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Two New Tetramethylammonium Zinc Phosphates: $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$, an Open Framework Phase Built up from a Low-Density 12-Ring Topology, and $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$, a Molecular Cluster

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The solution-phase syntheses and X-ray single crystal structures of $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$, two new tetramethylammonium (TMA) zinc phosphates, are described. $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ is a three-dimensional framework phase built up from ZnO_4, HPO_4, and H_2PO_4 tetrahedra sharing vertices. The polyhedral connectivity results in a novel, low-density framework topology, based on tetrahedral 12-rings. TMA cations provide extra-framework charge balancing, and occupy the 12-ring channel network. $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ is a "zero-dimensional" (molecular) phase built up from the same polyhedral units, formed into discrete anionic clusters. Crystal data: $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$, $M_r = 332.49$, monoclinic, space group Pc (No. 7), $a = 8.443$ (2) Å, $b = 13.779$ (4) Å, $c = 10.170$ (2) Å, $\beta = 91.91$ (2)°, $V = 1182.9$ (5) Å^3, $Z = 4$, $R(F) = 4.69\%$, $R_w(F) = 5.46\%$ [3284 observed reflections with $I > 3\sigma(I)$]. $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)_3$, $M_r = 430.49$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.950$ (2) Å, $b = 10.068$ (2) Å, $c = 10.263$ (2) Å, $\alpha = 61.649$ (9)°, $\beta = 76.04$ (2)°, $\gamma = 76.72$ (1)°, $V = 782.5$ (2) A^3, $Z = 2$, $R(F) = 4.22\%$, $R_w(F) = 4.77\%$ [3038 observed reflections with $I > 3\sigma(I)$]. © 1977 Academic Press

INTRODUCTION

Zincophosphate (ZnPO) open framework phases shows a substantial structural variety (1–16). Several direct analogous of aluminosilicate zeolites have been prepared, including the sodalite (2), zeolite-X (3), lithium-A (4), and edingtonite (5) framework topologies. A new chiral structure type (6), denoted framework code CZP by the International Zeolite Association, has been synthesized as single crystals. An especially interesting family of ZnPO phases of the general formula $M_3Zn_4O(PO_4)_3 \cdot nH_2O$ (7), where M = Li, Na, K, Rb … , shows a new type of zinc-rich framework topology, incorporating tetrahedral OZn_4 centers into spiro-5 ring systems. Several of these $M_3Zn_4O(PO_4)_3 \cdot nH_2O$ materials show a high degree of thermal stability, to at least 400°C, and undergo typical zeolitic dehydration/rehydration and ion-exchange reactions.

Using small organic cations as structure-directing agents in hydrothermal ZnPO syntheses leads to many novel organo-zincophosphate phases (8–16), whose crystal structures are strongly dependent on the identity of the organic species. Interesting features such as tetrahedral 3-rings (9) and infinite chains of –Zn–O–Zn–O– bonds (11, 14) are found in some of these structures. A tetrahedral 18-ring, the largest pore size observed in a zincophosphate so far, occurs in the guanidinium zinc phosphate $(CN_3H_6)_3 \cdot Zn_7(H_2O)_4(PO_4)_6 \cdot H_3O$ (15).

Here, we report the syntheses and structures of two new tetramethylammonium (TMA) zincophosphates. $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ consists of a novel, low-density, three-dimensional ZnPO framework topology, whereas $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ contains anionic zincophosphate molecular clusters.

EXPERIMENTAL

Synthesis. $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ was prepared from the reaction of 85% phosphoric acid (8.45 g), 25% tetramethylammonium hydroxide (TMAOH) solution (10.30 g), and zinc oxide (1.0 g), mixed together in a plastic bottle. Initially a white gel formed, which was homogenized by shaking. The gel was transferred to a sealed Teflon liner and heated in the oven at 80°C overnight. The liner was removed from the oven, and the clear solution was cooled to room temperature. Small, faceted, "brick-like" crystals (maximum linear dimension ~0.4 mm) of $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ formed in the cooled reaction mixture.

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$N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ was prepared from the reaction of 85% phosphoric acid (6.02 g) and 25% tetramethylammonium hydroxide solution (2.80 g). The mixture was shaken in a plastic bottle until homogeneous, followed by the addition of zinc oxide (1.00 g), resulting in a white gel. The bottle was shaken again to homogenize the gel. The gel was transferred to a Teflon liner and heated to 80°C overnight, The liner was removed from the oven, and the clear solution was cooled to room temperature. Upon cooling, well-faceted transparent crystals formed (maximum linear dimension ~0.6 mm) which were recovered by vacuum filtration.

