RAPID COMMUNICATION

$(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$: A Low-Density Framework Built Up from a Fully Connected (3, 4) Net of ZnO_4 Tetrahedra and HPO_3 Pseudo Pyramids

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$(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$, the first organically templated, three-dimensional zincophosphite framework, is built up from a fully connected (3, 4) net of ZnO_4 tetrahedra and HPO_3 pseudo pyramids, sharing vertices as Zn–O–P bonds. These units self-assemble around the piperidinium templates to result in a low-density anionic framework containing helical columns and 4-ring and 16-ring windows. Crystal data: $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$, $M_r = 688.39$, monoclinic, $C2/c$ (No. 15), $a = 16.3351(7)$ Å, $b = 9.2750(4)$ Å, $c = 17.2416(8)$ Å, $\beta = 117.987(1)°$, $V = 2306.8$ (3) Å³, $Z = 4$, $R = 0.032$, $R_w = 0.036$. © 2001 Academic Press

INTRODUCTION

As part of the current renaissance in the study of micro-porous solids (1), over 30 organically templated zincophos-phates (ZnPOs) have now been characterized (2), all of which contain a protonated organic template (usually an amine or amine derivative), Zn^{2+} cations, and (hydrogen) phosphate tetrahedra. These latter moieties link together in various ways to form inorganic networks which may be zero- (i.e., a cluster), one-, two-, or three-dimensional in nature. The degree of protonation of each phosphate group is important in determining how many P–O–Zn bonds are formed, because, when P–OH vertices are present, these groupings do not participate in links to Zn. Thus, rather than a tetrahedron, an $[HPO_4]^{2-}$ group could be regarded as an *anionic pseudo pyramid* (APP) in terms of the availability of three P–O links for network forming.

A more systematic way of introducing APP building units into polyhedral networks was suggested to us by the work of Clearfield *et al.* on zinc hydrogen phosphites (containing the $[HPO_3]^{2-}$ ion) templated by inorganic species (3), and we have recently described (4–6) several organically templated zincophosphites. Their structural features include Zn–N

(zinc-to-template) bonds (4), and for $[H_2N(CH_2)_2NH_2]_{0.5} \cdot$ $ZnHPO_3$ (5), a novel structure containing two independent, interpenetrating networks. $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_3)_2$ has strong one-dimensional character and contains 4-ring chains (6). In this paper we report the synthesis and structural characterization of $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$, a low-density, three-dimensional zincophosphite framework templated by piperidinium cations.

EXPERIMENTAL

Synthesis. $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ was prepared by combining 0.5 g of H_3PO_3, 0.24 g of ZnO, and 0.26 g of piperidine in 10 ml of water (starting template:Zn:P ratio ≈ 1:1:2). The reactants were sealed in a 23-ml capacity, Teflon-lined hydrothermal bomb and heated to 150°C for 2 days. Upon cooling over several hours, the solid product was recovered from the supernatant liquors by vacuum filtration and rinsed with acetone. It contained a mass of transparent plates and flakes of the title compound and a minor component identified as ZnO on the basis of powder data. Preparations under similar conditions starting from a stoichiometric 2:3:4 template:Zn:P ratio led to as-yet unidentified powder products.

Structure determination. Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 25 \pm 2°C$): ω scans, $2° < 2\theta < 65°$, 10,701 data collected, empirical absorption correction (min. 0.504, max. 0.962), 3390 of 4139 merged reflections ($R_{Int} = 0.028$) considered observed $[I > \sigma(I)]$, structure solution by direct methods (7), full-matrix least-squares refinement using CRYSTALS (8). The P–H and N–H hydrogen atoms were located in difference maps and the C–H hydrogen atoms were located geometrically. The H atoms were refined by riding on their appropriate parent atoms in their as-found or calculated positions (group atomic

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TABLE 1
Crystallographic Parameters for $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$

