

NaZnPO₄·H₂O, an Open-Framework Sodium Zincophosphate with a New Chiral Tetrahedral Framework Topology

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Two approaches to the synthesis and structure determination of NaZnPO₄·H₂O, a new open-framework, chiral, hydrated sodium zincophosphate phase, are reported. The ordered, alternating, vertex-sharing ZnO₄ and PO₄ groups in NaZnPO₄·H₂O form a new framework topology, which includes novel 4-ring “squares” and edge-sharing helices of 4-rings. The disordered extra-framework species (Na⁺, H₂O) are located in pear-shaped cavities (12-ring diameter), interconnected through 8-rings and 6-rings. Crystal data: NaZnPO₄·H₂O (I), *M_r* = 201.36, hexagonal, space group *P*6₁22 (No. 178), *a* = 10.4797(8) Å, *c* = 15.089(2) Å, *V* = 1435 Å³, *Z* = 12, *R* = 5.99%, *R_w* = 5.29% (709 observed reflections with *I* > 3σ(*I*)). NaZnPO₄·H₂O (II), *M_r* = 201.36, hexagonal, space group *P*6₅22 (No. 179), *a* = 10.412(2) Å, *c* = 15.184(2) Å, *V* = 1426 Å³, *Z* = 12, *R* = 6.90%, *R_w* = 8.10% (687 observed reflections with *I* > 4σ(*I*)).

Introduction

The prospect of synthesizing chiral molecular sieves is of great interest with respect to their possible applications in enantioselective separations and syntheses.¹ It is known that chiral silica (hand separated, large crystals of *l* and *d* quartz) adsorbs derivatives of (*R*)- and (*S*)-alanine enantioselectively.² Aluminosilicate zeolites and other open-framework, microporous compounds have surface areas some 10⁴ times larger than that of a similar quantity of quartz, thus the use of such phases as enantioselective sieves and catalysts could lead to very significant increases in the efficiency of such processes.¹

Although the geometrical principles and theoretical stabilities of tetrahedral frameworks are quite well understood,³ it is not yet possible to synthesize new framework topologies, chiral or otherwise, “on demand.” The structure-directing effect of metallic and organic cations has been demonstrated for various microporous families,^{4–7} but as noted by Davis and Lobo in their recent review,¹ most syntheses of microporous phases involve complex reaction mechanisms, and are poorly

understood.

Zeolite β⁸ is a rare example of an aluminosilicate with a helical pore structure. “Normal” zeolite β consists of random intergrowths of two polymorphs (A and B) of opposite chirality,⁹ but recent work¹⁰ suggests that modifying the synthesis conditions by the addition of a chiral template may lead to enhanced growth of polymorph A *versus* polymorph B.

In this paper we describe the hydrothermal synthesis and single crystal X-ray structural characterization of NaZnPO₄·H₂O, a hydrated sodium zincophosphate with a new, chiral, tetrahedral framework topology. Two crystals, denoted NaZnPO₄·H₂O (I) and NaZnPO₄·H₂O (II) were prepared and studied simultaneously by groups in Santa Barbara and Des Plaines, and for the reader's convenience, both approaches are described in this paper. Although the tetrahedral connectivities are the same for these two enantiomeric phases, there appear to be slight differences in the extraframework species.

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Experimental Section

Crystal I. Synthesis and Initial Characterization. Single crystals of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**) were prepared hydrothermally, as follows: 10 cm³ of water was added to a clear solution of 0.49 g of ZnO (6 mmol) in 3 cm³ of 5 M H_3PO_4 (15 mmol), followed by 6.85 g of 4 M NaOH (24 mmol), resulting in a pH of 11.5. After 2 days at 70 °C without stirring, the reaction yielded about 1 g of crystalline product, including a few spherical clusters of transparent, spearlike, hexagonal-prismatic rods of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**) (typical maximum linear dimension ≈ 0.6 mm). The crystals were recovered from the mother liquor by vacuum filtration and washed with acetone. These crystals are air and moisture stable. X-ray powder data for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**) have been presented previously.⁷ Unindexed powder data reported many years ago¹¹ for another phase of stoichiometry $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ do not match those for the $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ phase described here.

Thermogravimetric (TGA) measurements on $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**), carried out on a DuPont 9900 analyzer, showed a small weight loss occurring below 100 °C, attributable to surface effects, followed by a $\sim 10.0\%$ weight loss at 300 °C, and no further weight loss to 500 °C. The loss at 300 °C occurred in two distinct steps, of about 5% each. An X-ray powder pattern of the white post-TGA residue showed only the presence of monoclinic NaZnPO_4 .¹² The theoretical weight loss for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{NaZnPO}_4$ is 8.94%, and we hereafter assume a stoichiometry of exactly $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ for this phase.