Crystal structure determinations. The structures of $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ were determined by single-crystal X-ray methods. In each case, a suitable crystal (for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$: transparent block, dimensions ~$0.2 \times 0.2 \times 0.4$ mm: for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$: faceted lump, dimensions ~ $0.4 \times 0.4 \times 0.3$ mm) was mounted on a thin glass fiber with cyanocrylate adhesive, and room-temperature [25(2)°C] intensity data were collected on a Siemens P4 automated four-circle diffractometer (graphite-monochromated Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å). Peak search, centering, indexing, and least-squares refinement routines led to a monoclinic unit cell for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and a triclinic cell for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ (Table 1). Data were collected using the $\omega/2\theta$ scan model; three standard reflections, rescanned every 100 observations, showed no significant variation in intensity over the course of each data collection. Crystal absorption [range of equivalent transmission factors, 0.64–0.80 for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$; 0.72–0.75 for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$] was accounted for by the ψ scan method. During data reduction, the usual corrections for Lorentz and polarization effects were made and redundant reflections were merged, resulting in 3284 observed reflections [$R_{\mathrm{Int}} = 2.89\%$] for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and 3038 observed reflections [$R_{\mathrm{Int}} = 3.07\%$] for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$, based on an observability criterion of $I > 3\sigma(I)$. For $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$, the systematic absence condition $h0l$, $l \neq 2n$ indicated space groups Pc (No. 7) or $P2/c$ (No. 13).

Starting coordinates for the Zn, P, and some O atoms in $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ were located by direct methods using the program SHELXS86 (17) and the crystal structure model was successfully developed in space group Pc. No reasonable atomic configuration could be established in space group $P2/c$. The remaining O, N, and C atoms positions were readily located from difference Fourier maps and added to the structural model. No proton positions could be located from difference maps during the latter stages of refinement. Those protons associcated with the TMA cation were located geometrically [d(C–H) = 0.95 Å] and refined by riding on their respective C atoms. The final cycles of full-matrix least-squares refinement [program CRYSTALS (18)], using complex neutral-atom scattering factors (19), minimized the function $\sum w_i(F_o - F_c)^2$, with w_i described by a Tukey–Prince weighting scheme (20), and included anisotropic temperature factors for all the nonhydrogen atoms and a Larson-type secondary extinction correction (21). Data collection and crystallographic parameters for $N(CH_3)_4 \cdot Zn(HPO_4)$ (H_2PO_4) are summarized in Table 1.

TABLE 1
Crystallographic/Data Collection Parameters

	$N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$	$N(CH_3)_4 \cdot Zn(H_2PO_4)_3$
Emp. formula	$Zn_1P_2O_8N_1C_4H_{15}$	$Zn_1P_3O_{12}N_1C_4H_{18}$
Formula wt.	332.49	430.49
Crystal system	Monoclinic	Triclinic
a(Å)	8.443 (2)	8.950 (2)
b(Å)	13.779 (4)	10.068 (2)
c(Å)	10.170 (2)	10.263 (2)
α (°)	90	61.649 (9)
β (°)	91.91 (2)	76.04 (2)
γ (°)	90	76.72 (1)
V(Å^3)	1182.9 (5)	782.5 (2)
Z	4	2
Space group	Pc (No. 7)	$P\bar{1}$ (No. 2)
T(°C)	25 (2)	25 (2)
λ (Mo$K\alpha$) (Å)	0.71073	0.71073
ρ_{calc} (g/cm^3)	1.87	1.82
μ (cm^{-1})	24.17	19.54
Total data	4547	6365
Observed data[a]	3284	3038
Parameters	291	191
$R(F)$[b]	4.69	4.22
$R_w(F)$[c]	5.46	4.77

[a] $I > 3\sigma(I)$ after data merging.

[b] $R = 100 \times \sum ||F_o| - |F_c|| / \sum |F_o|$.

[c] $R_w = 100 \times [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

The $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ structure determination followed the same procedure as that outlined for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$. After starting Zn and P atoms coordinates were located by direct methods, the structure of $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ was developed in space group $P\bar{1}$ (No. 2), which was assumed for the remainder of the crystallographic analysis. The remaining O, N, and C atoms were located from difference maps and added to the refinement. No proton positions could be located. The weighting scheme was $w_i = 1/[\sigma(F)]^2$. Data collection and crystallographic parameters for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ are summarized in Table 1. Supplementary tables of anisotropic thermal factors and observed and calculated structure factors for these materials are available from the authors.

