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Tetrahedral-Network Organo-Zincophosphates: Syntheses and Structures of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$

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Abstract

The solution-mediated syntheses and single crystal structures of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ (**I**), $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ (**II**), and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$ (**III**) are described. These phases contain vertex-sharing ZnO_4 and HPO_4 tetrahedra, accompanied by doubly-protonated organic cations. Despite their formal chemical relationship, as members of the series of $t\cdot Zn_n(HPO_4)_{n+1}$ (t = template, n = 1–3), these phases adopt fundamentally different crystal structures, as one-dimensional, two-dimensional, and three-dimensional ZnO_4/HPO_4 networks, for **I**, **II**, and **III**, respectively. Similarities and differences to some other zinc phosphates are briefly discussed. Crystal data: $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, M_r = 389.54, monoclinic, space group $P2_1/n$ (No. 14), a = 9.864 (4) Å, b = 8.679 (4) Å, c = 15.780 (3) Å, β = 106.86 (2)°, V = 1294.2 (8) Å^3, Z = 4, $R(F)$ = 4.58%, $R_w(F)$ = 5.28% [1055 reflections with $I > 3\sigma(I)$]. $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, M_r = 494.84, monoclinic, space group $P2_1/c$ (No. 14), a = 8.593 (2) Å, b = 9.602 (2) Å, c = 17.001 (3) Å, β = 93.571 (8)°, V = 1400.0 (5) Å^3, Z = 4, $R(F)$ = 4.09%, $R_w(F)$ = 4.81% [2794 reflections with $I > 3\sigma(I)$]. $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, M_r = 694.25, monoclinic, space group $P2_1/n$ (No. 14), a = 9.535 (2) Å, b = 23.246 (4) Å, c = 9.587 (2) Å, β = 117.74 (2)°, V = 1880.8 (8) Å^3, Z = 4, $R(F)$ = 3.23%, $R_w(F)$ = 3.89% [4255 reflections with $I > 3\sigma(I)$].

Introduction

Many tetrahedral-network zincophosphates (ZnPOs) templated by organic cations have been described (1). Although the fundamental building units—ZnO_4 and PO_4 tetrahedra—are common to all these phases, their crystal structures are strongly but unpredictably dependent on the identity of the structure-directing organic species. The presence of "dangling" Zn–OH_2, P–O, and P–OH bonds (2), and three-coordinated framework O atoms, invariably to 2 Zn + 1 P (3) complicate the picture further, in terms of rationalising and predicting ZnPO crystal structures. Thus, exploratory synthesis continues to play a vital role in mapping out this phase space and seeking further correlations between preparations and crystal structures.

In this paper we report the solution-mediated syntheses and single-crystal structures of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, three new zinc hydrogen phosphate phases templated by the doubly-protonated, "bifunctional" organic cations 1,4-diazabicyclo[2.2.2]octane (dabco), $N_2C_6H_{14}$, and 1,3-diammonium propane, $H_3N(CH_2)_3NH_3$. These phases may be regarded as members of the series of $t\cdot Zn_n(HPO_4)_{n+1}$ (t = $[\text{template}]^{2+}$, n = 1–3). Despite their formal chemical relationship, these phases adopt fundamentally different crystal structures, as one-dimensional, two-dimensional, and three-dimensional ZnO_4/PO_4 networks, for $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, respectively. These phases are briefly compared and contrasted to known zinc phosphates.

Experimental

Syntheses: $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$: 10.08 g (90 mmol) dabco, 0.81 g (10 mmol) ZnO and 6.91 g (216 mmol) of H_2O were added to a teflon bottle. 10.35 g (90 mmol) of 85% H_3PO_4 wes added. A thixotropic mixture formed, resulting in a milky white solution upon mixing. The solution was heated in a sealed bottle at 70 C for 14 days. The product was recovered by vacuum filtration and washing with deionized H_2O, resulting in a few clear needle and rod shaped crystals.

$H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$: ZnO, TiO_2, 85% H_3PO_4 and 1,3-diaminopropane were mixed in a 2:1:10:2 ratio in 10 cc of water. This mixture was enclosed in a teflon-lined 23-ml hydrothermal bomb and heated to 150 C for three days. The product was vacuum filtered and washed with deionized H_2O, resulting in block-like crystals to 1 mm. Preparations omitting the TiO_2 powder led to other, unidentified products.