Crystal Structure Determination. A suitable, rodlike transparent crystal of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**), approximate dimensions $0.05 \times 0.05 \times 0.6$ mm, was selected for structure determination and mounted on a thin glass fiber with cyanoacrylate glue. Room-temperature [25(2) °C] intensity data were collected on a Huber automated diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). Initially, 25 reflections ($10^\circ < 2\theta < 20^\circ$) were located and centered, resulting in least-squares optimized hexagonal lattice parameters of $a = 10.4797(8)$ Å and $c = 15.089(2)$ Å ($V = 1435$ Å³). 1162 intensity data ($0 \rightarrow h, 0 \rightarrow k, -l \rightarrow l$) were collected in the θ - 2θ scanning mode for $0 < 2\theta < 65^\circ$. Three standard reflections monitored every 100 observations for intensity variation showed insignificant variation over the course of the experiment. Crystal absorption was monitored by ψ -scans, but no absorption correction was applied. The raw intensities were reduced to F and $\sigma(F)$ values by using a Lehmann-Larsen profile-fitting routine,¹³ and the normal corrections for Lorentz and polarization effects were made. All the data collection and reduction routines were based on the UCLA crystallographic computing package.¹⁴

The systematic-absence condition in the reduced data ($000l, l \neq 6n$) was comparable with the hexagonal Laue classes $6/m$ (enantiomorphic pair of space groups $P6_1$ and $P6_5$) and $6/mmm$ (enantiomorphic space groups $P6_122$ and $P6_522$). Comparison of would-be equivalent reflections¹⁵ indicated that the latter Laue class was probably the correct one [$R_{\text{int}} = 3.77$, 711 merged reflections, 709 considered observed according to the criterion $I > 3\sigma(I)$]. The structure of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**) was developed in space group $P6_122$ (No. 178). Starting positions for the framework Zn and P atoms and some of the framework oxygen atoms of the structure were obtained by direct methods from the program SHELXS-86.¹⁶ The other atomic species were progressively located from Fourier difference maps during the course of the refinement (program CRYSTALS¹⁵).

The fractional site occupancies of the guest species were all treated as variable parameters in the later refinement cycles, and final full-matrix refinements (76 parameters) were against F and included anisotropic temperature factors for all the framework atoms and a Larson-type secondary extinction correction.¹⁷ Attempts to simultaneously refine the fractional site occupancies and individual isotropic thermal factors of the guest atoms led to unstable refinements. Thus, the isotropic thermal factors of the guests were constrained to refine together, and the site occupation factors were allowed to refine independently. Neutral-atom scattering factors, taking account of anomalous dispersion terms, were obtained from the *International Tables*.¹⁵ At the end of the refinement, the Flack polarity parameter¹⁶ was refined but did not conclusively indicate the dominant presence of one enantiomorph (clockwise or counterclockwise sense of helix pitch) in the crystal studied.

Final residuals of $R(F) = 5.99\%$ and $R_w(F) = 5.23\%$ (Tukey-Prince¹⁷ weighting scheme described by a 2-term Chebychev polynomial), and S (goodness-of-fit) = 1.05 were obtained. Final Fourier difference maps revealed no regions of electron density (min = -1.0 , max = 2.0 e Å⁻³) which could be attributed to additional atomic sites, and analysis of the various trends in F_o versus F_c revealed no unusual effects. Tables of anisotropic thermal factors and observed and calculated structure factors are available as supporting information.

Crystal II. Synthesis. A mixture of 48.0 g of NaOH, 4.67 g of $\text{Mg}(\text{OH})_2$, 46.16 g of 85% H_3PO_4 , and 1055 g of H_2O was made up. A portion of this mixture was digested at 100 °C for 24 h, then isolated by filtration, and washed with water. Hexagonal prismatic crystals of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**II**), (dimensions 50–200 μm) were recovered. Scanning electron microscopy (EDAX) indicated no measurable amount of Mg in the crystals. There was insufficient sample of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**II**) to perform X-ray powder measurements.

Crystal Structure Determination. Data were collected on a rodlike crystal ($\sim 30 \times 30 \times 130$ μm) on an Enraf-Nonius CAD4 diffractometer (Cu K α radiation; $\lambda = 1.54184$ Å). Least-squares refinement of 25 centered reflection positions gave hexagonal lattice parameters of $a = 10.412(2)$ Å and $c = 15.184(2)$ Å ($V = 1426$ Å³). Four octants of data were collected for $0^\circ < 2\theta < 120^\circ$ (maximum $|\sin \theta|/\lambda = 0.56$) for $-11 < h < 11$, $-11 < k < 11$, and $0 < l < 17$. Standard reflections measured every 2 h showed a 4.7% decrease in intensity over the period of data collection (4415 intensity maxima scanned). Reflections were merged to 712 unique intensities (Friedel opposites not merged) with $R_{\text{int}} = 4.7\%$, of which 687 with $I > 4\sigma(I)$ were considered observed. Due to the well-defined crystal shape, a Gaussian absorption correction ($\mu = 10.78$ mm⁻¹; transmission factor range = 0.46–0.76) was applied at the data reduction stage.

Systematic absences ($000l, l \neq 6n$) and intensity statistics suggested possible space groups of $P6_1$, $P6_5$, $P6_122$, or $P6_522$. The best refinement (stable convergence, lowest residuals) was obtained in space group $P6_522$ (No. 179). This space group is the enantiomeric partner of $P6_122$ used for the $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (**I**) refinement. Initial Zn and P atom positions were found by direct methods, and the other atom positions were found by subsequent least-squares and Fourier difference syntheses. Positional parameters and anisotropic thermal parameters were refined for all atoms. The expected composition, based on chemical analysis, is $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$. Only 34% of the Na⁺ and 35% of the water oxygen atoms were located; the rest of these species are apparently disordered. Final residuals of $R = 6.9\%$, $R_w = 8.1\%$, $R_g (=wR) = 12.4\%$, and $S = 1.59$ were obtained. All data analysis was carried out using the Shelxtl Plus package.²¹

