lie in the range expected for this type of anions.

Table 6  
Selected inter-atomic distances (Å) in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**)

[Zn(1)O <sub>4</sub> ] tetrahedron		[Zn(2)O <sub>4</sub> ] tetrahedron		[P(1)O <sub>4</sub> ] tetrahedron	
Zn(1)–O(3)	1.93(2)	Zn(2)–O(9) <sup>i</sup>	1.86(2)	P(1)–O(1)	1.57(2)
Zn(1)–O(4) <sup>ii</sup>	1.93(2)	Zn(2)–O(10)	1.97(2)	P(1)–O(2)	1.50(2)
Zn(1)–O(8)	1.93(2)	Zn(2)–O(13)	1.93(2)	P(1)–O(3)	1.53(1)
Zn(1)–O(18)	1.93(2)	Zn(2)–O(17)	1.92(2)	P(1)–O(4)	1.49(2)
[P(2)O <sub>4</sub> ] tetrahedron		[P(3)O <sub>4</sub> ] tetrahedron		[P(4)O <sub>4</sub> ] tetrahedron	
P(2)–O(5)	1.46(2)	P(3)–O(9)	1.51(2)	P(4)–O(13)	1.53(1)
P(2)–O(6)	1.57(3)	P(3)–O(10)	1.52(2)	P(4)–O(14)	1.56(2)
P(2)–O(7)	1.54(3)	P(3)–O(11)	1.59(1)	P(4)–O(15)	1.56(1)
P(2)–O(8)	1.50(2)	P(3)–O(12)	1.53(2)	P(4)–O(16)	1.48(2)
[P(5)O <sub>4</sub> ] tetrahedron		[N <sub>2</sub> C <sub>9</sub> H <sub>22</sub> ] <sup>2+</sup> (A) cation			
P(5)–O(17)	1.51(3)	N(1A)–C(1A)	1.52(4)	C(1A)–C(8A)	1.59(4)
P(5)–O(18)	1.49(3)	N(1A)–C(5A)	1.51(3)	C(1A)–C(9A)	1.52(5)
P(5)–O(19)	1.52(3)	N(2A)–C(3A)	1.44(4)	C(5A)–C(4A)	1.55(4)
P(5)–O(20)	1.57(2)	C(3A)–C(2A)	1.54(5)	C(5A)–C(6A)	1.53(4)
		C(3A)–C(4A)	1.51(4)	C(5A)–C(7A)	1.45(4)
		C(1A)–C(2A)	1.47(5)		
[N <sub>2</sub> C <sub>9</sub> H <sub>22</sub> ] <sup>2+</sup> (B) cation					
N(1B)–C(1B)	1.51(3)	C(3B)–C(4B)	1.45(4)	C(5B)–C(4B)	1.58(4)
N(1B)–C(5B)	1.60(3)	C(1B)–C(2B)	1.51(4)	C(5B)–C(6B)	1.47(4)
N(2B)–C(3B)	1.52(4)	C(1B)–C(8B)	1.60(4)	C(5B)–C(7B)	1.57(4)
C(3B)–C(2B)	1.50(4)	C(1B)–C(9B)	1.45(4)		

Symmetry codes: i =  $-x + 3/2, y + 1/2, -z + 1$ ; ii =  $-x + 3/2, y - 1/2, -z + 2$ .

Table 7  
Hydrogen bond scheme in  $[\text{N}_2\text{C}_9\text{H}_{22}]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**II**)

N(O)–H...O	H...O (Å)	N(O)...O (Å)	N(O)HO (°)
O(1)–H(1)...O(19)	2.03	2.59(3)	125.8
O(14)–H(14)...O(12) <sup>i</sup>	1.96	2.57(3)	129.7
O(7)–H(7)...O(4) <sup>ii</sup>	2.26	2.78(3)	121.9
O(20)–H(20)...O(3) <sup>ii</sup>	1.91	2.70(3)	161.2
O(6)–H(6)...O(W)	2.28	2.88(5)	130.1
O(15)–H(15)...O(19)	1.70	2.51(3)	167.9
Ow–Hw(1)...O(12)	2.3	3.10(5)	133
N(1A)–H(1A1)...O(5) <sup>iv</sup>	2.10	2.94(3)	155.3
N(1A)–H(1A2)...O(16) <sup>v</sup>	1.84	2.71(3)	161.4
N(2A)–H(2A1)...O(3) <sup>ii</sup>	2.21	3.01(3)	149.9
N(2A)–H(2A2)...Ow	2.38	3.05(5)	132.5
N(2A)–H(2A3)...O(2) <sup>iv</sup>	1.93	2.80(4)	163.7
N(1B)–H(1B1)...O(5) <sup>vi</sup>	1.85	2.74(2)	171.3
N(1B)–H(1B2)...O(16)	2.30	3.09(3)	145.9
N(1B)–H(1B2)...O(13)	2.37	3.18(3)	149.3
N(2B)–H(2B1)...O(2) <sup>iv</sup>	2.03	2.87(3)	157.0
N(2B)–H(2B2)...O(12) <sup>iii</sup>	2.15	2.98(4)	154.8
N(2B)–H(2B3)...O(10)	1.91	2.74(3)	155.3