$(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$: ZnO, TiO_2, 85% H_3PO_4 and 1,4-diazabicyclo[2.2.2]octane (dabco) were mixed in a 4:1:4:2 ratio in 10 cc of water. This mixture was enclosed in a teflon-lined 23-ml hydrothermal bomb and heated to 150 C for three days. The product was vacuum filtered and washed with deionized H_2O, resulting in clear, chunky crystals.

Structure determinations: Suitable single crystals [$(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, translucent lump, ~0.1 × 0.3 × 0.4 mm; $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, clear block, ~0.3 × 0.3 × 0.4 mm; $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, clear chunk, ~0.4 × 0.5 × 0.5 mm] were mounted on thin glass fibers with cyanoacrylate 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), as summarised in Table 1. The application of peak-search, centering, indexing and least-squares refinement routines led to a primitive monoclinic unit cell in each case. Intensity data [for the weakly scattering $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $2 < 2\theta < 45$; for $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, $2 < 2\theta < 60$] were collected using the $\theta/2\theta$ scan mode. Three check reflections, remeasured every 100 observations, showed no significant variation in intensity over the course of each data collection. Empirical corrections for crystal absorption [for $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, range of equivalent transmission factors = 0.490–0.759; $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ 0.517–0.818; $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$ 0.676–0.839] were applied on the basis of ψ scans.

Data merging for $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ resulted in 1696 reflections (R_{Int} = 0.026), with 1162 of these observed according to the criterion $I > 3\sigma(I)$. The systematic absences ($h0l$, $h+l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14). For $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ [3936 merged data; 2794 observed; R_{Int} = 0.047], the systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/c$. For $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, there were 5110 merged data, of which 4255 were observed (R_{Int} = 0.025) with the systematic absences indicating space group $P2_1/n$.

Direct methods (4) established enough of each structure (Zn, P, some O atoms) to enable the remaining non-hydrogen atoms to be located from difference maps without difficulty. Hydrogen atoms associated with the doubly-protonated template molecules were located geometrically [d(N–H) =0.95 Å, d(C–H) = 0.95 Å] and refined by riding on their N and C atoms. Some H atoms associated with P–O bonds were located from Fourier syntheses and refined by riding on their O atoms. The final cycles of full-matrix least-squares refinement [program CRYSTALS (5)], using complex, neutral-atom scattering factors (6), minimized the function $\Sigma\ w_i\ (F_o - F_c)^2$, with w_i described by a three-term Chebychev polynomial (7), and included anisotropic temperature factors for all the non-hydrogen atoms and a Larson-type secondary extinction correction (8). Refinement details are summarised in Table 1. Supplementary data (hydrogen atom coordinates, anisotropic thermal factors and observed and calculated structure factors) are available from the authors.

Results

Crystal Structure of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$: Final atomic positional and thermal parameters are listed in Table 2, with selected bond distance/angle data in Table 3. $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ is a new dabco–zinc hydrogen phosphate hydrate with strong one-dimensional character based on chains of ZnO_4 and HPO_4 tetrahedra, fused together *via* Zn–O–P bonds. An ORTEP-3 (9) view of the asymmetric unit of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ is shown in Figure 1, and the complete crystal structure in Figure 2.

Zn1 makes four Zn–O–P linkages to nearby phosphorus atoms, with typical (1) geometrical parameters [d_{av}(Zn–O) = 1.924 (4) Å]. Both P atoms form the centers of hydrogen phosphate groups with d_{av}(P1–O) = 1.534 (5) Å and d_{av}(P2–O) = 1.531 (5) Å. Each of these entities participates in two P–O–Zn links, and has two terminal P–O bonds. Assuming that the organic species is doubly protonated, then two "framework" protons are required for charge-balancing purposes. Variations in terminal P–O bond lengths and individual P–O bond valences (10) suggest that the P1–O7 and P2–O5 bonds are protonated, *i.e.*, there are two HPO_4 groups in this phase. The eight distinct framework oxygen atoms thus divide into four Zn–O–P bridges [θ_{av} = 141.5°] and four terminal P–O vertices. The N–C and C–C geometrical parameters for the dabco cation are typical (2). A water molecule of hydration (oxygen atom O10) is present. H atoms associated with this O atom were not located, but hydrogen bonding may well be present, based on the presence of short O10···O1 and O10···O7 contacts of 2.851 (9) and 2.87 (1) Å, respectively.

