

Variations on the (3,4)-Net *Motif* in Organo-Zincophosphite Chemistry: Syntheses and Structures of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$

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DEDICATED TO GALEN D. STUCKY ON HIS 65TH BIRTHDAY

The solution-mediated syntheses and single-crystal structures of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (I) and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (II) are reported. These phases contain networks of vertex-sharing ZnO_4 tetrahedra and HPO_3 pseudopyramids accompanied by organic cations and water molecules. Despite their similar formulae, these phases adopt different crystal structures, in terms of three-dimensional and two-dimensional $\text{ZnO}_4|\text{HPO}_3$ networks, for I and II, respectively. Their similarities and differences to other zinc phosphites and phosphates are briefly discussed. Crystal data: $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$, $M_r = 654.23$, triclinic, $P\bar{1}$ (No. 2), $a = 7.5121$ (3) Å, $b = 8.9927$ (4) Å, $c = 15.1530$ (6) Å, $\alpha = 90.256$ (1)°, $\beta = 93.391$ (1)°, $\gamma = 111.091$ (1)°, $V = 953.04$ (7) Å³, $Z = 2$, $R(F) = 0.048$, $wR(F^2) = 0.121$. $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$, $M_r = 610.22$, monoclinic, $C2/c$ (No. 15), $a = 8.9310$ (4) Å, $b = 14.4308$ (6) Å, $c = 14.3669$ (6) Å, $\beta = 104.624$ (1)°, $V = 1791.64$ (13) Å³, $Z = 4$, $R(F) = 0.033$, $wR(F^2) = 0.087$. © 2002 Elsevier Science (USA)

INTRODUCTION

Organically templated zincophosphates (ZnPOs) containing an extended inorganic network built up from vertex-linked ZnO_4 and PO_4 tetrahedra show great structural diversity, with some 50 examples now known (1–6). Much of the early work on these phases was carried out by Stucky and co-workers, who revealed the fundamental, structure-directing role of N–H...O (template-to-framework) hydrogen bonding (7), and notable structural features such as tetrahedral three rings and direct Zn–N (zinc-to-template) bonds (8).

We are now exploring the chemistry of organically templated zincophosphites containing networks of ZnO_4

tetrahedra and pseudopyramidal $[\text{HPO}_3]^{2-}$ building units (9–14). The phases $(\text{NC}_5\text{H}_{12})_2 \cdot \text{Zn}_3(\text{HPO}_3)_4$ (13) and $(\text{CN}_4\text{H}_7)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4$ (14) are of particular interest here. Their three-dimensional frameworks can be described topologically in terms of a (3, 4) *connected net* (15) in which every Zn species participates in four Zn–O–P bonds, every P atom makes three P–O–Zn links, and all the framework O atoms are bi-coordinate to one Zn and one P. The terminal P–H vertex does not participate in bonding to other atoms. Thus, for zincophosphites based on a (3, 4) connected net, there are no terminal, or “dangling” Zn–OH₂, P–O, or P–OH bonds, which are commonly seen in ZnPOs (7, 8).

In this paper, we report the solution-mediated syntheses and single-crystal structures of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (I) and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (II), two new zinc phosphite frameworks based on a (3,4) connected net templated by “multifunctional” organic cations (i.e. those with more than one donor nitrogen atom for forming N–H...O hydrogen bonds to the framework). These phases are briefly compared and contrasted to known phases, focusing on structural aspects of the (3, 4) connected net. The concept of secondary building units (SBUs) is borrowed from aluminosilicate zeolite structural chemistry to assist in analyzing these frameworks.

EXPERIMENTAL

Syntheses

$(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ was prepared from 0.50 g (5 mmol) biguanidine, 0.407 g (5 mmol) ZnO (Spectrum), 0.85 g (10 mmol) H_3PO_3 (Alfa) and 9.00 g (500 mmol) H_2O . These components were loaded into an HDPE bottle which was shaken and placed in an 82°C oven for 6 days: the pH of the supernatant liquid at the time of recovery was 7. The recovered solids consisted of a wad of sticky gum that

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contained some embedded crystals (estimated yield < 5%) of the title compound.