RESULTS AND DISCUSSION

Crystal structure of $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$. Final atomic positional and thermal parameters for $N(CH_3)_4 \cdot$

$Zn(HPO_4)(H_2PO_4)$ are listed in Table 2, with selected bond distance/angle data in Table 3. $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$ is a new organo-zincophosphate consisting of a three-dimensional network of vertex-linked ZnO_4 and PO_4 tetrahedra incorporating TMA cations into its pores. Although it is very "open," the $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$ structure shows no particular similarity to aluminosilicate or aluminophosphate phases. A CAMERON (22) representation of the bonding unit of $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$ is shown in Fig. 1 and the complete crystal structure is illustrated in Fig. 2.

There are 32 component nonhydrogen atoms in $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$ (i.e., two formula units per asymmetric unit). The two distinct zinc atoms each make four Zn–O–P bonds to different nearby phosphorus atoms, with average Zn–O bond distances of 1.932 (3) Å and 1.930 (3) Å for Zn(1) and Zn(2), respectively. There are four distinct phosphorus atoms in $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$: All of these are tetrahedrally coordinated by oxygen, and each P atom makes two P–O–Zn bonds, with the other two P–O vertices being "terminal." Average P–O distances of 1.535 (3), 1.527 (3), 1.534 (3), and 1.531 (3) Å result for P(1), P(2), P(3), and P(4), respectively, in good agreement with previous studies of similar entities in related materials (8–16). The 16 framework O atoms divide into eight bicoordinate zinc-to-phosphorus bridges [average Zn–O–P bond angle 134.9°] and eight terminal oxygen atoms attached only to P (Table 3). Charge-balancing considerations dictate that the $[Zn_2P_4O_{16}]^{8-}$ framework unit requires six protons, in addition to the two extra-framework univalent TMA cations. Bond length/bond strength considerations (23, 24) suggest that the P(1)- and P(3)-centered groups are hydrogen phosphate entities and the P(2)- and P(4)-centered groups are dihydrogen phosphate moieties.

TABLE 2
Final Atomic Coordinates/Thermal Factors for $N(CH_3)_4{\cdot}Zn(HPO_3)(H_2PO_4)$

Atom	x	y	z	U_{eq}[a]
Zn (1)	0.1211 (2)	0.07358 (5)	0.5396 (1)	0.0197
Zn (2)	0.6228 (2)	0.36910 (5)	0.6504 (1)	0.0187
P (1)	– 0.1894 (2)	0.1938 (1)	0.5285 (2)	0.0203
P (2)	0.1503 (3)	0.1133 (1)	0.2258 (2)	0.0201
P (3)	0.3108 (3)	0.2732 (1)	0.5591 (2)	0.0218
P (4)	0.6539 (3)	0.4630 (1)	0.3599 (2)	0.0120
O (1)	– 0.0959 (7)	0.1057 (3)	0.5745 (6)	0.0241
O (2)	– 0.2454 (7)	0.2535 (3)	0.6425 (5)	0.0259
O (3)	– 0.3382 (7)	0.1524 (4)	0.4498 (6)	0.0309
O (4)	– 0.0939 (7)	0.2540 (3)	0.4306 (5)	0.0246
O (5)	0.1568 (8)	0.0584 (4)	0.3530 (5)	0.0305
O (6)	– 0.0099 (9)	0.1700 (5)	0.2124 (6)	0.0408
O (7)	0.1673 (8)	0.0557 (3)	0.1029 (5)	0.0240
O (8)	0.2836 (9)	0.1910 (4)	0.2209 (5)	0.0354
O (9)	0.2578 (7)	0.1753 (4)	0.6074 (5)	0.0299
O (10)	0.4057 (7)	0.3278 (4)	0.6631 (5)	0.0282
O (11)	0.1624 (7)	0.3388 (4)	0.5283 (7)	0.0330
O (12)	0.4054 (7)	0.2644 (4)	0.4313 (5)	0.0281
O (13)	0.6637 (8)	0.4556 (4)	0.5061 (5)	0.0301
O (14)	0.4906 (9)	0.4255 (5)	0.3050 (6)	0.0407
O (15)	0.785 (1)	0.3978 (5)	0.2969 (6)	0.0421
O (16)	0.6751 (8)	0.5646 (3)	0.3117 (5)	0.0248
N (1)	0.1295 (9)	0.6126 (5)	0.4424 (7)	0.0320
N (2)	0.628 (1)	0.8799 (5)	0.4780 (7)	0.0352
C (1)	0.006 (1)	0.5905 (8)	0.537 (1)	0.0454
C (2)	0.115 (1)	0.5453 (7)	0.3247 (8)	0.0410
C (3)	0.113 (2)	0.7149 (6)	0.395 (1)	0.0465
C (4)	0.286 (1)	0.5990 (9)	0.506 (1)	0.0523
C (5)	0.490 (2)	0.899 (1)	0.394 (1)	0.0652
C (6)	0.635 (2)	0.7734 (7)	0.510 (1)	0.0628
C (7)	0.622 (1)	0.9346 (6)	0.604 (1)	0.0453
C (8)	0.776 (1)	0.9074 (8)	0.408 (1)	0.0482