Symmetry codes: i =  $-x + 3/2, y + 1/2, -z + 1$ ; ii =  $-x + 3/2, y - 1/2, -z + 2$ ; iii =  $-x + 3/2, y - 1/2, -z + 1$ ; iv =  $x, y - 1, z$ ; v =  $x - 1/2, y - 1/2, z$ ; vi =  $x + 1/2, y - 1/2, z$ .

### 3.1.1. Structure of $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$ (**I**)

The structure of **I** is characterized by isolated  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  clusters where one central  $[\text{ZnO}_4]$

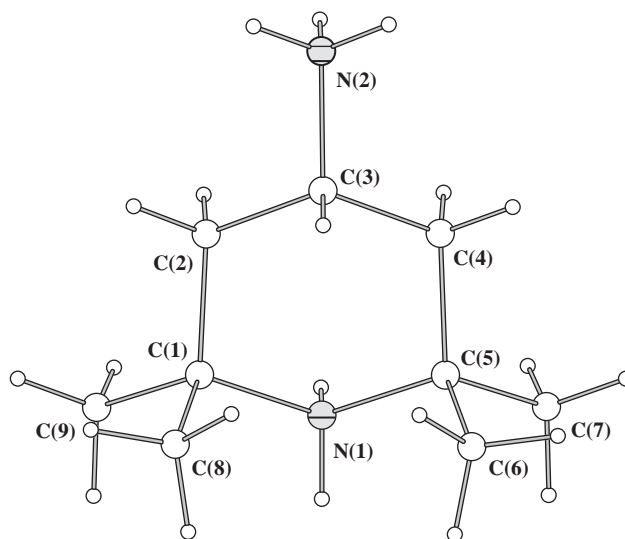


Fig. 2. View of the 4-amino-2,2,6,6-tetramethylpiperidinium cation in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$ .

tetrahedron shares its four corners with four  $[\text{H}_2\text{PO}_4]$  tetrahedra (Fig. 3a). Two strong intracluster hydrogen bonds take part to the stability of these clusters, also involved in six other strong intercluster hydrogen bonds; O...O distances range from 2.574(2) to 2.692(2) Å. Clusters form infinite pseudo-sheets parallel to the (001) plane at  $z \approx 1/2$ . These inorganic

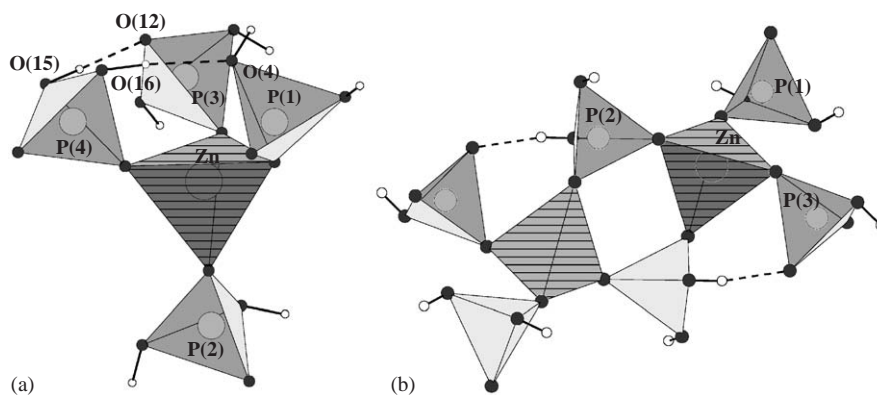


Fig. 3. (a)  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  cluster in  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$ ; and (b)  $[\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{4-}$  cluster in  $[\text{N}_2\text{C}_6\text{H}_{18}] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$  [6].