$\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ was synthesized as follows: 3.56 g of $\text{Zn}(\text{NO}_3)_2$, 14.9 g of ethylene glycol, and 0.89 g 1,3-diaminopropane were sequentially added to 24 mL of 1 M H_3PO_3 solution with stirring. After 30 min, a clear solution containing some white solids resulted. A teflon lined, 23-mL, hydrothermal bomb was 2/3 filled with the mixture, sealed and heated to 180°C for 4 days. After cooling overnight, the solid product was recovered by vacuum filtration and washed with deionized H_2O and acetone to result in a dark brown mass of plate-like crystals of the title compound and small amounts of other, unidentified products. So far, pure $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ has not been prepared by empirical, minor variations of the synthesis procedure; in the absence of ethylene glycol it has not been prepared at all.

Structure Determinations

A crystal of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (transparent plate, $\sim 0.05 \times 0.29 \times 0.33$ mm) was mounted on a thin glass fiber with cyanoacrylate adhesive, and room-temperature [$25 \pm 2^\circ\text{C}$] intensity data were collected on a Bruker SMART1000 CCD diffractometer (graphite-monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å). After preliminary scans indicated satisfactory crystal quality and a triclinic unit cell, a hemisphere of intensity data was collected using an ω scan increment of 0.3° (16), resulting in 9756 measured intensities for $2^\circ \leq 2\theta \leq 60^\circ$. Data merging resulted in 5416 unique reflections ($R_{\text{int}} = 0.028$) of which 4524 were considered “observed” according to the criterion $I > 2\sigma(I)$. An absorption correction was applied on the basis of multiply measured and symmetry-equivalent reflections (17), with a resulting correction factor range of 0.519–0.894. Intensity statistics suggested space group $P\bar{1}$. Crystal data are summarized in Table 1.

A similar data collection protocol was applied to $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ as shown in Table 1: slightly translucent, chunky plate, $\sim 0.08 \times 0.18 \times 0.35$ mm, *C*-centered monoclinic cell, ω -scan width = 0.3° , 15,319 measured intensities ($2^\circ \leq 2\theta \leq 60^\circ$), 5212 unique reflections ($R_{\text{int}} = 0.030$), 3922 with $I > 2\sigma(I)$, empirical absorption correction factor range of 0.644–0.862. The systematic absences indicated space groups *Cc* or *C2/c*.

Direct methods (18) established enough of each structure (Zn and P, some O atoms) to enable the remaining non-hydrogen atoms to be located from difference maps without difficulty. For **I**, a satisfactory solution was obtained in space group $P\bar{1}$ (No. 2) and for **II** *C2/c* (No. 15) was assumed. Hydrogen atoms associated with the hydrogen phosphite moieties and template molecules were located geometrically [$d(\text{P-H}) = 1.32$ Å] and refined by riding on their parent atoms. The 1,3-diammonium propane template

TABLE 1
Crystallographic Parameters

	$(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$	$\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$
Empirical formula	$\text{Zn}_3\text{P}_4\text{O}_{13}\text{N}_6\text{C}_2\text{H}_{18}$	$\text{Zn}_3\text{P}_4\text{O}_{13}\text{N}_2\text{C}_3\text{H}_{18}$
Formula weight	654.23	610.22
Crystal system	Triclinic	Monoclinic
<i>a</i> (Å)	7.5121 (3)	8.9310 (4)
<i>b</i> (Å)	8.9927(4)	14.4308 (6)
<i>c</i> (Å)	15.1530 (6)	14.3669 (6)
α (°)	90.256 (1)	90
β (°)	93.391 (1)	104.624 (1)
γ (°)	111.091 (1)	90
<i>V</i> (Å ³)	953.04 (7)	1791.64 (13)
<i>Z</i>	2	4
Space group	$P\bar{1}$ (No. 2)	<i>C2/c</i> (No. 15)
<i>T</i> (C)	25 ± 2	25 ± 2
λ (MoK α) (Å)	0.71073	0.71073
<i>R</i> (<i>F</i>) ^a	0.048	0.033
w <i>R</i> 2(<i>F</i> ²) ^b	0.121	0.087

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]}{\sum w|F_o|^2}^{1/2}$$

in **II** was found to be partially disordered over two orientations and modelled as such. H atoms associated with the extra-framework water molecules were not located for either phase. The final cycles of full-matrix least-squares refinement with SHELXL-97 (19) included anisotropic temperature factors for all the undisordered non-hydrogen atoms and led to satisfactory convergence. Further details of the crystal structures (tables of atomic coordinates and anisotropic thermal factors) are available from the authors.