[a] $U_{eq}\ (Å^2) = [U_1 U_2 U_3]^{1/3}$.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$

Zn (1)–O (1)	1.925 (6)	Zn (1)–O (5)	1.939 (5)
Zn (1)–O (7)	1.931 (4)	Zn (1)–O (9)	1.934 (5)
Zn (2)–O (2)	1.946 (5)	Zn (2)–O (10)	1.926 (6)
Zn (2)–O (13)	1.927 (5)	Zn (2)–O (16)	1.921 (5)
P (1)–O (1)	1.517 (5)	P (1)–O (2)	1.505 (5)
P (1)–O (3)	1.583 (6)	P (1)–O (4)	1.536 (5)
P (2)–O (5)	1.498 (5)	P (2)–O (6)	1.565 (7)
P (2)–O (7)	1.490 (5)	P (2)–O (8)	1.555 (6)
P (3)–O (9)	1.507 (5)	P (3)–O (10)	1.514 (5)
P (3)–O (11)	1.572 (6)	P (3)–O (12)	1.544 (5)
P (4)–O (13)	1.492 (5)	P (4)–O (14)	1.565 (7)
P (4)–O (15)	1.573 (7)	P (4)–O (16)	1.495 (5)
N (1)–C (1)	1.46 (1)	N (1)–C (2)	1.52 (1)
N (1)–C (3)	1.50 (1)	N (1)–C (4)	1.47 (1)
N (2)–C (5)	1.46 (1)	N (2)–C (6)	1.50 (1)
N (2)–C (7)	1.49 (1)	N (2)–C (8)	1.49 (1)
Zn (1)–O (1)–P (1)	128.2 (3)	Zn (2)–O (2)–P (1)	131.9 (3)
Zn (1)–O (5)–P (2)	141.9 (3)	Zn (1)–O (7)–P (2)	138.5 (3)
Zn (1)–O (9)–P (3)	135.4 (3)	Zn (2)–O (10)–P (3)	126.2 (3)
Zn (2)–O (13)–P (4)	142.6 (4)	Zn (2)–O (16)–P (4)	134.3 (3)

The two distinct tetrahedral TMA cations have typical geometrical parameters, with $d_{av}[N(1)–C] = 1.488\ (6)$ Å and $d_{av}[N(2)–C] = 1.485\ (5)$ Å. There are no template to framework H-bonding linkages for this species, unlike the situation in most other ZnPOs templated by small organic species, where structurally important N–H ⋯ O hydrogen bonds from a protonated amine group to a framework oxygen atom donor are seen to occur (8–12).

The three-dimensional framework of $N(CH_3)_4{\cdot}Zn(HPO_4)(H_2PO_4)$ is built up from ZnO_4 and PO_4 units sharing vertices. There are no Z–O–Zn or P–O–P bonds in the structure. Separate, zigzag chains of Zn(1)/P(2) (at 0, 0, 0 and equivalent positions) and Zn(2)/P(4) zinc/dihydrogen phosphate tetrahedra (at 1/2, 1/2, 0 and equivalent positions) propagate in the [001] direction. These two chains are

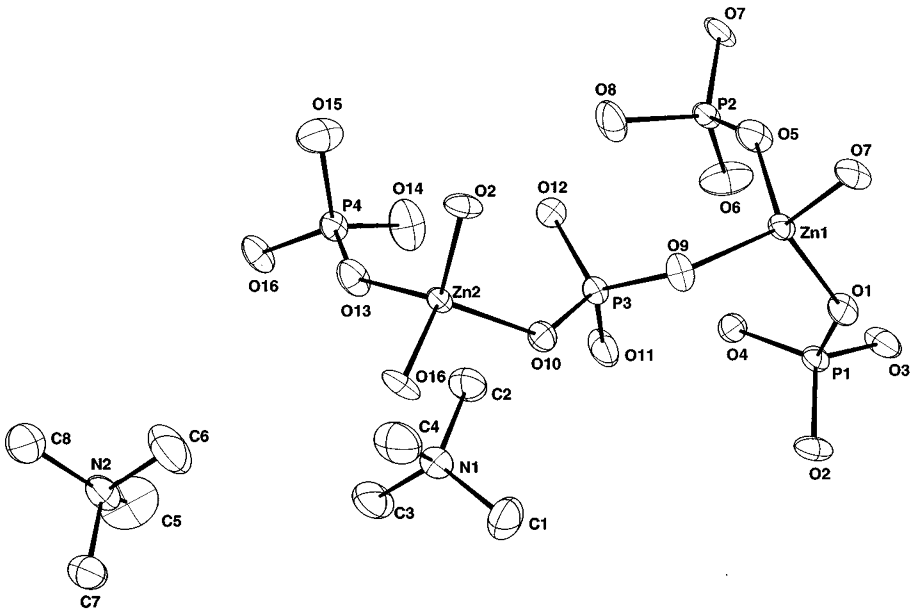

FIG. 1. View of a fragment of the $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ structure showing the atom labeling scheme (50% thermal ellipsoids).