The polyhedral connectivity in $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, results in corner sharing, anionic 4-ring (4 nodal tetrahedral atoms) chains of stoichiometry $[Zn(HPO_4)_2]^{2-}$, which propagate along [010]. The doubly protonated dabco cations occupy inter-chain sites and bond to the zincophosphate chains through N–H···O hydrogen bonds. Based on the geometrical placement of the hydrogen atoms, both N–H protons are involved in such linkages, as N1–H1···O8 [d(H···O) = 1.77 Å, d(N···O) = 2.706 (9) Å] and N2–H2···O6 [1.72 Å, 2.668 (9) Å], thus the dacbo cation crosslinks adjacent [010] $[Zn(HPO_4)_2]^{2-}$ chains.

Crystal Structure of $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$: Final atomic positional and thermal parameters and selected geometrical data are listed in Tables 4 and 5, respectively. $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ is a new 1,3-diammonium propane zinc hydrogen phosphate with strong two-dimensional character consisting of infinite, anionic $[Zn_2(HPO_4)_3]^{2-}$ sheets sandwiching 1,3-diammonium-propane cations. The bonding unit and atom labelling scheme for $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ is shown in Figure 3, and the complete crystal structure in Figure 4.

The tetrahedral zinc and phosphorus atoms in this phase have typical geometrical parameters (1): d_{av}(Zn1–O) = 1.935 (2) Å; d_{av}(Zn2–O) = 1.926 (2) Å; d_{av}(P1–O) = 1.530 (2) Å; d_{av}(P2–O) = 1.528 (2) Å; d_{av}(P3–O) = 1.533 (2) Å. Each Zn centre makes four Zn–O–P bonds. P1 and P2 make three P–O–Zn links, and one terminal P–OH bond, whereas P3 makes two links to Zn and has two terminal P–O bonds. The P1–O4H, P2–O8H, and P3–O12H entities were located from Fourier maps. The presence of three HPO_4 groups is consistent with the charge balancing criterion, which requires three framework H atoms. The average Zn–O–P bond angle (eight contributors) is 130.3 . N–C and C–C bond length for the template are unexceptional (1). Torsion angles of 177.9 for the N1–C1–C2–C3 and 179.3 for the C1–C2–C3–N2 groupings of the 1,3-diammonium-propane chain result.

The ZnO_4 and HPO_4 groups in $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ fuse together to result in infinite sheets which propagate normal to [001] (Figure 5). Four rings and 12 rings are apparent in these sheets.

Template-to-framework hydrogen bonding interactions appear to be significant in stabilising the layered nature of the $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$ structure. All six N–H vertices make H bonds to zincophosphate chain oxygen atoms (Table 5) which variously form parts of Zn–O–P and P–OH groups. Because of the canted arrangement of the $[H_3N(CH_2)_3NH_3]^{2+}$ species (Figure 4), both N1 and N2 are involved in O···H–N–H···O *inter*-layer interactions. Thus, we might visualise that *each end* of the $[H_3N(CH_2)_3NH_3]^{2+}$ cation is serving to pillar the anionic zincophosphate layers by "typical" hydrogen bonding interactions (1). The three zincophosphate layer P–OH bonds also serve as H bond donors; two of these bonds are *intra*-layer, and one [O8–H102···O11] is *inter*-layer.

Crystal Structure of $(N_2C_6H_{14}) \cdot Zn_3(HPO_4)_4$: Final atomic positional and thermal parameters are listed in Table 6, with selected bond distance/angle data in Table 7. $(N_2C_6H_{14}) \cdot Zn_3(HPO_4)_4$ is a new phase based on a three-dimensional network of vertex-sharing ZnO_4 and HPO_4 tetrahedra, accompanied by doubly-protonated dabco cations. The bonding unit of $(N_2C_6H_{14}) \cdot Zn_3(HPO_4)_4$ is shown in Figure 6, and the complete crystal structure in Figure 7.