RESULTS

Crystal Structure of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$

Selected bond distance/angle data are listed in Table 2. Figure 1 shows the atomic connectivity of this new guanidinium–zinc–phosphite hydrate. The three distinct zinc atoms each make four bonds to nearby P atoms via oxygen bridges with typical (10) geometrical parameters [$d_{\text{av}}(\text{Zn1-O}) = 1.931$ (2) Å, $d_{\text{av}}(\text{Zn2-O}) = 1.933$ (2) Å, $d_{\text{av}}(\text{Zn3-O}) = 1.941$ (2) Å]. Each of the four distinct P atoms make three P–O–Zn bonds with $d_{\text{av}}(\text{P1-O}) = 1.513$ (3) Å, $d_{\text{av}}(\text{P2-O}) = 1.515$ (3) Å, $d_{\text{av}}(\text{P3-O}) = 1.501$ (3) Å, and $d_{\text{av}}(\text{P4-O}) = 1.513$ (3) Å. The fourth tetrahedral vertex about each P atom is assumed to be a P–H bond, as invariably observed in phosphites (20). Thus, there are no terminal links to O associated with either the zinc or phosphorus species. The average Zn–O–P bond angle for the 12 contributors is 137.6° (spread of values 128.9–147.0°). A water molecule of hydration (atom O13) is present. Assuming the normal charges for the framework species, both

TABLE 2
Selected Bond Distances (Å)/Angles (°) for
(CN₃H₆)₂ · Zn₃(HPO₃)₄ · H₂O

Zn1–O8	1.920(3)	Zn1–O1	1.923(3)	
Zn1–O9	1.933(3)	Zn1–O5	1.948(3)	
Zn2–O7	1.896(3)	Zn2–O4	1.934(2)	
Zn2–O10	1.946(3)	Zn2–O3	1.956(2)	
Zn3–O2	1.933(3)	Zn3–O11	1.935(3)	
Zn3–O12	1.942(3)	Zn3–O6	1.955(2)	
P1–O1	1.506(3)	P1–O2	1.507(3)	
P1–O3	1.527(2)	P2–O4	1.505(3)	
P2–O5	1.518(3)	P2–O6	1.523(2)	
P3–O8	1.481(3)	P3–O7	1.503(3)	
P3–O9	1.519(3)	P4–O10	1.512(3)	
P4–O11	1.512(3)	P4–O12	1.514(3)	
P1–O1–Zn1	140.98(18)	P1–O2–Zn3	140.21(19)	
P1–O3–Zn2	132.45(16)	P2–O4–Zn2	147.03(17)	
P2–O5–Zn1	128.93(16)	P2–O6–Zn3	129.19(15)	
P3–O7–Zn2	144.8(2)	P3–O8–Zn1	146.4(3)	
P3–O9–Zn1	131.87(18)	P4–O10–Zn2	137.36(17)	
P4–O11–Zn3	139.30(19)	P4–O12–Zn3	132.73(17)	
N1–H11 ... O12	0.95	2.16	3.031(4)	152
N1–H12 ... O2	0.95	2.11	3.032(4)	162
N2–H21 ... O11	0.95	2.11	3.031(4)	163
N2–H22 ... O3	0.95	2.20	3.131(4)	168
N3–H31 ... O10	0.95	1.95	2.891(5)	170
N3–H32 ... O13	0.95	1.95	2.876(5)	164
N4–H41 ... O4	0.95	2.14	3.044(5)	159
N5–H52 ... O9	0.95	2.00	2.938(4)	170
N6–H61 ... O5	0.95	2.09	3.002(5)	161
N6–H62 ... O1	0.95	2.12	3.071(5)	174

Note. For the hydrogen bonds, the four values refer to the N–H, H ... O, N ... O separations (Å) and the N–H ... O bond angle (°), respectively.

guanidinium moieties are protonated as [CN₃H₆]⁺ groups. The average C–N bond length of 1.322 Å is similar to that seen in guanidinium-templated zinc phosphates (21) and indicates that the usual delocalized model resulting in a C–N bond order of 1.33 is appropriate here.