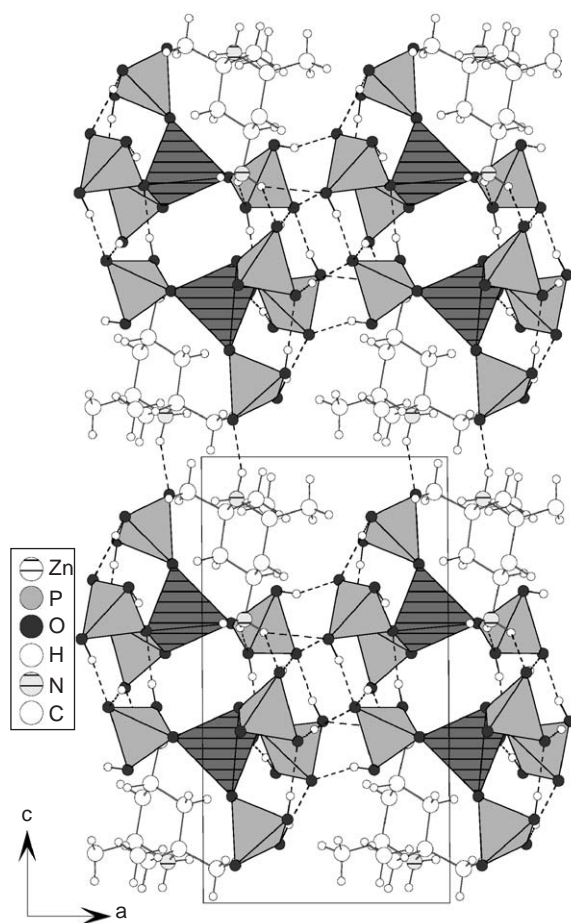


Fig. 4. Projection of the structure of  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  along the *b*-axis, showing the intracuster and intercluster hydrogen bonds.

pseudo-layers are held together by N–H...O hydrogen bond interactions which involve the amine cations (Fig. 4). The main geometrical features of hydrogen bonds are given in Table 4.

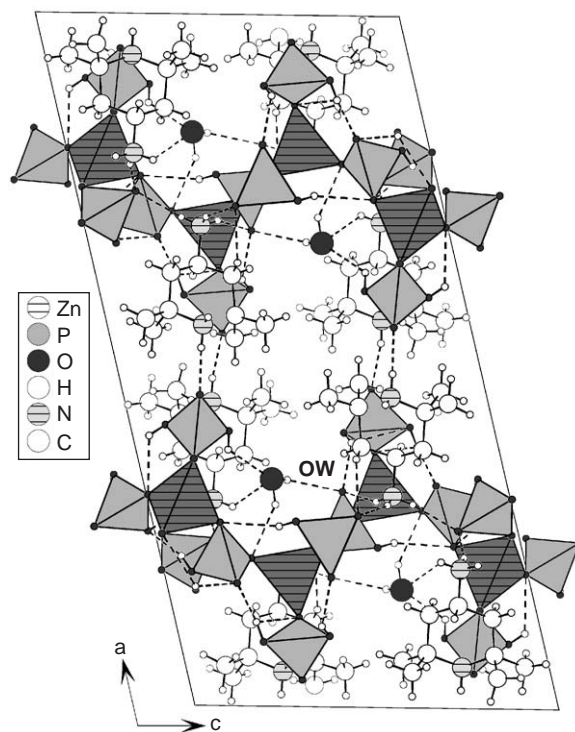


Fig. 5. [010] Projection of the structure of  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ .

### 3.1.2. Structure of $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ (II)

The structure of **II** is characterized by inorganic layers at  $x \approx 1/4$  and  $3/4$  (Fig. 5). They are built up from  $[\text{ZnO}_4]$  and  $[(\text{H}_2/\text{H})\text{PO}_4]$  tetrahedra. Each  $[\text{ZnO}_4]$  tetrahedron shares three oxygen atoms with three  $[\text{HPO}_4]$  tetrahedra and one oxygen atom with one  $[\text{H}_2\text{PO}_4]$  tetrahedron. Alternating  $[\text{Zn}(1)\text{O}_4]$  and  $[\text{HP}(1)\text{O}_4]$  tetrahedra generate linear chains along *b*-axis. Similarly, vertex-sharing  $[\text{Zn}(2)\text{O}_4]$  and  $[\text{HP}(3)\text{O}_4]$  tetrahedra form corrugated chains which are also parallel to [010]. Both