crosslinked from zinc to zinc, normal to [001], by the P(1)- and P(3)-centered hydrogen phosphate groups. This connectivity results in a distinctive two-dimensional channel system, with intersecting 12-ring pore systems propagating along [100] and [001]. Each of the TMA cations is associated with a framework 12-ring (12 tetrahedral atoms, or 24 atoms in total, six Zn, six P, and 12 O), as shown in Fig. 3. The smallest identifiable loop configuration in this structure, starting at either Zn or P, is a 12-ring, with strictly alternating Zn and P nodes—there are no 4-, 6-, or 8-rings present in this structure, as found for most other zincphosphate frameworks templated by organic cations (8–16).

By the criterion of framework density (25), defined as the number of nodal tetrahedral atoms per 1000 Å^3, $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ has an exceptionally open structure, with a FD value of 10.2, equal to the lowest FD value observed so far all-tetrahedral networks (16). It should be noted however, that the $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ framework is "interrupted"—not all the tetrahedral groups make four bonding connections to their neighbors, thus direct comparison with aluminosilicate networks should be made with care. $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ is closely related to $N(CH_3)_4 \cdot ZnH_3(PO_4)_2$ (16), the latter material having an essentially identical FD value and a similar 12-ring based framework topology. In $N(CH_3)_4 \cdot ZnH_3(PO_4)_2$, which crystallizes in a face-centered orthorhombic unit cell (12, 16), the location of the H atoms on the hydrogen/dihydrogen phosphate groups and the orientation of the TMA cation appear to be less well defined than the corresponding species in $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$. It is not yet known whether $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and $N(CH_3)_4 \cdot ZnH_3(PO_4)_2$ can structurally transform.

Crystal structure of $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$. Final atomic positional and thermal parameters for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ are listed in Table 4, with selected bond distance/angle data in Table 5. $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ is a new "zero-dimensional" zincophosphate consisting of anionic $[Zn(H_2PO_4)_3]_2^{2-}$ clusters accompanied by TMA cations.

TABLE 4
Final Atomic Coordinates/Thermal Factors for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$

Atom	x	y	z	U_{eq}[a]
Zn (1)	0.11066 (6)	0.21892 (6)	0.35718 (6)	0.0226
P (1)	− 0.1616 (1)	0.1035 (1)	0.6307 (1)	0.0246
P (2)	− 0.1264 (1)	0.5151 (1)	0.2013 (1)	0.0241
P (3)	0.3243 (1)	0.4310 (1)	0.3558 (1)	0.0258
O (1)	− 0.0023 (4)	0.1479 (4)	0.5565 (4)	0.0328
O (2)	0.1715 (4)	0.0639 (3)	0.2882 (4)	0.0316
O (3)	− 0.0066 (3)	0.3816 (3)	0.2002 (3)	0.0278
O (4)	0.2915 (4)	0.2960 (4)	0.3500 (4)	0.0322
O (5)	− 0.2737 (4)	0.1773 (4)	0.5099 (4)	0.0422
O (6)	− 0.2270 (4)	0.1651 (4)	0.7503 (4)	0.0379
O (7)	− 0.2642 (3)	0.4700 (4)	0.3234 (3)	0.0293
O (8)	− 0.1914 (4)	0.6004 (4)	0.0487 (4)	0.0370
O (9)	− 0.0477 (4)	0.6332 (4)	0.2085 (5)	0.0438
O (10)	0.3728 (4)	0.3794 (4)	0.5112 (4)	0.0407
O (11)	0.1938 (4)	0.5616 (4)	0.3248 (4)	0.0374
O (12)	0.4723 (4)	0.4849 (5)	0.2381 (4)	0.0461
N (1)	0.3391 (5)	− 0.0803 (5)	0.8363 (5)	0.0350
C (1)	0.3946 (8)	− 0.0309 (7)	0.6721 (6)	0.0513
C (2)	0.4681 (9)	− 0.172 (1)	0.9222 (8)	0.0743
C (3)	0.290 (2)	0.055 (1)	0.863 (1)	0.0921
C (4)	0.214 (1)	− 0.174 (1)	0.887 (1)	0.1067

[a] U_{eq} (Å^2) $= [U_1 U_2 U_3]^{1/3}$.