The polyhedral connectivity in (CN₃H₆)₂ · Zn₃(HPO₃)₄ · H₂O results in an anionic, three-dimensional network of stoichiometry [Zn₃(HPO₃)₄]²⁻ encapsulating the extra-framework species in eight-ring channels (formed from eight polyhedral building units made up from four ZnO₄ and four HPO₃ moieties) which propagate along [100] (Fig. 2). The framework can be schematically decomposed (Fig. 3) into sheets arranged in the (101) plane linked by way of Zn2–O4–P2 bonds (which possess the largest Zn–O–P bond angle in this structure) but this description does not necessarily imply that these sheets form as a distinct step in the synthesis mechanism (*vide infra*).

The guanidinium cations interact with the zincophosphate framework by way of N–H ... O hydrogen bonds (Table 2). Based on our model of geometrically placed H atoms, 10 out of 12 N–H entities are involved in these

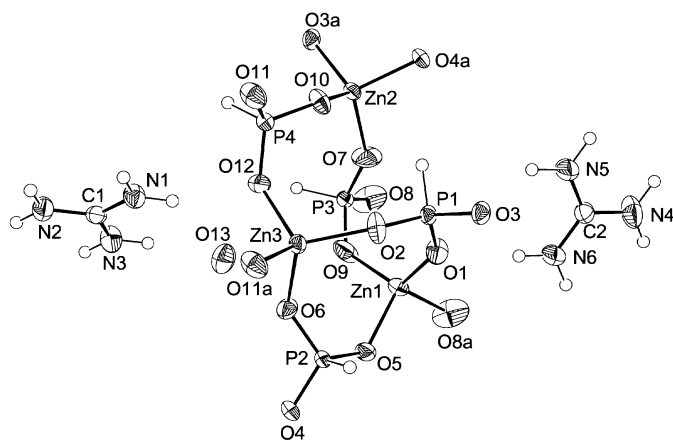


FIG. 1. Fragment of (CN₃H₆)₂ · Zn₃(HPO₃)₄ · H₂O (50% thermal ellipsoids for the non-hydrogen atoms) showing the atom labelling scheme. Symmetry-generated atoms are indicated by, e.g., O3a.

interactions, with the H ... O separation varying from 1.95 to 2.20 Å. As also seen in zincophosphates templated by guanidinium cations (21), the [CN₃H₆]⁺ species in (CN₃H₆)₂ · Zn₃(HPO₃)₄ · H₂O form closely associated pairs, such that the planes of the two moieties are essentially

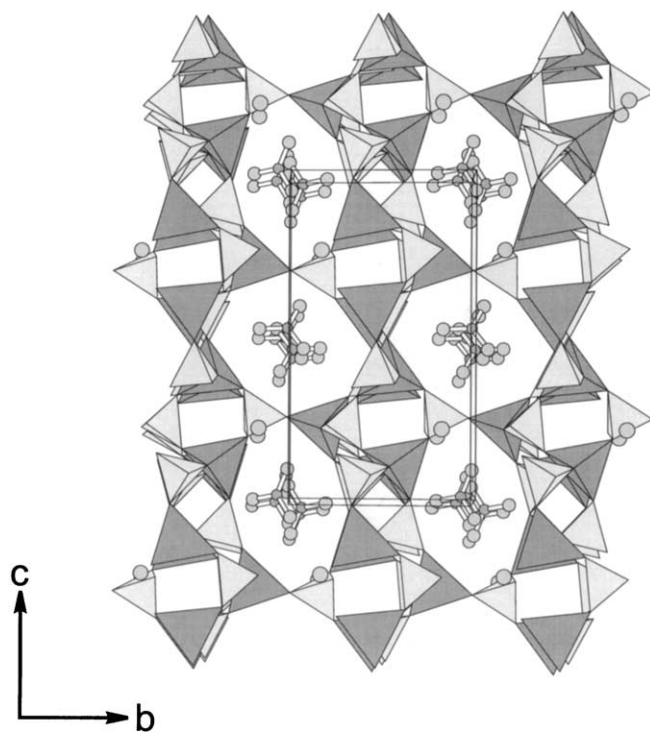


FIG. 2. View down [100] of the (CN₃H₆)₂ · Zn₃(HPO₃)₄ · H₂O crystal structure with the framework represented by polyhedra (ZnO₄ dark shading; HPO₃ light shading) and extra-framework atoms by spheres of arbitrary radius (template H atoms omitted for clarity). This view shows the regular eight-ring channels propagating in the [100] direction.