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Table 1. Atomic Positional/Thermal Parameters for NaZnPO₄·H₂O (I)

atom	x	y	z	U _{eq} ^a	occ ^b
Na(1)	0.668(1)	0.336	1/4	0.037(3) ^c	0.53(3)
Na(2)	0.602(3)	0.336(3)	0.235(1)	0.037(3) ^c	0.24(1)
Zn(1)	0.8414(1)	0.6827	1/4	0.0183	
Zn(2)	0.5071(1)	0.4929	5/12	0.0198	
P(1)	0.8324(3)	0.5912(4)	0.4409(2)	0.0203	
O(1)	0.805(1)	0.5403(9)	0.3439(5)	0.0230	
O(2)	1.0485(9)	0.8019(9)	0.2185(5)	0.0255	
O(3)	0.689(1)	0.571(1)	0.4808(6)	0.0328	
O(4)	0.873(1)	0.489(1)	0.4910(6)	0.0311	
O(5) ^d	0.07(2)	0.033	1/12	0.037(3)	0.10(3)
O(6) ^d	0.410(4)	0.302(4)	0.161(2)	0.037(3) ^c	0.29(2)
O(7) ^d	0.076(6)	0	0	0.037(3) ^c	0.24(3)
O(8) ^d	0.425(4)	0.247(4)	0.117(2)	0.037(3) ^c	0.30(2)

^a U_{eq}(Å²) = (U₁U₂U₃)^{1/3}. ^b Fractional site occupancy, if not unity.
^c U_{iso}(Å²). ^d Oxygen atom of water molecule (protons not located).

Table 2. Bond Distances^a (Å) for NaZnPO₄·H₂O (I)

Na(1)–O(1) × 2	2.36(1)	Na(1)–O(3) × 2	2.841(9)
Na(1)–O(4) × 2	2.42(2)	Na(1)–O(6) × 2	2.88(3)
Na(2)–O(1)	2.69(2)	Na(2)–O(1)	2.23(2)
Na(2)–O(3)	2.45(2)	Na(2)–O(4)	2.55(2)
Na(2)–O(4)	2.49(2)	Na(2)–O(8)	2.41(3)
Zn(1)–O(1) × 2	1.953(6)	Zn(1)–O(2) × 2	1.946(7)
Zn(2)–O(3) × 2	1.920(8)	Zn(2)–O(4) × 2	1.975(7)
P(1)–O(1)	1.535(7)	P(1)–O(2)	1.529(8)
P(1)–O(3)	1.531(8)	P(1)–O(4)	1.530(8)
O(5)–O(2)	3.101(9)	O(5)–O(2)′	2.9(1)
O(5)–O(5)′	2.58(3)	O(6)–O(1)	3.06(3)
O(6)–O(3)	2.89(3)	O(6)–O(4)	3.09(3)
O(6)–O(6)′	3.11(6)	O(6)–O(7)	3.09(5)
O(6)–O(8)	2.73(5)	O(7)–O(2)	2.85(3)
O(7)–O(6)	3.09(6)	O(7)–O(7)′	2.638(8)
O(7)–O(8)	3.25(5)	O(8)–O(1)	3.22(3)
O(8)–O(4)	2.92(3)	O(8)–O(4)	2.83(3)
O(8)–O(6)	2.73(5)	O(8)–O(7)	3.25(5)

^a Apparent short contacts resulting from disorder have been omitted.

Table 3. Framework-Atom Bond Angles (deg) for NaZnPO₄·H₂O (I)

O(1)–Zn(1)–O(1)′	97.1(4)	O(1)–Zn(1)–O(2) × 2	113.2(3)
O(1)–Zn(1)–O(2) × 2	109.9(3)	O(2)–Zn(1)–O(2)′	112.5(4)
O–Zn(1)–O	109.3[6.2] ^a		
O(3)–Zn(2)–O(3)′	121.1(6)	O(3)–Zn(2)–O(4) × 2	118.4(4)
O(3)–Zn(2)–O(4) × 2	99.5(4)	O(4)–Zn(2)–O(4)′	98.8(5)
O–Zn(2)–O	109.3[11.0] ^a		
O(1)–P(1)–O(2)	111.1(4)	O(1)–P(1)–O(3)	109.2(4)
O(2)–P(1)–O(3)	109.0(5)	O(1)–P(1)–O(4)	107.2(5)
O(2)–P(1)–O(4)	112.6(4)	O(3)–P(1)–O(4)	107.6(5)
O–P(1)–O	109.5[2.1] ^a		
Zn(1)–O(1)–P(1)	119.6(4)	Zn(1)–O(2)–P(1)	127.4(4)
Zn(2)–O(3)–P(1)	123.9(5)	Zn(2)–O(4)–P(1)	137.7(6)
Zn–O–P	127.2[7.7] ^a		

^a Average bond angle, with standard deviation in brackets, about central atom.