The tetrahedral ZnO_4 and HPO_4 moieties in $(N_2C_6H_{14}) \cdot Zn_3(HPO_4)_4$ have typical geometrical parameters, with average bond lengths as follows: Zn1 1.937 (1) Å, Zn2 1.919 (1) Å, Zn3 1.935 (1) Å, P1 1.533 (2) Å, P2 1.532 (2) Å, P3 1.532 (2) Å, P4 1.528 (2) Å. Each of the Zn centres makes four Zn–O–P bonds. All the P atoms make three P–O–Zn bonds and one terminal P–OH bond, as required by the charge balancing criterion, which requires four framework H atoms. Three of these H atoms were located from difference maps, and the fourth was implied by the long P3–O12 bond. The average Zn–O–P bond angle, based on 12 contributors, is 132.6 . N–C and C–C bond lengths for the dabco template are typical (2).

The ZnO_4 and HPO_4 groups in $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ fuse together to result in a three-dimensional framework which contains 12-rings propagating along [001]. Based on atom-to-atom measurements, these highly-squashed rings are ~4.0 × 17.5 Å in size. Four rings and eight rings are also present in this topology. A notable feature of the structure is the grouping of three edge-sharing 4-rings (Figure 8).

The doubly protonated dabco cations bond to the zincophosphate network through N–H···O hydrogen bonds, as N1–H1···O5 [d(H···O) = 1.87 Å, d(N···O) = 2.801 (3) Å] and N2–H2···O6 [1.92 Å, 2.809 (4) Å], based on the geometrical placement of the hydrogen atoms. In this structure, the dabco cation occupies and bridges across an [001] 12-ring. Two P–OH···O bonds are also involved in stabilising the 12-ring channels, as O8–H16···O12 [1.85 Å, 2.702 (4) Å] and O16–H18–O1 [1.66 Å, 2.599 (4) Å]. The third definitely located P–OH···O bond in this structure weakly bonds across a 6-ring, as O4-H15···O14 [2.26 Å, 3.035 (4) Å].

Discussion

Three new organically-templated zincophosphates, $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$, have been prepared as single crystals from solution mediated reactions and structurally characterised by X-ray methods. They consist of the typical polyhedral units of ZnO_4 and HPO_4 tetrahedra, sharing vertices (1). Only Zn–O–P bonds occur as inter-tetrahedral linkages in these phases, despite the less-than-unity Zn:P atomic ratio found in each phase. Some terminal P–O and P–OH vertices occur, as previously observed in related compounds (1). Based on chemical composition, they form a family of phases $t\cdot Zn_n(HPO_4)_{n+1}$ (t = [template]$^{2+}$, $n = 1$–3). However, their structures are completely different and the chain, layer, and network structures described above result. Similar results have been achieved for vanadium phosphates, where the dimensionality of the vanadophosphate network can be controlled by choice of template (11).

$(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ is closely related to $RbZn(HPO_4)(H_2PO_4)\cdot H_2O$ (12) and $NH_4Zn(HPO_4)(H_2PO_4)\cdot H_2O$ (13), with all three phases showing the same corner-sharing 4-ring ZnPO chain architecture. The rubidium and ammonium phases achieve charge balance with an additional framework proton, as an H_2PO_4 group. In $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $RbZn(HPO_4)(H_2PO_4)\cdot H_2O$, and $NH_4Zn(HPO_4)(H_2PO_4)\cdot H_2O$, the ZnPO chains all propagate in the same direction. Conversely, in $(NC_2H_8)\cdot Zn(HPO_4)(H_2PO_4)\cdot 1/2H_2O$ (14), similar ZnPO chains adopt a crisscross *motif* between layers. $H_3N(CH_2)_3NH_3\cdot Zn(HPO_4)_2$ (1) adopts a distinctly different structure, based on *edge*-shared tetrahedral 4-rings. This topology is also adopted by the one-dimensional organo-aluminophosphate $C_{10}N_2H_9\cdot Al(PO_4)(H_2PO_4)$ (15). Both the corner shared and edge-shared 4-ring *motifs* are well known as subunits in three-dimensional aluminosilicate structures (16). Other phases with a 1:2 Zn:P ratio, such as $N(CH_3)_4\cdot Zn(HPO_4)(H_2PO_4)$ (17) and $(CN_3H_6)_2\cdot Zn(HPO_4)_2$ (18), form a radically different type of three-dimensional structure in which the H_2/HPO_4 groups serve as “spacers” between tetrahedral ZnO_4 nodes, leading to fragile, but exceptionally low-density structures based on tetrahedral 12 rings.