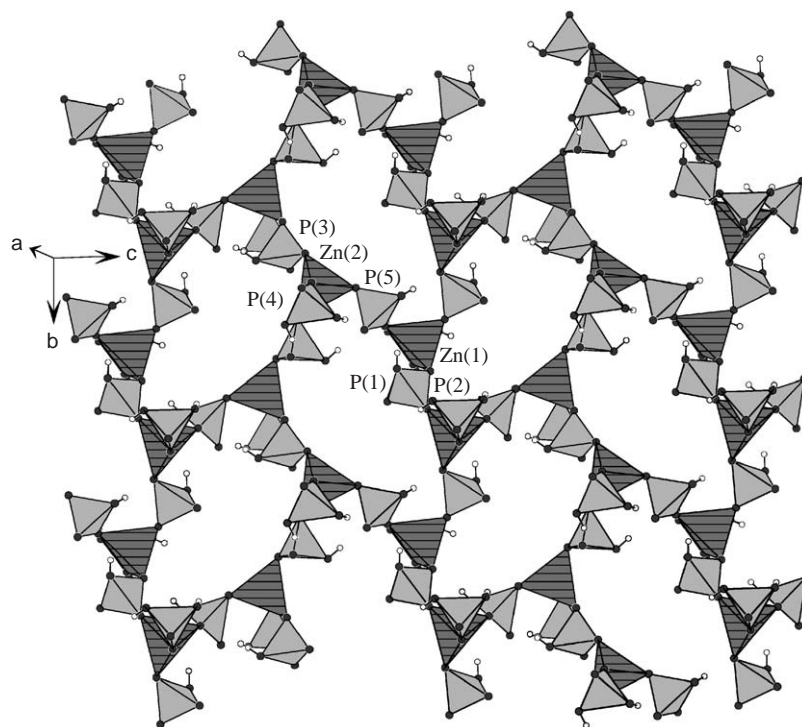


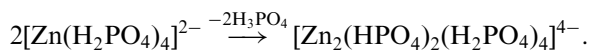
Fig. 6. View of one  $\infty[\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2]^{4-}$  layer lying at  $x \approx 1/4$ .

types of chains are connected together via  $[\text{HP}(5)\text{O}_4]$  tetrahedra and lead to a (2D) network based on distorted 12-membered rings (Fig. 6). The  $[\text{H}_2\text{PO}_4]$  tetrahedra lie above and below these layers while the organic cations and the water molecules are inserted between the inorganic sheets (Fig. 5).

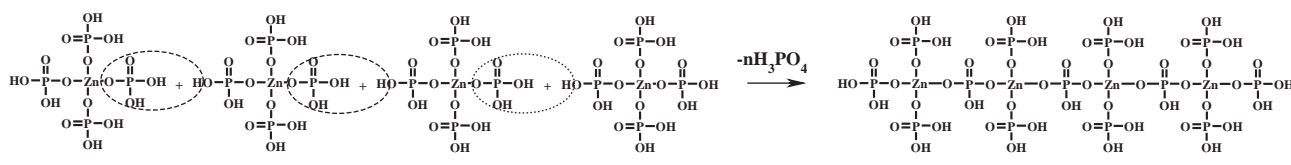
### 3.1.3. Discussion

Only four (0D) organically templated ZnPO were previously identified with similar  $[\text{Zn}_2(\text{H}_2\text{PO}_4)_6]^{2-}$ ,  $[\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{4-}$  or  $[\text{Zn}_2(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_2]^{6-}$  clusters (Fig. 3b) [1,2,6,7]. All these clusters consist of 4-membered rings of alternating  $[\text{ZnO}_4]$  and  $[(\text{H}_2/\text{H})\text{PO}_4]$  tetrahedra with two additional terminal phosphoryl

follows:



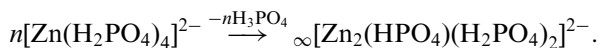
Thus, most of ZnPO with one-, two-, and three-dimensional networks can be obtained from  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  as starting building blocks. The (1D)  $[\text{N}_2\text{C}_6\text{H}_{14}] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$  [13], the as-synthesized (2D) compound (II), and the (3D)  $[\text{N}(\text{CH}_3)_4] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$  [14],  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$  [15] and  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}(\text{HPO}_4)_2]$  [15] support this assumption;  $\infty[\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]^{2-}$  chains are first derived from the condensation of  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  clusters as follows:



groups linked to each zinc tetrahedron. Until now, these cyclic units were considered to be the starting building blocks of the vast majority of (ZnPO) with higher network dimensions, as illustrated by the schematic reaction pathway proposed by Neeraj et al. [12].