Crystal Structure

Crystal I. NaZnPO₄·H₂O (I) is a new open-framework sodium zinc phosphate hydrate: Final atomic positional and thermal parameters for NaZnPO₄·H₂O (I) are presented in Table 1, with selected geometrical data given in Tables 2 and 3. The asymmetric unit of NaZnPO₄·H₂O (I) consists of 7 “framework” atoms (2 Zn, 1 P and 4 O atoms) and 6 “guest”, species (2 Na, 4 O atoms, the latter parts of water molecules). Views of the framework-atom asymmetric unit and the unit cell

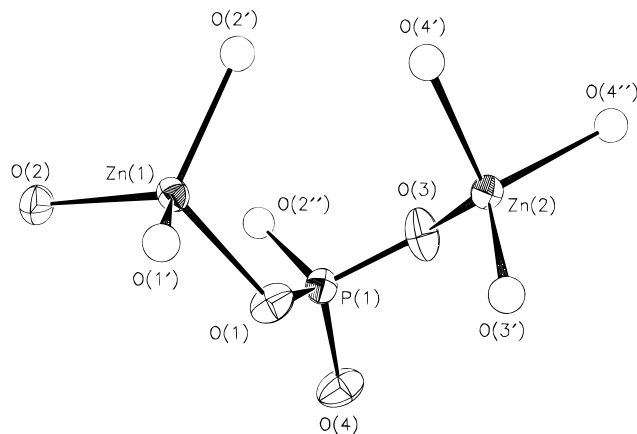


Figure 1. ORTEP view of the framework-atom asymmetric unit of NaZnPO₄·H₂O (I), showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

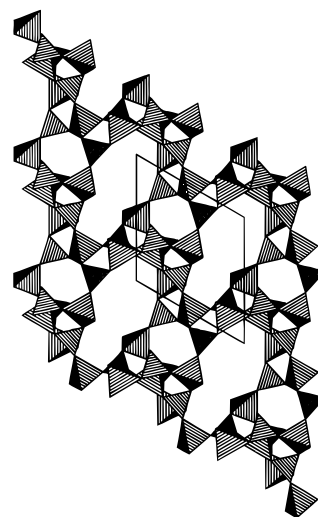


Figure 2. Polyhedral representation of a slab of the unit-cell of NaZnPO₄·H₂O (I) (0.4 < z < 1.1), viewed down the c direction, showing the large pear-shaped cavities.

of NaZnPO₄·H₂O (I) are given in Figures 1 and 2, respectively.

The Zn and P framework atoms in NaZnPO₄·H₂O (I) show typical crystallochemical behavior, consistent with their environments in other tetrahedral zincophosphate structures.^{22,23} The two zinc atoms, both of which occupy special positions with site symmetry ..2, are tetrahedrally coordinated to their O atom neighbors, with $d_{av}[Zn(1)–O] = 1.950(4)$ Å and $d_{av}[Zn(2)–O] = 1.948(4)$ Å. Both of the ZnO₄ tetrahedra are somewhat “squashed” from regular 43m local symmetry, as indicated in Table 3, and Zn(2) is more distorted than Zn(1). The single, crystallographically independent, tetrahedral phosphorus atom (general position), with $d_{av}(P–O) = 1.531(4)$ Å, bonds to 4 different zinc atoms [2 each of Zn(1) and Zn(2)] via oxygen-atom bridges. The spread of O–P–O angles about “ideal” tetrahedral geometry in the PO₄ moiety is notably smaller than the O–Zn–O angles in the ZnO₄ tetrahedra (Table 3). The four framework oxygen atoms partake in Zn–O–P links with $\theta_{av} = 127.2^\circ$ (standard deviation of mean = 7.7°),

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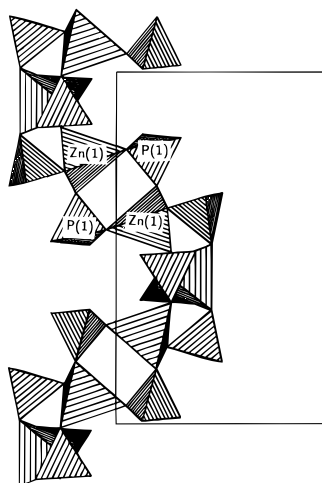


Figure 3. Polyhedral view down [100] of the connectivity of the Zn(1) and P(1) tetrahedral helix in NaZnPO₄·H₂O (I), with selected tetrahedra labeled, indicating the linked-4-ring repeat unit. The helix propagates in the [001] direction, with a periodicity equal to the *c* unit-cell dimension.

thus maintaining perfect Zn/P ordering and alternation over the tetrahedral nodes. All of these O atoms also make bonds with one or more of the guest sodium cations and/or water molecules, as indicated in Table 2. The small Zn(1)–O(1)–P(1) bond angle of 119.6(4)° is perhaps attributable to a short Na(2)–O(1) bond [*d* = 2.23(2) Å], akin to the situation in organozincophosphate tetrahedral structures,²³ where the more acute Zn–O–P bond angles may be correlated with the H-bonding the O atom makes to the protonated template molecules. However, in this case, the relatively strained nature of the tetrahedral framework may also be responsible for the large spread of Zn–O–P bond angles. Bond-valence-summation (BVS) values are consistent with the framework atomic assignments: Brese–O’Keeffe BVS values²⁴ for Zn(1) and Zn(2) are 2.06 and 2.08, respectively (expected value = 2.00), with an equivalent value of 4.87 for P(1) (expected 5.00). Tetrahedral distortions, δ , measured in terms of the distortion of the central atom from the centroid of its four oxygen-atom neighbors are as follows: $\delta[\text{Zn}(1)] = 0.11$ Å; $\delta[\text{Zn}(2)] = 0.17$ Å; $\delta[\text{P}(1)] = 0.03$ Å, again indicating that the PO₄ group is more regular than the ZnO₄ units.