The layered $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$ complements the one-dimensional $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_4)_2$ and the two-dimensional $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2$ templated by the same cation (1). A notable difference between these three phases is in the geometry of the 1,3-diammonium propane template cation. In $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_4)_2$ and $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2$, the organic species is highly contorted, whereas in $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$ it is in the almost ideal, "straight" configuration as quantified in terms of torsion angles which are near to 180 . The same molecule adopts an essentially identical conformation in $H_3N(CH_2)_3NH_3 \cdot (H_2PO_4)_2$ with similar N–H···O hydrogen bonding linkages (19). Although the $[H_3N(CH_2)_3NH_3]^{2+}$ cation has a quite different conformation, there appears to be a rather similar templating effect for the layered $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2$ and $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$. For the former (1), a strong correlation between N–H···O bonds and 12-ring holes in adjacent zincophosphate layers is apparent; for the latter, the situation is described above.

$(N_2C_6H_{14}) \cdot Zn_3(HPO_4)_4$ complements other complex three-dimensional dabco–zinc phosphates including $(N_2C_6H_{14}) \cdot Zn_2(HPO_4)_3$ (2), $(N_2C_6H_{14}) \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ (2), $(N_2C_2H_{14})_2 \cdot Zn_5(PO_4)_2(HPO_4)_4 \cdot H_2O$ (20), and $(N_2C_2H_{13}) \cdot Zn_3(PO_4)(HPO_4)_2$ (20). One point of commonality may be identified in terms of the presence of the ubiquitous 4-ring subunit (21). However, these five structures have little further similarity in terms of their overall architectures. $(N_2C_2H_{13})\cdot Zn_3(PO_4)(HPO_4)_2$ contains Zn–N(template) bonds, which are so-far unique in open-framework zincophosphates.

Overall, it would be optimistic to claim any clear structure-directing effect for these cations at this stage. Clearly, template-to-framework hydrogen bonding is important, but there are many other structural variables involved, including the Zn:P ratio, presence of "dangling," terminal P–O, P–OH, Zn–OH_2 bonds, and framework charge. Indeed, the variety of structures obtainable in this area of chemistry is one of its most striking features. We are continuing to explore these materials, with one goal being the synthesis of more "zeolite-like" [materials containing a 1:1 Zn:P ratio with Zn–O–P bridges linking *all* the ZnO_4 and PO_4 groups and no dangling bonds] organically-templated zincophosphates (22).

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Figure Captions

Figure 1. Fragment of the $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ structure (50% thermal ellipsoids) showing the atom labelling scheme. Symmetry-related atoms are indicated by, *e.g.*, O2a.

Figure 2. View down [010] of the $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$ crystal structure with H atoms omitted for clarity.

Figure 3. Fragment of the $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ structure showing the atom labelling scheme (50% thermal ellipsoids). Symmetry-related atoms are indicated by, *e.g.*, O1a.

Figure 4. View down [100] of the $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ structure (H atoms omitted for clarity).

Figure 5. Topological [Zn (small filled circle) to P (larger open circle)] connectivity of a $[Zn_2(HPO_4)_3]^{2-}$ layer in $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$, showing the presence of four rings and 12 rings.

Figure 6. Fragment of the $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$ structure (50% thermal ellipsoids) showing the atom labelling scheme. Symmetry-related atoms are indicated by, *e.g.*, O3a.

Figure 7. View down [001] of the $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$ crystal structure with the $Zn_3(HPO_4)_4$ framework represented in skeletal form, showing only the Zn to P connectivity. Pairs of dabco cations occupy the 12 ring windows.

Figure 8. Detail of the zincophosphate framework of $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$ showing a triplet of edge-sharing four rings and a 12 ring window.