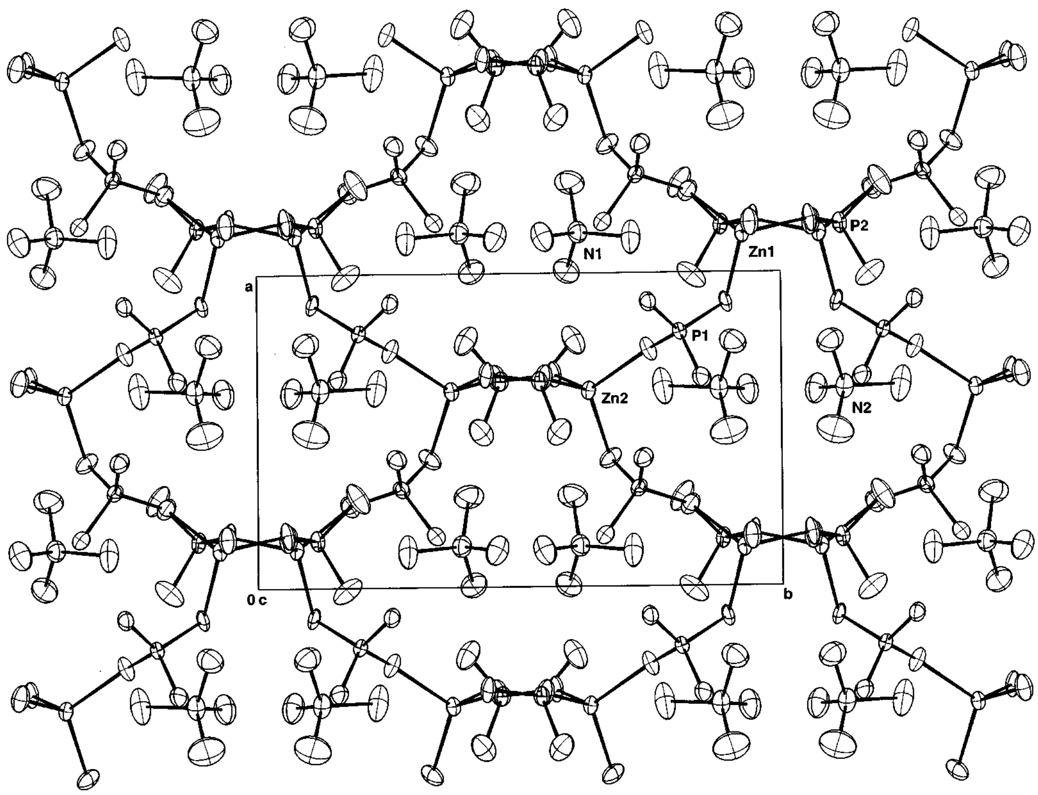

FIG. 2. View down *c* of the unit cell packing of $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$, showing the 12-ring channel system propagating along [001]. Note that the N(1) and N(2) centered TMA cations segregate into their own 12-ring channels.

The bonding unit of $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ is shown in Fig. 4, and the complete crystal structure is in Fig. 5.

The zinc atom in $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ is tetrahedral with $d_{av}[Zn–O] = 1.934$ (2) Å. Each of the four Zn–O vertices also bonds to a phosphorus center, resulting in an average Zn–O–P bond angle of 133.7°. There are three distinct P atoms with $d_{av}[P(1)–O] = 1.534$ (2) Å, $d_{av}[P(2)–O] = 1.536$ (2) Å, and $d_{av}[P(3)–O] = 1.551$ (2) Å. P(1) makes two P–O–Zn connections and has two terminal P–O links. P(2) and P(3) make one P–O–Zn link and have three terminal bonds to O in their tetrahedral coordination spheres. The $[ZnP_3O_{12}]^{7-}$ unit requires six protons for charge balance, in addition to the TMA counter cation. Phosphorus–oxygen bond length/bond strength considerations suggest that each of the three P atoms has two P–OH vertices; i.e., there are three dihydrogen phosphate groups in this phase.

The TMA species shows extensive thermal motion in three of its four carbon atoms. A TLS analysis (26) suggested that this motion was well accounted for by a librational motion essentially about the N(1)–C(1) bond axis. An alternative model which assumed two orientations for the C(2), C(3), and C(4) atoms led to virtually identical residuals to the simple model and statistically equal populations of the two conformations.