The topology of this anionic zincophosphate framework is a new chiral tetrahedral network and has not been previously observed in either aluminosilicate or aluminophosphate nets. One way to consider the building-up of the structure is to note that the Zn(1)O₄ and P(1)O₄ units [linked via Zn(1)–O(1)–P(1) and Zn(1)–O(2)–P(1) bonds] form one-dimensional helical chains, which propagate in the polar *c* direction (Figure 3). The chains themselves are built up from strings of tetrahedral 4-ring linkages: In each 4-ring, Zn(1) and P(1) tetrahedra alternate, and the 4-rings are linked into infinite strings through the Zn(1) tetrahedra. Thus, a Zn(1) tetrahedron is linked to its two Zn(1)’ neighbors in the helical chain via two bridging P(1)O₄ tetrahedra in each direction. This infinite 4-ring connectivity is commonly seen in other tetrahedral structures, such as the sodalite²⁵ framework; however, its *helical* configu-

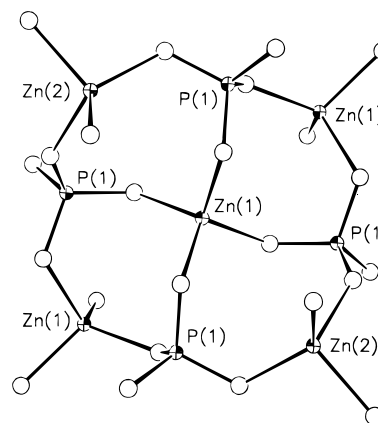


Figure 4. Detail of the 4-ring square in NaZnPO₄·H₂O (I), with Zn and P atoms labeled, showing the central Zn(1)O₄ unit bonded into an 8-ring of neighboring TO₄ groups (see text).

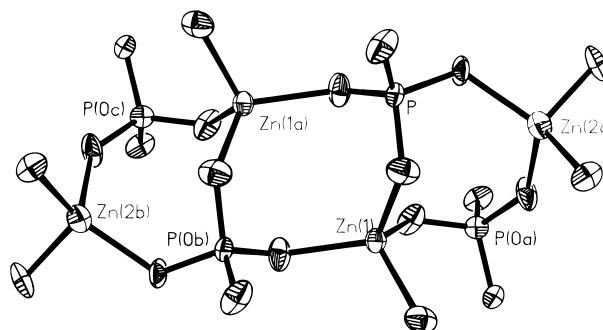


Figure 5. Triple 4-ring building unit in NaZnPO₄·H₂O (II).

ration here appears to be unique. Linkage between adjacent helices, perpendicular to the [001] direction, is provided by the oxygen-atom links between the P(1)–O₄ and Zn(2)O₄ groups [via O(3) and O(4)], thus forming a three-dimensional network.

An unprecedented structural feature of this tetrahedral *T*-atom connectivity is the presence of “squares” of 4-rings (Figure 4), in which a central Zn(1) tetrahedron is effectively surrounded by, or “bonded into”, an 8-ring of alternating ZnO₄ and PO₄ groups [two Zn(1)- and two Zn(2)-centered ZnO₄ moieties]. This building unit, in which the central, “nodal” Zn(1) atom makes *four* 4-ring loops and *two* 6-ring loops with its *T*-atom neighbors, has not been seen in any other three-dimensional tetrahedral structures. The circuit symbol,²⁶ which enumerates the six, distinct, smallest *T*-atom loop pathways (including the central atom itself) starting and finishing at Zn(1) is therefore [4,4,4,4,6,6]. Conversely, Zn(2), the linking atom between helices, makes *two* 4-ring and *four* 8-ring loops (circuit symbol [4,4,8,8,8,8]). The loop configuration for P(1) in NaZnPO₄·H₂O (I) is *three* 4-rings, *two* 6-rings, plus *one* 8-ring ([4,4,4,6,6,8]).

The guest species in NaZnPO₄·H₂O (I) consist of six distinct atomic sites (Table 1), occupied by sodium

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(26) Newsam, J. M. Personal communication, 1994. For a 4-connected *T*-atom in a continuous net, linked to adjacent *T*-atoms denoted *a*, *b*, *c*, and *d*, there are six distinct loop pathways from the central atom: out through *a*, back through *b*; out through *a*, back through *c*; out through *a*, back through *d*; out through *b*, back through *c*; out through *b*, back through *d*; out through *c*, back through *d*. The circuit symbols for the three distinct tetrahedral atoms in NaZnPO₄·H₂O (I) are listed in this order. Circuit symbols for all known tetrahedral nets are listed in the *Zeofile* database distributed by J. M. Newsam, San Diego.