Table 1: Crystallographic/Data Collection Parameters

	$(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$	$H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$	$(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$
Emp. formula	$ZnP_2O_9N_2C_6H_{18}$	$Zn_2P_3O_{12}N_2C_3H_{15}$	$Zn_3P_4O_{16}N_2C_6H_{18}$
Formula wt.	389.54	494.84	694.25
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	9.864 (4)	8.593 (2)	9.535 (2)
b (Å)	8.679 (4)	9.602 (2)	23.246 (4)
c (Å)	15.780 (3)	17.001 (3)	9.587 (2)
β (°)	106.86 (2)	93.571 (8)	117.74 (2)
V (Å^3)	1294.2 (8)	1400.0 (5)	1880.8 (8)
Z	4	4	4
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
T (°C)	25 (2)	25 (2)	25 (2)
λ (Mo $K\alpha$) (Å)	0.71073	0.71073	0.71073
ρ_{calc} (g/cm^3)	2.00	2.35	2.45
μ (cm^{-1})	22.3	39.1	43.1
Total data	2528	4827	6342
Observed data[a]	1055	2794	4255
Parameters	183	201	282
$R(F)$[b]	4.58	4.09	3.23
$R_w(F)$[c]	5.28	4.81	3.89

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

[b] $R = 100 \times \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$

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

Table 2: Atomic Coordinates/Thermal Factors for $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$

Atom	*x*	*y*	*z*	U_{eq}[a]
Zn1	0.44346(9)	0.2480(1)	0.00314(5)	0.0183
P1	0.2622(2)	0.5427(2)	-0.07694(12)	0.0162
P2	0.4067(2)	-0.0575(2)	0.11522(12)	0.0162
O1	0.2805(6)	0.3840(6)	-0.0331(3)	0.0252
O2	0.6010(6)	0.3746(6)	0.0643(3)	0.0264
O3	0.4721(6)	0.1458(7)	-0.0981(3)	0.0272
O4	0.4065(7)	0.1099(6)	0.0884(4)	0.0379
O5	0.4295(6)	-0.0614(7)	0.2189(3)	0.0274
O6	0.2638(6)	-0.1327(6)	0.0762(3)	0.0262
O7	0.1647(6)	0.6383(7)	-0.0320(4)	0.0274
O8	0.1838(6)	0.5316(6)	-0.1758(3)	0.0265
O10	-0.1365(8)	0.679(1)	-0.0958(5)	0.0637
N1	0.1130(7)	0.0359(7)	-0.2399(4)	0.0208
N2	-0.0719(7)	0.0739(8)	-0.1613(4)	0.0245
C1	0.1608(9)	-0.043(1)	-0.1514(5)	0.0311
C2	0.0571(9)	0.0073(11)	-0.0996(5)	0.0315
C3	0.095(1)	0.2046(9)	-0.2259(6)	0.0271
C4	-0.036(1)	0.226(1)	-0.1957(6)	0.0320
C5	-0.0247(9)	-0.030(1)	-0.2939(5)	0.0292
C6	-0.1268(9)	-0.0343(11)	-0.2392(5)	0.0308

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

Table 3: Selected Bond Distances(Å) and Angles ( ) for $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$

Zn1-O1	1.943(5)	Zn1-O2	1.920(5)
Zn1-O3	1.919(5)	Zn1-O4	1.914(5)
P1-O1	1.530(5)	P1-O2	1.490(6)
P1-O7	1.585(6)	P1-O8	1.531(6)
P2-O3	1.510(6)	P2-O4	1.515(6)
P2-O5	1.585(5)	P2-O6	1.513(6)
N1-C1	1.51(1)	N1-C3	1.50(1)
N1-C5	1.492(11)	N2-C2	1.478(11)
N2-C4	1.51(1)	N2-C6	1.52(1)
C1-C2	1.546(12)	C3-C4	1.509(12)
C5-C6	1.505(12)		

Zn1-O1-P1	131.3(3)	Zn1-O2-P1	155.9(4)
Zn1-O3-P2	134.4(3)	Zn1-O4-P2	144.4(4)

Table 4: Atomic Coordinates/Thermal Factors for $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$