Empirical formula	$Zn_3P_4O_{12}N_2C_{10}H_{28}$
M_r	688.39
Crystal symmetry	Monoclinic
Space group	$C2/c$ (No. 15)
a (Å)	16.3351(7)
b (Å)	9.2750(4)
c (Å)	17.2416(8)
β (°)	117.987(1)
V (Å^3)	2306.8(3)
Z	4
D_c (g/cm^3)	1.982
μ (cm^{-1})	34.3
T (K)	298(2)
R^a	0.032
R_w^b	0.036

[a] $R = \sum ||F_o| - |F_c||/\sum|F_o|$.
[b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ (calculated w_i).

isotropic thermal factor for the C–H species), as appropriate. Crystal data are summarized in Table 1. Supplementary data (atomic positional and thermal parameters, structure factors) are available from the author.

RESULTS AND DISCUSSION

There are 16 unique nonhydrogen atoms (2 Zn, 2 P, 6 O, 5 C, N) in $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$, all of which occupy general positions except Zn1, which has 2-fold symmetry (Fig. 1). The inorganic component of the structure is built up
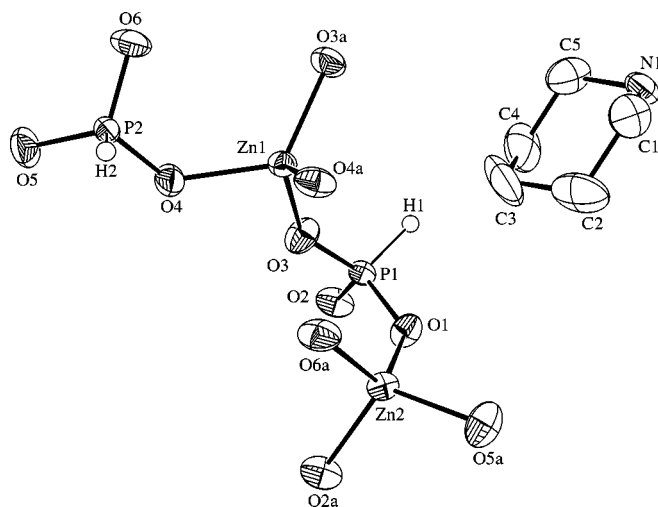
FIG. 1. View of the bonding unit in $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ showing the atom labeling scheme (50% thermal ellipsoids; template H atoms omitted for clarity; symmetry-generated atoms indicated by O2a, etc.). Selected bond distances (Å) and angles (°), with esds in parentheses: Zn1–O3 1.9313(15), Zn1–O4 1.9455(15), Zn2–O1 1.9709(14), Zn2–O2 1.9530(15), Zn2–O5 1.9202(17), Zn2–O6 1.9099(16), P1–O1 1.5285(15), P1–O2 1.5007(14), P1–O3 1.5078(16), P2–O4 1.5174(15), P2–O5 1.5071(16), P2–O6 1.5034(15), Zn2–O1–P1 130.82(9), Zn2–O2–P1 137.5(1), Zn1–O3–P1 143.37(12), Zn1–O4–P2 125.28(9), Zn2–O5–P2 144.30(12), Zn2–O6–P2 150.18(12).