(24) Brese, N. E.; O’Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

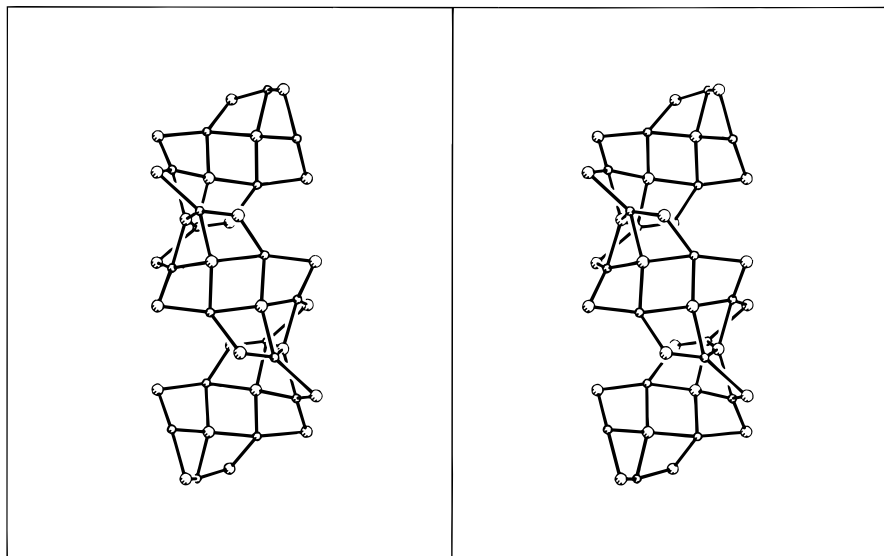


Figure 6. Stereoview of the tetrahedral helix in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II). Large circles represent Zn atoms, small circles P atoms. Framework oxygen atoms omitted for clarity.

Table 4. Atomic Positional/Thermal Parameters for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	occupancy
Zn(1)	0.84243(12)	0.68486(24)	0.75	0.0228(10)	1.0
Zn(2)	0.49697(14)	0.99393(28)	0.75	0.0311(11)	1.0
P(1)	0.17041(29)	0.40605(35)	0.06011(18)	0.0220(12)	1.0
O(1)	0.1976(10)	0.4597(9)	0.1566(5)	0.034(4)	1.0
O(2)	0.0519(9)	0.2464(9)	0.0547(5)	0.033(4)	1.0
O(3)	0.3130(9)	0.4229(10)	0.0201(5)	0.030(3)	1.0
O(4)	0.1292(10)	0.5030(10)	0.0075(6)	0.036(4)	1.0
Na	0.6713(7)	0.3425(14)	0.75	0.111(10)	0.34(2)
O(5)	0.5908(31)	0.7113(34)	0.3441(34)	0.092(21)	0.34(4)

cations, water molecules (oxygen atoms), or possibly a mixture of both. All the guest sites are partially occupied, with fractional site occupancies as noted in Table 1. The difficulties in accurately modeling disordered sodium ion/water molecule sites in aluminosilicate zeolites is well-known,²⁷ and the two species are probably mobile and interchangeable over the extraframework sites in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (I). The Na(1) and Na(2) sites were attributed to sodium-cation character on the basis of favorable guest-atom to framework-oxygen-atom contacts (Table 2). These locations have unexceptional average bond distance and BVS parameters: $d_{\text{ave}}[\text{Na}(1)-\text{O}] = 2.625(7)$ Å, $\text{BVS}[\text{Na}(1)] = 1.04$; $d_{\text{ave}}[\text{Na}(2)-\text{O}] = 2.470(9)$ Å, $\text{BVS}[\text{Na}(2)] = 1.05$. However, these sites account only for ~50% of the sodium cations required for charge balancing the anionic framework, and the remaining sodium cations are presumably distributed over the other extraframework sites [formally oxygen atoms (water molecules) O(5) through O(8)]. The high degree of disorder of the guest atoms (Table 2) makes analysis of the bonding environments of these sites problematical²⁸ and no efforts were made to elucidate possible H-bonding configurations.

Crystal II. Final atomic coordinates for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) are given in Table 4, with selected interatomic distance and angle data in Tables 5–7. $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) is essentially the enantiomorphic equivalent of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (I) (Figure 6, see below). Views of the highly puckered 12-ring with “side pocket”

Table 5. Bond Distances (Å) for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II)

atom pair	distance	atom pair	distance
Zn(1)–O(1)	1.956(8)	P–O(1)	1.543(8)
Zn(1)–O(2)	1.946(9)	P–O(2)	1.497(8)
Zn(2)–O(3)	1.921(8)	P–O(3)	1.531(10)
Zn(2)–O(4)	1.950(10)	P–O(4)	1.508(12)
Na–O(1)	2.303(12)	Na–O(4)	2.452(13)
Na–O(3)	2.907(5)	Na–O(5)	2.876(38)

Table 6. Framework-Atom Bond Angles (deg) for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II)

atoms	angle(s)	atoms	angle(s)
O(1)–Zn(1)–O(1)	96.4(0.5)	O(1)–P–O(2)	110.8(0.4)
O(1)–Zn(1)–O(2)	110.4(0.4), 113.4(0.4)	O(1)–P–O(3)	110.1(0.5)
O(2)–Zn(1)–O(2)	112.0(0.3)	O(1)–P–O(4)	108.8(0.6)
O(3)–Zn(2)–O(3)	121.6(0.4)	O(2)–P–O(3)	108.6(0.6)
O(3)–Zn(2)–O(4)	100.8(0.4), 115.0(0.3)	O(2)–P–O(4)	111.4(0.5)
O(4)–Zn(3)–O(4)	102.6(0.5)	O(3)–P–O(4)	107.3(0.5)
Zn(1)–O(1)–P	118.7(0.5)	Zn(2)–O(3)–P	123.4(0.4)
Zn(1)–O(2)–P	128.4(0.7)	Zn(2)–O(4)–P	142.7(0.5)

Table 7. Sodium Cation Bond Angles (deg) in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II)

atoms	angle(s)	atoms	angle(s)
O(1)–Na–O(1)	78.5(0.6)	O(3)–Na–O(4)	53.5(0.3), 116.8(0.5)
O(1)–Na–O(3)	82.0(0.3), 106.4(0.4)	O(3)–Na–O(5)	62.7(1.0), 115.4(1.1)
O(1)–Na–O(4)	107.4(0.3), 156.3(0.3)	O(4)–Na–O(4)	76.7(0.6)
O(1)–Na–O(5)	72.6(0.8), 124.1(0.9)	O(4)–Na–O(5)	79.1(0.9), 85.7(0.9)
O(3)–Na–O(3)	169.5(0.6)	O(5)–Na–O(5)	160.6(1.3)

and 8-ring pore openings in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) are given in Figures 7 and 8, respectively. Because of their puckering, their free dimensions are smaller than 12- and 8-ring pores in aluminosilicate zeolites (Table 8).