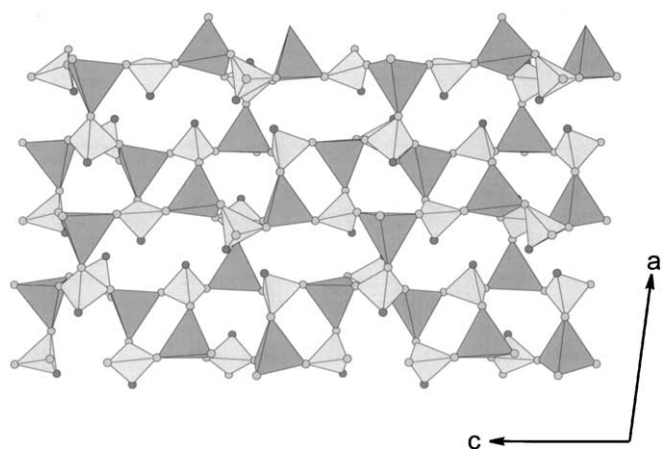


FIG. 3. View down [010] of one polyhedral layer in $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ showing the connectivity of the ZnO_4 and HPO_3 moieties. The light spheres at the corners of the tetrahedra represent O atoms (as parts of Zn-O-P links) and the dark spheres H atoms (as parts of terminal P-H bonds).

parallel. The $\text{C1} \cdots \text{C1}'$ separation of 3.37 \AA is exceptionally small and compares well to the situation predicted by molecular dynamic studies (22) which suggest that in solution, an energy minimum occurs when parallel pairs of $[\text{CN}_3\text{H}_6]^+$ cations are separated by $\sim 3.3 \text{ \AA}$. This can be

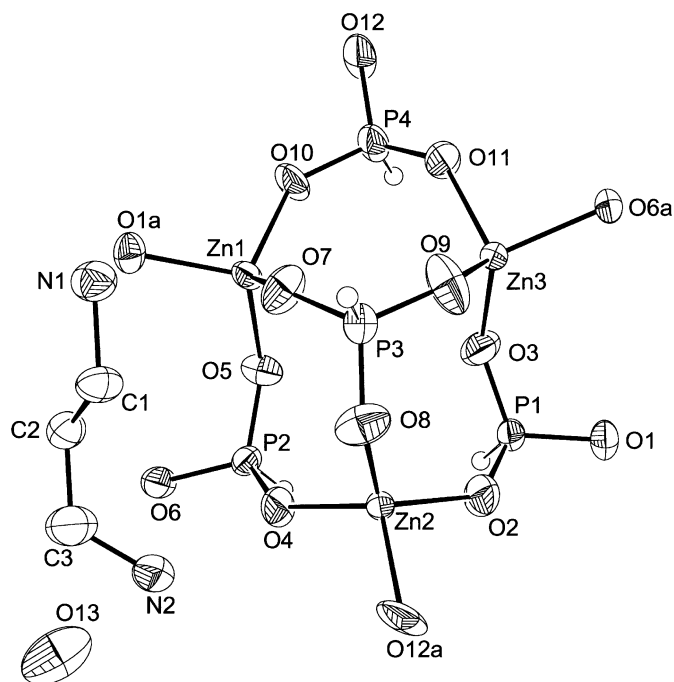


FIG. 4. Fragment of $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (50% thermal ellipsoids) showing the atom labelling scheme with template H atoms and disordered C and N atoms (minor component) omitted for clarity. Symmetry-generated atoms are indicated by, e.g., O1a.