$N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ is a molecular phase and appears to be unique among zincophosphates. Two $Zn(H_2PO_4)_3$ formula units combine to form an anionic $[Zn_2(H_2PO_4)_6]^{2-}$ dimer. This results in a tetrahedral 4-ring formed of alternating ZnO_4 and $H_2P(1)O_4$ tetrahedra, with two "hanging" dihydrogen phosphate groups [phosphorus

TABLE 5
Selected Bond Distances (Å) and Angles (°) for $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$

Zn (1)–O (1)	1.914 (3)	Zn (1)–O (2)	1.926 (3)
Zn (1)–O (3)	1.974 (3)	Zn (1)–O (4)	1.922 (3)
P (1)–O (1)	1.502 (3)	P (1)–O (2)	1.497 (3)
P (1)–O (5)	1.575 (4)	P (1)–O (6)	1.563 (3)
P (2)–O (3)	1.518 (3)	P (2)–O (7)	1.506 (3)
P (2)–O (8)	1.569 (3)	P (2)–O (9)	1.552 (4)
P (3)–O (4)	1.485 (3)	P (3)–O (10)	1.564 (4)
P (3)–O (11)	1.507 (3)	P (3)–O (12)	1.563 (4)
N (1)–C (1)	1.499 (7)	N (1)–C (2)	1.480 (7)
N (1)–C (3)	1.462 (9)	N (1)–C (4)	1.471 (9)
Zn (1)–O (1)–P (1)	136.2 (2)	Zn (1)–O (2)–P (1)	130.9 (2)
Zn (1)–O (3)–P (2)	131.2 (2)	Zn (1)–O (4)–P (3)	136.6 (2)

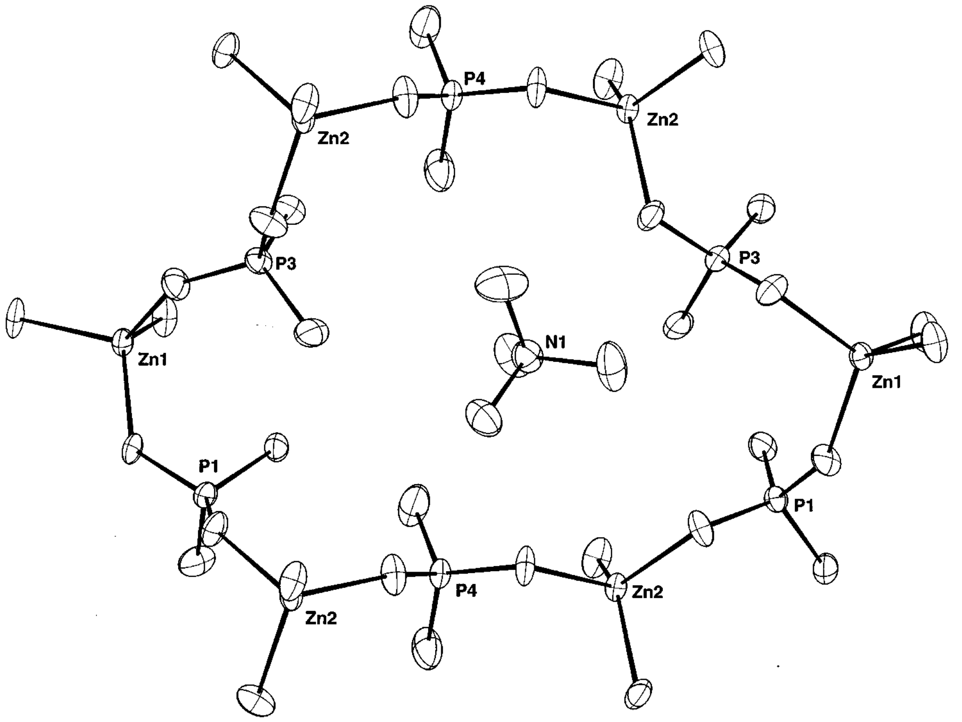

FIG. 3. Detail of the $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ structure showing the tetrahedral 12-ring associated with the N(1)-centered TMA cation.

atoms P(2) and P(3)] attached to each of the Zn centers (Fig. 4). There is a inversion center at the midpoint of the central 4-ring. The clusters stack along [010], probably involving intercluster H-bonding interactions. Along [100], the ZnPO clusters and TMA cations form a sandwich like structure (Fig. 5).