from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo pyramids, sharing vertices, as Zn–O–P bonds (Fig. 2). Both Zn1 and Zn2 make four links to nearby P atoms $[d_{av}(Zn1–O) = 1.939(2)$ Å, $d_{av}(Zn2–O) = 1.939(2)$ Å] and
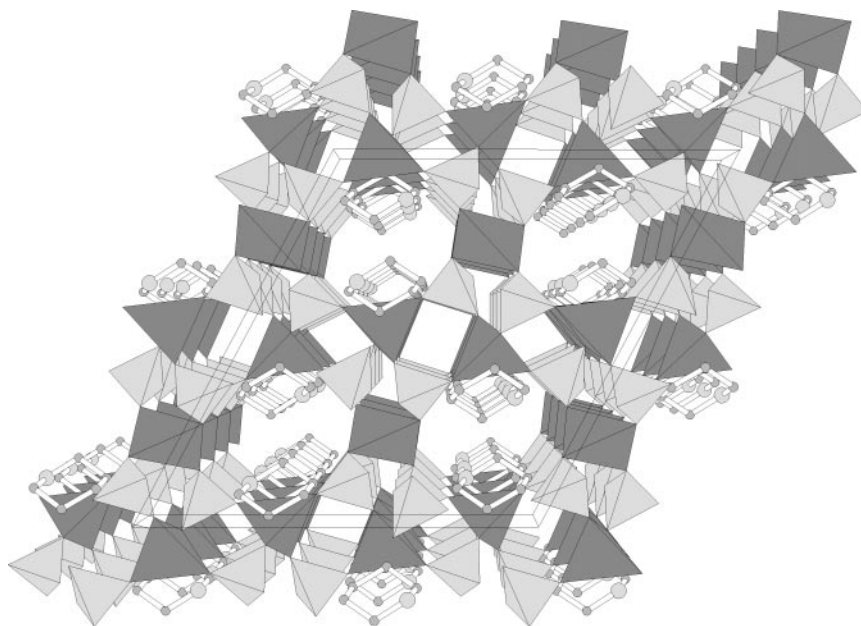
FIG. 2. View down [010] of the $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ structure showing the polyhedral connectivity of ZnO_4 (dark shading) and HPO_3 (light shading) groups encapsulating the extra-framework piperidinium cations.

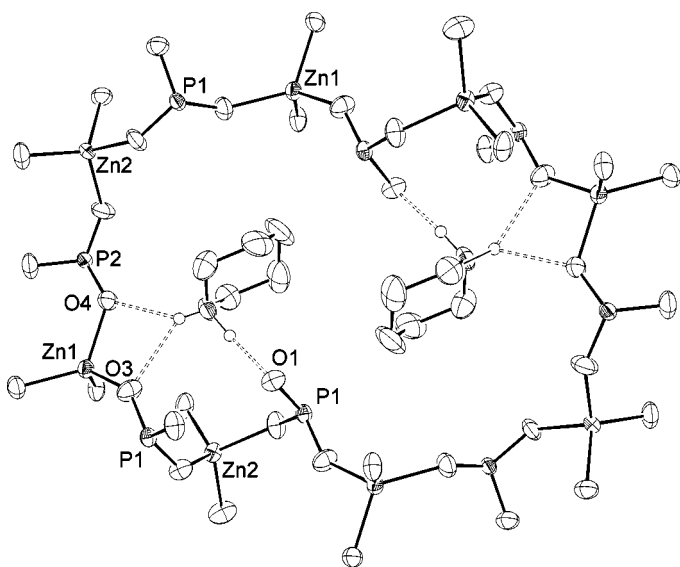**FIG. 3.** View of a 16-ring cavity in $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ with template-to-framework H bonds indicated by dotted lines. All H atoms except those associated with N1 are omitted for clarity.

P1 and P2 make three P–O–Zn links $[d_{av}(P1-O) = 1.512(2)\,Å$, $d_{av}(P2-O) = 1.509(2)\,Å]$, thus there are no "terminal" P–O bonds. As expected (9) for the hydrogen phosphite group, P–H bonds make up the fourth vertex of each $[HPO_3]^{2-}$ tetrahedron. The six O atoms all serve as bicoordinate Zn–O–P bridges, with an average bond angle of 138.6°.

The piperidinium cation has typical N–C and C–C geo-metrical parameters (10) and adopts a chair conformation. It interacts with the zincophosphite network by way of one short, strong N–H···O hydrogen bond, as N1–H3···O1 $[d(N-H) = 0.99\,Å$, $d(H···O) = 1.88\,Å$, $d(N···O) = 2.869$ $(3)\,Å$, $\theta(N-H···O) = 171°]$, and a longer and weaker bifur-cated N1–H4···(O3,O4) linkage $[d(N-H) = 0.80\,Å$, $d(H···O3) = 2.35\,Å$, $d(H···O4) = 2.25\,Å$, $d(N···O3) =$ $3.024(3)\,Å$, $d(N···O4) = 2.869(3)\,Å$, $\theta(N-H···O3) = 143°$, $\theta(N-H···O4) = 135°]$. These H bonds serve to anchor the organic species to the wall of an elliptical 16-membered cavity, which has atom-to-atom dimensions $\sim 5.94 \times 12.97\,Å$. Two piperidinium cations occupy each cavity (Fig. 3). The minimum nonbonding C···C contact between adjacent molecules is $\sim 4.6\,Å$.