TABLE 3
Selected Bond Distances (\AA)/Angles ($^\circ$)
for $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$

Zn1-O10	1.915(2)	Zn1-O7	1.921(2)	
Zn1-O5	1.924(2)	Zn1-O1	1.942(2)	
Zn2-O8	1.913(3)	Zn2-O2	1.919(2)	
Zn2-O12	1.926(2)	Zn2-O4	1.942(2)	
Zn3-O9	1.914(3)	Zn3-O3	1.926(2)	
Zn3-O11	1.927(2)	Zn3-O6	1.945(2)	
P1-O3	1.512(2)	P1-O2	1.512(2)	
P1-O1	1.521(2)	P2-O5	1.514(2)	
P2-O4	1.519(2)	P2-O6	1.520(2)	
P3-O9	1.502(3)	P3-O7	1.503(2)	
P3-O8	1.513(3)	P4-O11	1.459(3)	
P4-O12	1.476(3)	P4-O10	1.509(2)	
P1-O1-Zn1	133.68(14)	P1-O2-Zn2	134.59(16)	
P1-O3-Zn3	135.96(16)	P2-O4-Zn2	137.26(15)	
P2-O5-Zn1	137.64(15)	P2-O6-Zn3	132.61(15)	
P3-O7-Zn1	141.56(17)	P3-O8-Zn2	131.66(16)	
P3-O9-Zn3	134.27(18)	P4-O10-Zn1	140.12(16)	
P4-O11-Zn3	138.76(19)	P4-O12-Zn2	139.9(2)	
N1-H5 \cdots O2	0.95	2.20	2.992(4)	141
N1-H6 \cdots O10	0.95	2.17	2.948(4)	138
N1-H6 \cdots O12	0.95	2.33	3.222(4)	156
N1-H7 \cdots O1	0.95	1.98	2.895(4)	160
N2-H8 \cdots O6	0.95	1.99	2.924(5)	168
N2-H9 \cdots O13	0.95	1.83	2.768(6)	167
N2-H10 \cdots O4	0.95	1.97	2.908(4)	169

Note. For the hydrogen bonds, the four values refer to the N-H, H \cdots O, N \cdots O separations (\AA) and the N-H \cdots O bond angle ($^\circ$), respectively.

rationalized in terms of electrostatic cation-cation repulsion being overcome by favorable solvation effects. The $\text{C2} \cdots \text{C2}'$ separation of 3.64 \AA is comparable to that seen in phases such as $(\text{CN}_3\text{H}_6)_2 \cdot (\text{VO}_2)_3(\text{PO}_4)(\text{HPO}_4)$, where pairs of guanidinium cations act cooperatively to template a novel, layered, vanadium (V) phosphate (23).

Crystal Structure of $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$

Selected bond distance/angle data are presented in Table 3. $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ is a new, layered, zincophosphate templated by 1,3 diammonium propane cations as illustrated in Figs. 4 and 5.

The three distinct zinc atoms form the centers of ZnO_4 tetrahedra and make four Zn-O-P bonds with normal geometrical parameters [$d_{\text{av}}(\text{Zn1-O}) = 1.923(2) \text{ \AA}$, $d_{\text{av}}(\text{Zn2-O}) = 1.925(2) \text{ \AA}$, $d_{\text{av}}(\text{Zn3-O}) = 1.928(2) \text{ \AA}$]. Each of the four distinct P atoms makes three links to Zn via O with $d_{\text{av}}(\text{P1-O}) = 1.515(3) \text{ \AA}$, $d_{\text{av}}(\text{P2-O}) = 1.518(3) \text{ \AA}$, $d_{\text{av}}(\text{P3-O}) = 1.506(3) \text{ \AA}$, and $d_{\text{av}}(\text{P4-O}) = 1.481(3) \text{ \AA}$, with the fourth vertex assumed to be a P-H bond, with $d(\text{P-H}) = 1.32 \text{ \AA}$. Thus, as seen for $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$, there are no terminal Zn-O or P-O links in $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$. The average Zn-O-P