The Zn–O and P–O average bond distances in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) are 1.944(3) and 1.518(5) Å, respectively. The ZnO_4 tetrahedra are distorted from ideal geometry and have O–Zn–O bond angles from 97° to 121°. PO_4 tetrahedra are more regular with the O–P–O bond angle spread being 107–111°.

In $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II), the sodium cation is located in the side pocket and has a site occupancy of 0.34.

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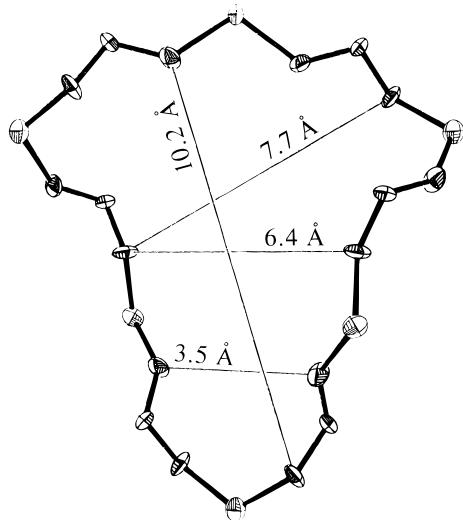


Figure 7. 12-ring in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) viewed down [001] with selected $\text{O} \cdots \text{O}$ distances noted.

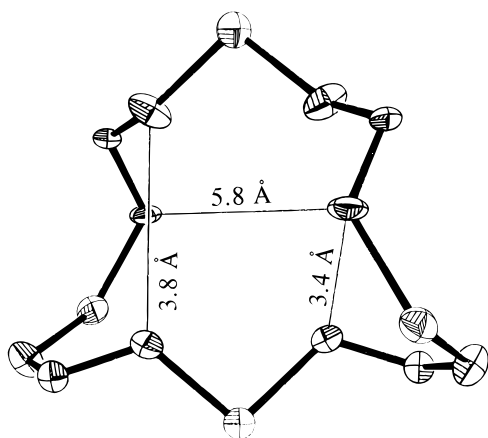


Figure 8. 8-ring in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) viewed down [110] with selected $\text{O} \cdots \text{O}$ distances noted.

Table 8. Channel Dimensions (Å) in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) and Related Phases

phase	direction	ring size	dimension
FAU	$\langle 111 \rangle$	12	7.4
LTL	[001]	12	7.1
MOR	[001]	12	6.5×7.0
$\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$	[001]	12	3.7×7.5
MOR	[010]	8	2.6×5.7
$\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$	$\langle 100 \rangle$	8	1.1×3.1

Because the water molecule [oxygen atom O(5)] has the same occupancy as the sodium atom, the two are probably associated. The apparent sodium coordination geometry (Figure 9) is a highly distorted square prism with four short and four long Na–O distances. Large anisotropy in the thermal ellipsoids for the sodium atom and water molecule (oxygen atom) may well indicate that they are disordered over adjacent sites, and that the true symmetry is $P6_5$. However, if the symmetry is lowered to $P6_3$, then all atoms, including the sodium species, refine to the same locations. No further species could be located from difference maps, and the remaining sodium cations and water molecules (66%) are presumably highly disordered.

Discussion

$\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ is a new sodium zincophosphate hydrate which crystallizes in a unique chiral framework

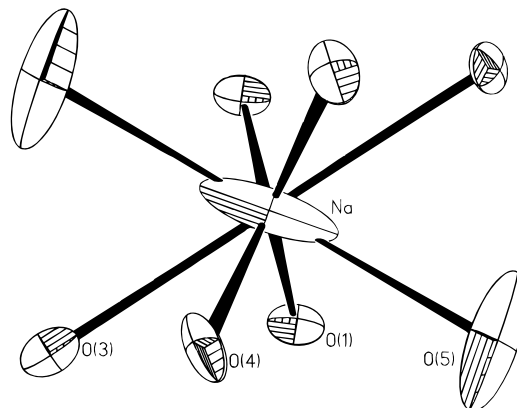


Figure 9. Na coordination geometry in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II). O(1), O(3), and O(4) are framework oxygen atoms; O(5) is part of a water molecule.

type built up from squares of 4-rings. The crystal structures determined for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (I) and $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) are enantiomorphic with respect to the Zn/P/O framework species. We note that $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (I) and $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (II) were refined in one of the pairs of enantiomorphic space groups listed earlier for possible chiral zeolite structures.¹ There are slight differences in the locations of the extraframework species and the unit-cell dimensions for these two phases. Whether these are a reflection of the different synthesis conditions (*vide supra*) for the two modifications of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ is not yet known.