Atom	*x*	*y*	*z*	U_{eq}[a]
Zn1	0.75902(5)	0.51877(5)	0.47819(3)	0.0132
Zn2	0.67667(5)	0.13227(5)	0.52116(3)	0.0132
P1	0.99029(11)	0.25402(11)	0.48902(6)	0.0131
P2	0.55594(11)	0.40868(11)	0.60954(6)	0.0117
P3	0.54496(11)	-0.10326(11)	0.62802(6)	0.0128
O1	1.1323(4)	0.3077(3)	0.53784(19)	0.0206
O2	0.8922(4)	0.3686(4)	0.44933(19)	0.0215
O3	0.8966(4)	0.1599(4)	0.5391(2)	0.0277
O4	1.0479(4)	0.1707(4)	0.4169(2)	0.0286
O5	0.6702(4)	0.5151(4)	0.57929(18)	0.0207
O6	0.3934(3)	0.4722(3)	0.61202(17)	0.0185
O7	0.5515(4)	0.2755(4)	0.5633(2)	0.0280
O8	0.6104(4)	0.3751(4)	0.69667(18)	0.0230
O9	0.6599(4)	-0.0496(3)	0.5707(2)	0.0203
O10	0.3829(4)	-0.1232(4)	0.59012(19)	0.0269
O11	0.5392(4)	-0.0120(4)	0.70074(18)	0.0237
O12	0.6098(4)	-0.2476(3)	0.66138(19)	0.0241
N1	-0.2408(4)	0.1643(4)	0.7917(2)	0.0201
N2	0.2714(5)	0.1779(5)	0.6731(3)	0.0265
C1	-0.1140(6)	0.0845(6)	0.7585(3)	0.0289
C2	0.0139(5)	0.1799(5)	0.7307(3)	0.0223
C3	0.1414(6)	0.0910(5)	0.7004(3)	0.0265

[a] U_{eq} (Å^2) = $1/3[U_1+U_2+U_3]$

Table 5: Selected Bond Distances(Å)[a] and Angles ( ) for $H_3N(CH_2)_3NH_3 \cdot Zn_2(HPO_4)_3$

Zn1-O1	1.937(3)	Zn1-O2	1.924(3)
Zn1-O5	1.924(3)	Zn1-O6	1.955(3)
Zn2-O3	1.914(3)	Zn2-O7	1.912(3)
Zn2-O9	1.948(3)	Zn2-O10	1.931(3)
P1-O1	1.522(3)	P1-O2	1.518(3)
P1-O3	1.509(3)	P1-O4	1.569(3)
P2-O5	1.528(3)	P2-O6	1.527(3)
P2-O7	1.500(3)	P2-O8	1.559(3)
P3-O9	1.520(3)	P3-O10	1.510(3)
P3-O11	1.518(3)	P3-O12	1.585(3)
N1-C1	1.473(6)	N2-C3	1.492(6)
C1-C2	1.528(7)	C2-C3	1.505(6)
N1-H1···O6	1.98, 2.840(5)	N1-H2···O2	2.20, 2.864(5)
N1-H3···O8	1.91, 2.844(5)	N2-H4···O11	2.17, 2.951(5)
N2-H5···O12	2.15, 3.019(6)	N2-H6···O1	1.89, 2.816(5)
O4-H101···O9	1.87, 2.763(5)	O8-H102···O11	1.67, 2.479(4)
O12-H103···O5	1.84, 2.738(5)		
Zn1-O1-P1	126.28(19)	Zn1-O2-P1	138.8(2)
Zn2-O3-P1	123.3(2)	Zn1-O5-P2	127.7(2)
Zn1-O6-P2	124.40(18)	Zn2-O7-P2	144.4(2)
Zn2-O9-P3	130.53(19)	Zn2-O10-P3	127.2(2)

[a] For the hydrogen bonds, the two distances correspond to the H···O and *X*···O separations, respectively, for an *X*–H···O bond.

Table 6: Atomic Coordinates/Thermal Factors for $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$