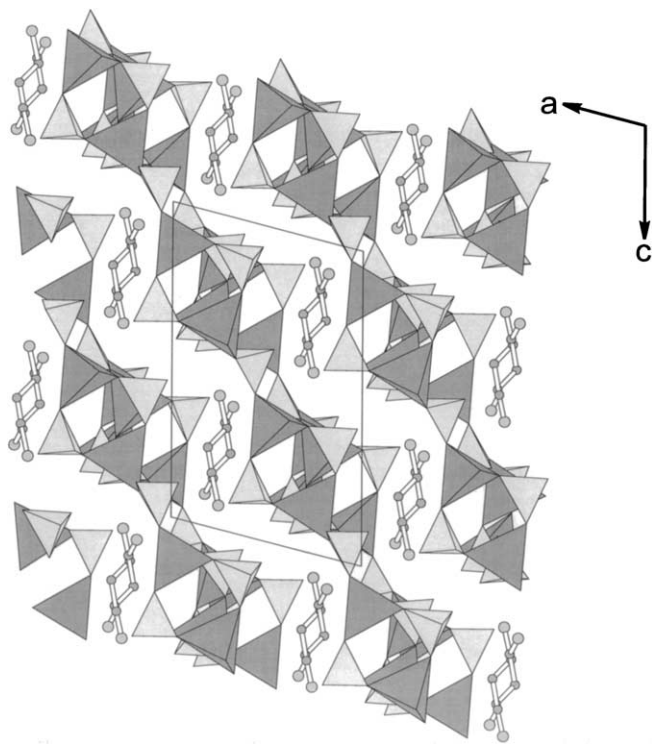


FIG. 5. View down [010] of $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ showing the (101) sheets separated by the organic species. Atom/polyhedron representation as in Fig. 2.

bond angle is 136.50° (spread of values 131.7–141.6 for the 12 contributors). A water molecule of hydration (atom O13) is present. Assuming the normal charges for the framework species, the template cation is doubly protonated, as the 1,3-diammonium propane species.

The polyhedral connectivity in $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ can be analyzed in terms of very contorted four-ring ladders (24) built up from the Zn1, Zn2, Zn3, P1, P2, and P3 centered polyhedra which propagate along [010]. The P4-centered phosphite group crosslinks the ladders by bonding to Zn1 and Zn3 (same ladder) and Zn2 (adjacent ladder) to result in an infinite sheet of stoichiometry $[\text{Zn}_3(\text{HPO}_3)_4]^{2-}$ (Fig. 6) containing quite regular and very squashed eight-ring pores. The pores alternate in the [010] direction and the sheets propagate in the (101) plane. The organic species interacts with the zincophosphate sheets by way of N–H \cdots O bonds (Table 3). The interactions involving N2 appear to be well defined and result in O \cdots H–N2–H \cdots O inter-sheet links. Those involving N1 are less certain, perhaps due to the partial disorder of the template molecule.

DISCUSSION

Two new organically templated zincophosphites have been prepared by hydrothermal methods and structurally

characterized. The framework components of the structures of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ reveal the characteristic building blocks of vertex-sharing ZnO_4 tetrahedra and HPO_3 pseudopyramids as seen already in related phases (10–14). However, their overall structures bear no particular resemblance to other zincophosphites templated by the same cations. Thus, the novel guanidinium zincophosphite $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}(\text{HPO}_3)_2$ reported recently (12) contains a zincophosphite framework composed solely of 12 rings. In this phase, the guanidinium cations show a particularly good templating “fit” to the framework 12-ring windows, quite distinct from the 8-ring template–framework interactions in $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$.

The other zincophosphite (11) templated by 1,3-diammonium propane cations, $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}(\text{HPO}_3)_2$, is a one-dimensional (chain) structure and is closely related to various zincophosphates (25, 26). This general behavior is very similar to that observed in zincophosphates, where several entirely different structures can arise for the same templating cation.

Although the dimensionalities of the frameworks of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (three-dimensional, i.e., continuous) and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (layered) are different, their structures are quite closely related and can be analyzed in terms of the (3, 4) connected net motif. It is also helpful to borrow the terminology of aluminosilicate