However, it is very easy to show that these cyclic units (Fig. 3b) result from the condensation of two  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  polyanions (Fig. 2a), found in I, as

The condensation reaction is



Successive chains are then connected by a further condensation of  $[\text{H}_2\text{PO}_4]$  tetrahedra, represented in II by the  $(\text{HP}(5)\text{O}_4)^{2-}$  units for example, in order to form the

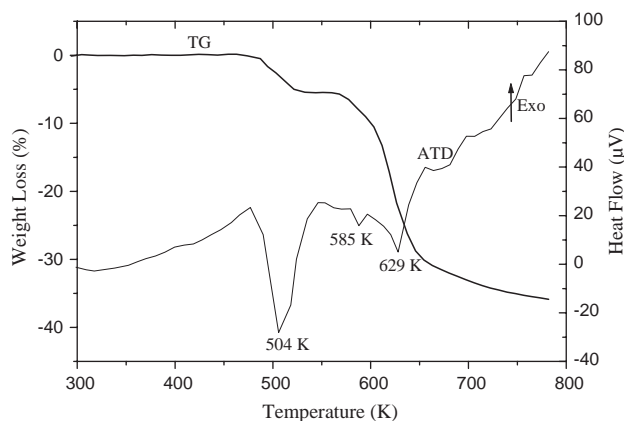
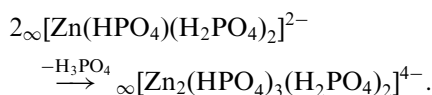


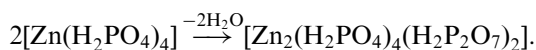
Fig. 7. TGA–DTA curves showing thermal behaviour of  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$ .

observed layers in **(II)** or the 3D network in  $[\text{N}(\text{CH}_3)_4] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$  [14],  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$  [15] and  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}(\text{HPO}_4)_2]$  [15]. For **(II)**, the condensation reaction is



### 3.2. Thermal analysis of **I**

The thermogravimetric analysis of  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  reveals a total weight loss of 36.9% (calculated: 37.7%) in two steps between 475 and 773 K (Fig. 7). The weight loss of 5.5% (calculated: 5.9%) in the 480–550 K region is in good agreement with the departure of two water molecules coming from the dehydration of  $(\text{H}_2\text{PO}_4)^-$  groups, according to the reaction:



The second weight loss occurring in the region 566–773 K (observed: 31.4%), corresponds to the loss of the two remaining water molecules and of the organic template (calculated: 31.8%). Thus, we can note that the degradation of the organic molecule starts while the loss of water molecules is not achieved. After calcination at 873 K, **I** is converted to an amorphous phase.

## 4. Conclusion

Two new ZnPO:  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  **I** and  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})]_2 \cdot [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  **II** have

been synthesized hydrothermally with 4-amino-2.2.6.6-tetramethylpiperidine as organic template. In both compounds, the amine cations adopt the same geometrical configuration.

To our knowledge,  $[\text{H}_2(\text{N}_2\text{C}_9\text{H}_{20})] \cdot [\text{Zn}(\text{H}_2\text{PO}_4)_4]$  (**I**), is the first (0D) organically templated ZnPO obtained with isolated  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  units. It is shown that the previously known inorganic cluster  $[\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{4-}$  derives from the condensation of two  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  polyanions. Thus, it is likely to be thought that  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  clusters are the precursors for a large number of open-framework ZnPO. The (1D) condensation of the  $[\text{Zn}(\text{H}_2\text{PO}_4)_4]^{2-}$  units leads, in a first step, to  $\infty [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]^{2-}$  chains observed in  $[\text{N}_2\text{C}_6\text{H}_{14}] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$ . The (2D) condensation build the  $\infty [\text{Zn}_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2]^{4-}$  layers found in the structure of **II**. A final condensation leads to a (3D) network illustrated by  $[\text{N}(\text{CH}_3)_4] \cdot [\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$ ,  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$  and  $[\text{N}_3\text{CH}_6] \cdot [\text{Zn}(\text{HPO}_4)_2]$ .

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