Atom	x	y	z	$U_{eq}{}^a$
Zn1	0.53789(4)	0.062059(16)	0.66432(4)	0.0146
Zn2	0.77144(4)	0.132774(16)	0.37704(4)	0.0148
Zn3	0.87360(4)	0.226624(16)	1.09671(4)	0.0154
P1	0.54094(9)	0.17871(4)	0.50164(9)	0.0148
P2	0.75547(9)	0.09971(3)	1.03238(9)	0.0133
P3	0.23179(9)	-0.01297(4)	0.46630(9)	0.0153
P4	1.07834(9)	0.20413(4)	0.44911(9)	0.0152
O1	0.4507(3)	0.13111(11)	0.5367(3)	0.0267
O2	0.5803(3)	0.16138(12)	0.3727(3)	0.0244
O3	0.4459(3)	0.23393(11)	0.4614(3)	0.0222
O4	0.7058(3)	0.18723(13)	0.6538(3)	0.0290
O5	0.6061(3)	0.08387(11)	0.8840(3)	0.0202
O6	0.8464(3)	0.14937(11)	1.0084(3)	0.0254
O7	0.7139(3)	0.11151(12)	1.1627(3)	0.0264
O8	0.8658(3)	0.04463(11)	1.0723(3)	0.0265
O9	0.3528(3)	0.01534(11)	0.6163(3)	0.0238
O10	0.2918(3)	-0.02470(15)	0.3488(3)	0.0357
O11	0.1542(4)	-0.06433(13)	0.4982(3)	0.0379
O12	0.0881(3)	0.03080(11)	0.3753(3)	0.0255
O13	0.9257(3)	0.19271(12)	0.4548(3)	0.0294
O14	1.0548(3)	0.23493(13)	0.3006(3)	0.0319
O15	1.1937(3)	0.23645(12)	0.5938(3)	0.0255
O16	1.1505(4)	0.14264(12)	0.4509(4)	0.0366
N1	0.6539(3)	-0.10396(13)	0.0616(3)	0.0216
N2	0.8735(4)	-0.1400(2)	0.0187(5)	0.0526
C1	0.6377(5)	-0.16734(17)	0.0390(6)	0.0357
C2	0.6464(5)	-0.0757(2)	-0.0795(5)	0.0361
C3	0.8090(5)	-0.0899(2)	0.2027(4)	0.0321
C4	0.7727(8)	-0.1883(3)	0.0123(11)	0.0877
C5	0.7790(7)	-0.0977(4)	-0.1069(7)	0.0838
C6	0.9412(5)	-0.1119(3)	0.1744(5)	0.0473

$^aU_{eq}$ (Å^2) = 1/3[$U_1+U_2+U_3$]

Table 7: Selected Bond Distances(Å) and Angles ( ) for $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$

Zn1-O1	1.954(2)	Zn1-O5	1.960(2)
Zn1-O9	1.936(2)	Zn1-O10	1.897(3)
Zn2-O2	1.923(2)	Zn2-O7	1.928(2)
Zn2-O11	1.917(3)	Zn2-O13	1.908(2)
Zn3-O3	1.958(2)	Zn3-O6	1.951(2)
Zn3-O14	1.923(3)	Zn3-O15	1.907(2)
P1-O1	1.532(3)	P1-O2	1.504(2)
P1-O3	1.514(2)	P1-O4	1.582(3)
P2-O5	1.517(2)	P2-O6	1.524(3)
P2-O7	1.501(2)	P2-O8	1.586(3)
P3-O9	1.513(2)	P3-O10	1.507(3)
P3-O11	1.509(3)	P3-O12	1.600(2)
P4-O13	1.505(2)	P4-O14	1.514(3)
P4-O15	1.509(2)	P4-O16	1.583(3)
N1-C1	1.487(5)	N1-C2	1.475(5)
N1-C3	1.504(5)	N2-C4	1.461(9)
N2-C5	1.489(9)	N2-C6	1.474(5)
C1-C4	1.505(7)	C2-C5	1.496(8)
C3-C6	1.498(5)		
Zn1-O1-P1	127.75(15)	Zn2-O2-P1	132.17(15)
Zn3-O3-P1	125.56(15)	Zn1-O5-P2	140.15(14)
Zn3-O6-P2	127.00(15)	Zn2-O7-P2	151.54(17)
Zn1-O9-P3	132.64(15)	Zn1-O10-P3	140.09(18)
Zn2-O11-P3	135.18(19)	Zn2-O13-P4	134.23(17)
Zn3-O14-P4	125.31(16)	Zn3-O15-P4	120.21(15)

Tetrahedral-Network Organo-Zincophosphates: Syntheses and Structures of $(N_2C_6H_{14})\cdot Zn(HPO_4)_2\cdot H_2O$, $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_3$ and $(N_2C_6H_{14})\cdot Zn_3(HPO_4)_4$

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Supplementary Material