The two hydrothermal syntheses for $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ described above are typical of those used to prepare other microporous zincophosphates.^{7,22,23} Although no chiral templates were present, a chiral crystal was produced in both cases. Thus, under the synthesis conditions used here, there is no reason to suspect, that on a *bulk scale*, one enantiomer of $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ is favored over the other, since no chiral templating agents are involved. However, reasonably large single crystals may be prepared by the two methods noted above. As seen with other *continuous* zincophosphate nets linked by two-coordinate oxygen-atom bridges,^{22,25} complete Zn/P ordering and alternation is maintained in this framework configuration, which only contains even-number loops of T atoms (4-, 6-, 8-, and 12-rings). Odd-membered rings, including 3-rings, are found in other types of tetrahedral ZnPO structures⁷ and feature Zn–(OH)–Zn hydroxide bridges²⁹ or Zn–O(P)–Zn “bridging” links.³⁰

The novel building unit in $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$, the 4-ring square, is somewhat puckered, and the participating ZnO_4 and PO_4 groups are distorted to the extents noted above. We have studied structural and stability trends in $\text{Na}_3(\text{ABO}_4)_3 \cdot 4\text{H}_2\text{O}$ -type sodalite phases,³¹ and the $\text{Na}_3(\text{ZnPO}_4)_3 \cdot 4\text{H}_2\text{O}$ zincophosphate sodalite appears to be prone to greater tetrahedral distortions than the other sodalite types, which may be due to the *combination* of the large (Zn) + small (P) size T-atoms involved. The size difference, Δ , between the ionic radii³² of Zn^{II} and

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(31) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Keder, N. L.; Zaremba, C. M.; Srdanov, V. I.; Nicol, J. M.; Stucky, G. D. *Inorg. Chem.* **1994**, *33*, 2472.

Table 9. Framework Densities for NaZnPO₄·H₂O (II) and Related Phases

phase	density	
	g/cm ³	<i>T</i> /1000Å ³
FAU	1.27	12.7
LTL	1.61	16.4
MOR	1.70	17.2
NaZnPO ₄ ·H ₂ O	2.24	16.8

P^V is ~0.43 Å, compared to Δ = 0.22 Å for [Al + P] and Δ = 0.13 Å for [Al + Si] tetrahedral-atom combinations. This suggests that in NaZnPO₄·H₂O, the [Zn + P] *T*-atom combination results in a new tetrahedral framework which is not accessible in other ordered *T*-atom combinations. However, the role of the nonframework species is also significant: The NaZnPO₄·H₂O framework is stable at ambient conditions but irreversibly collapses to a condensed structure on dehydration. This behavior is consistent with the reduced thermal stability found for most other zincophosphate phases^{7,22} as compared to aluminosilicate structures.

NaZnPO₄·H₂O has a framework density (FD)³³ of ~16.7 *T*-atoms/1000 Å³, comparable to FD values of the LTL (Linde type-L), MOR (mordenite), ATS (MAPO-36), and BPH (beryllophosphate-H) zeolitic frameworks.³⁴ The density of the ZnPO₄ framework part of the NaZnPO₄·H₂O structure (Na and H₂O species omitted) is 2.24 g/cm³. If Zn and P were replaced by Al and Si for the same topology, a density of 1.66 g/cm³ would result, which is again comparable to LTL and MOR (Table 9). Thus, the NaZnPO₄·H₂O framework is about as open as those of LTL and MOR aluminosilicate zeolites. Tetrahedral coordination sequence (CS) values³⁵ have been elucidated for known tetrahedral-

Table 10. Tetrahedral Coordination Sequences for NaZnPO₄·H₂O

atom	<i>N</i> ₁	<i>N</i> ₂	<i>N</i> ₃	<i>N</i> ₄	<i>N</i> ₅	<i>N</i> ₆	<i>N</i> ₇	<i>N</i> ₈	<i>N</i> ₉	<i>N</i> ₁₀	ρ ₁₀ ^a
Zn(1)	4	8	16	33	52	73	112	160	190	214	862
Zn(2)	4	10	20	33	56	85	114	144	192	242	900
P(1)	4	9	18	32	54	83	113	149	191	234	887

^a Topological density value (J. M. Newsam, personal communication, 1994).

framework structures,³⁴ and the CS values for NaZnPO₄·H₂O are listed in Table 10. The small *N*₂ value of 8 for Zn(1) is matched only in interrupted frameworks (−CHI, −CLO, −PAR, −ROG) or those built up from 4 = 1 (EDI, NAT, THO) or spiro-5 (LOV) building units, or in the novel AFY framework.

Conclusion

The synthesis and single-crystal structure of NaZnPO₄·H₂O, which has a new chiral framework structure, are described. This phase was prepared by two different methods, neither of which involved chiral templating agents. NaZnPO₄·H₂O, which is about as open as the Linde Type L and mordenite aluminosilicate zeolite structures, contains novel 4-ring squares, which have not been observed in any other microporous phase.

Supporting Information Available: Tables of anisotropic thermal factors (1 page) and observed and calculated structure factors for NaZnPO₄·H₂O (I) and NaZnPO₄·H₂O (II) (5 pages). Ordering information is given on any current masthead page.

Acknowledgment. John Newsam (BIOSYM Corp., San Diego) kindly calculated the circuit symbol and coordination sequence values for NaZnPO₄·H₂O using the CATALYSIS option of the BIOSYM molecular modeling package. We thank the National Science Foundation for partial financial support.

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