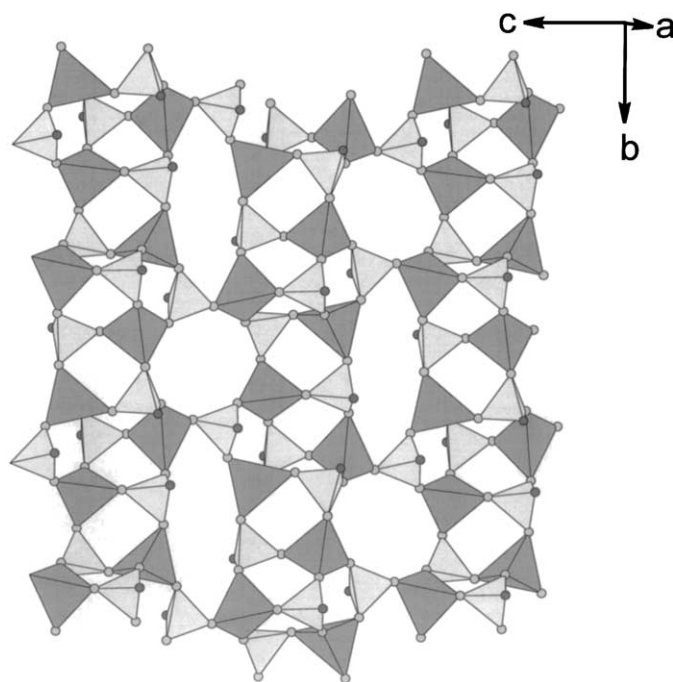


FIG. 6. Polyhedral view normal to (101) of a layer in $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$, with atom/polyhedron representations as in Fig. 3.

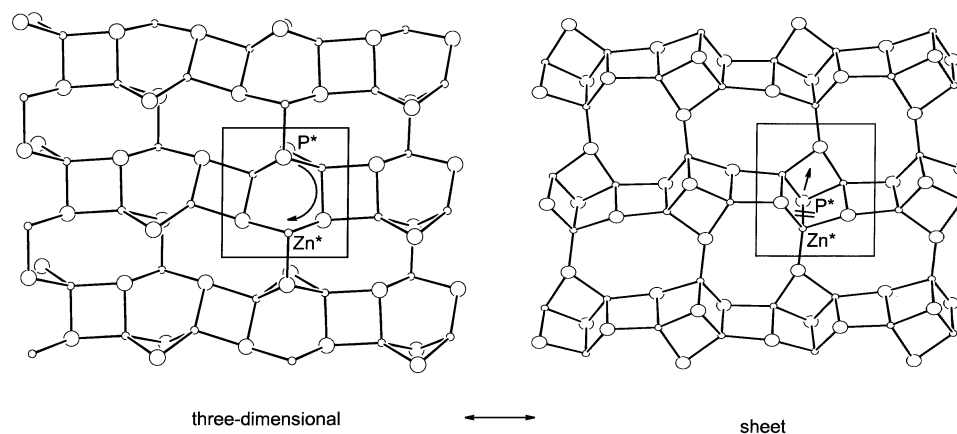


FIG. 7. Topological comparison of a (101) slice of $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (left) and a layer of $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ (right) with Zn–O–P bonds represented by lines. The small spheres represent Zn atoms, the large spheres P atoms. The rectangles show the SBUs for each structure (see text). On the left-hand diagram, the atoms denoted Zn* and P* are involved in Zn*–P* inter-sheet links (as Zn–O–P bonds) leading to a three-dimensional structure. The curly arrow shows the nominal transformation of this three-dimensional framework to a layered topology by means of breaking a Zn*–P* bond and reforming the same bond in sheet. The right-hand diagram explicitly shows how a single in-layer or intra-sheet Zn*–P* linkage (via O) is broken in the transformation to the left-hand structure.

zeolite structures to amplify this point. In each structure (Fig. 7), we may identify a (pseudo) secondary building unit (27) or SBU, which is the smallest polyhedral grouping, that when repeated through the appropriate symmetry, generates the whole framework. In diagrammatic form, this can be simplified to a collection of nodes connected by lines, where the nodes represent the Zn and P atoms and the lines the Zn–O–P bonds (which, of course, are not actually linear). For $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$, the SBU can be described as a bifurcated six ring (compare also Fig. 1), whilst the SBU for $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ is the unusual $6 \equiv 1$ type (compare Fig. 4) previously seen in the beryllophosphate phase $\text{NaK}(\text{BePO}_4)_2 \cdot 2.8\text{H}_2\text{O}$ (28). Figure 7 further shows that the two frameworks are related by the breaking and reforming of just one Zn–O–P bond which transforms the three-dimensional guanidinium structure into the layered 1,3-diammonium propane structure. However, there is no evidence, as yet, that such a transformation is actually chemically possible. Indeed, the fact that $(\text{CN}_3\text{H}_6)_2 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ contains corner-shared four-ring chains and $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot \text{H}_2\text{O}$ contains edge-shared four-ring chains may indicate that the two ZnPO networks can be differentiated at a very early stage of the reaction (29). We are now following the lead of Rao *et al.* (30) in beginning to investigate the possibilities of transforming zincophosphate structures by hydrothermal means.

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