The polyhedral connectivity in $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ results in an anionic, three-dimensional zincophosphite framework encapsulating channels and cavities occupied by the extraframework organic cations. We may envisage the structure to be built up from sheets of 4-ring chains (Zn2-, P1-, P2-centered polyhedra) alternatively propagating along [110] and [1$\bar{1}$0] with respect to the c direction, crosslinked by the Zn1O$_4$ tetrahedra into an infinite net-work. When viewed down [010], the cations appear to be
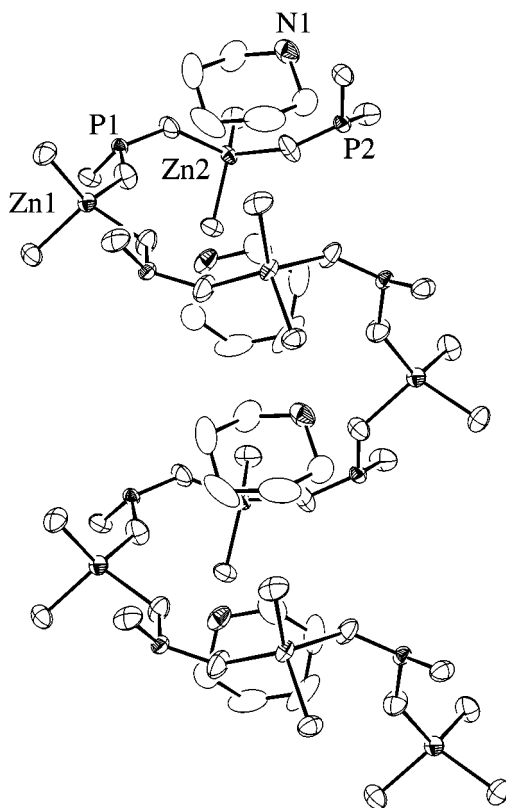

FIG. 4. Side-on view of a [010] helix of ZnO$_4$ and HPO$_3$ groups in $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ encapsulating a chain of piperidinium cations.

associated with polyhedral 8 rings built up from four ZnO$_4$ and four HPO$_3$ units (Fig. 2). In reality, these are *helical* chains (Fig. 4) although crystal symmetry dictates that there must be an equal number of clockwise and counterclock-wise spirals. The amount of void space (11) encapsulated by the $(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ framework is exceptionally large, at 1242.8 Å^3, or 53.8% of the unit cell volume. The framework density (12), defined as the number of nodal Zn and P atoms per 1000 Å^3, is 12.2.

$(NC_5H_{12})_2 \cdot Zn_3(HPO_3)_4$ is the first three-dimensional zincophosphite to be prepared by us, and as such is an interesting example of a network made up from four-coordi-nate (ZnO$_4$) and three-coordinate (phosphite) building blocks, with all vertices shared *via* bicoordinate O atom bridges, which naturally leads to the 3:4 Zn:P ratio. Little systematic study has been made of such so-called 3:4 nets (13), with two examples being $M_3B_7O_{13}X$ (M = divalent cation, X = halide) boracite-type phases containing BO$_4$ tetrahedra and BO$_3$ triangles and Na$_2$Zn$_3(CO_3)_4 \cdot 3H_2O$ (14) containing ZnO$_4$ tetrahedra and CO$_3$ triangles, but their cubic or pseudo-cubic structures are totally different from that of the title compound where the organic template plays a structure-directing role in forming a low-density network.

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