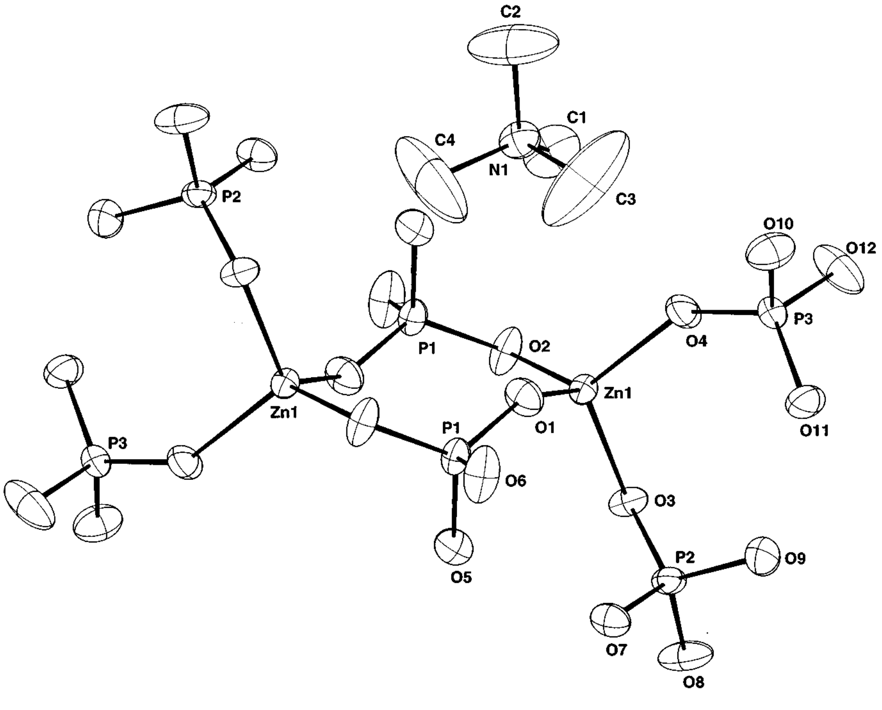

FIG. 4. View of a fragment of the $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ structure showing the atom labeling scheme (50% thermal ellipsoids).

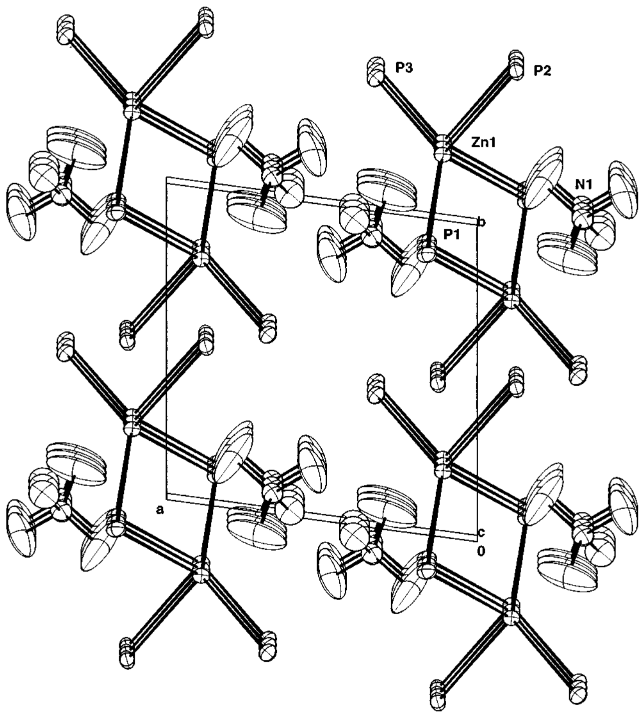

FIG. 5. Packing diagram for the $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ structure in skeletal representation showing Zn to P connectivity (O atoms omitted). View direction down [001].

The Zn/P/O connectivity in $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$ shows similarities to that of the "polymeric" $Zn[PO_2(OC_2H_5)_2]_2$ phase (27), which is built up from infinite chains of 4-rings of ZnO_4 and PO_4 units (the latter as part of diethylphosphate entities), with the zinc atoms forming the nodes of the 4-ring chains.

CONCLUSIONS

Two new tetramethylammonium zincophosphates, $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$ and $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$, have been prepared as single crystals and structurally characterized. Both consist of the typical tetrahedral building blocks found in other zincophosphate framework phases (1–16). As with the organo-zincophosphates templated by other molecules, the TMA templating species has led to unique structural types. It is difficult to rationalize any local templating effect for this cation because of its approximately spherical shape and the lack of any H-bonds formed. A previous ZnPO co-templating synthesis involving sodium and TMA cations led to a zeolite-X framework (3), with the TMA species possibly occupying cuboctahedral β-cages, akin to its behavior in solidate analogues (28). The behavior of the TMA species in the present study is quite different, and for $N(CH_3)_4 \cdot Zn(HPO_4)(H_2PO_4)$, a novel low-density framework structure based on a 12-ring *motif* results. Conversely, a molecular cluster is formed in $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$, perhaps due to the 1:3 Zn:PO_4 ratio, which requires most of the P–O bonds to be protonated to offset its high negative charge.

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