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The Low-Temperature Synthesis and Characterization of Two Layered Materials Containing 3-Ring Groupings: $NaH(ZnPO_4)_2$ and $CsH(ZnPO_4)_2$

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Two zinc phosphate layered materials, each containing unique 3-rings yet differing hydrogen bonding schemes, have been prepared by hydrothermal methods and characterized by single-crystal X-ray diffraction, TGA, and MAS NMR. These phases consist of a two-dimensional network of ZnO_4 and PO_4 tetrahedra, linked through oxygen vertices, to form structures whose interlayers are occupied by charge-balancing cations. The layers are notable because of the formation of 3-rings comprised of the tetrahedral atoms, Zn and P, and the oxygen atoms, resulting in "terminal" –OH bonds off the P(2) atom, in the sodium analog, and off the P(1) atom in the cesium analog. The topology of the layers is controlled by the templating cation. While the small interlayer sodium cation allows for hydrogen bonding between the layers which results in "puckered" sheets, the larger cesium cation does not allow interlayer hydrogen bonding, resulting in flat sheets. Sodium hydrogen zinc orthophosphate ($NaH(ZnPO_4)_2$) is a triclinic crystal: space group $P\bar{1}$ (no. 2), with a = 8.641 (2), b = 8.817 (3), and c = 5.1268 (9) Å; α = 100.401 (8)°, β = 105.684 (8)°, and γ = 96.924 (9)°; V = 363.9 (1) Å^3 and Z = 2, with R = 5.21% and R_w = 4.96% for 1873 observed reflections, according to the criterion $I > 3\sigma(I)$. Cesium hydrogen zinc orthophosphate ($CsH(ZnPO_4)_2$) is orthorhombic: space group *Abma* (no. 64), with a = 7.739 (8), b = 6.594 (7), and c = 15.94 (2) Å; α = 90°, β = 90°, and γ = 90°; V = 813.56 (5) Å^3 and Z = 4, with R = 4.56% and R_w = 5.23% for 762 observed reflections, according to the criterion $I > 3\sigma(I)$.

Introduction

Recently, many novel zinc phosphate systems have been prepared and reported. These new materials are all based upon the bonding of tetrahedral ZnO_4 and PO_4 units to form a large number of frameworks. The well known and studied aluminosilicates, with their alternating Al and Si (in a 1 : 1 ratio) tetrahedral atoms, form $(AlSiO_4)^-$ building blocks that serve as models for equivalent $(ZnPO_4)^-$ frameworks (*1*). However, these zinc phosphates differ from their aluminosilicate predecessors inasmuch as they form under much milder conditions, yet are very dependent on exact synthetic conditions for their phase purity. The two primary variables we have characterized so far are the pH (2–14) and reaction temperature (−18 to 70°C) (*1*). Depending upon the reaction conditions and the presence or absence of organic templates, materials of known and unique three-dimensional structures can be synthesized. These include analogs of zeolite X, RHO, and sodalite, whose structures are comprised of 4-, 6-, and

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8-rings of bonded $ZnO_4$and PO_4 tetrahedra (*1*). The materials presented here are synthesized under those conditions stated above. However, these two-dimensional layered crystals have a uncommon characteristic: their structural topologies include 3-rings.

Related structures have been reported earlier. A 3D microporous zincosilicate framework, VPI-7, contains a 3-ring building block, the spiro-5 unit, which is comprised of (Zn,Si)–O atoms (*2*). Similar to this is lovedarite, a beryllosilicate mineral (*3*). Other 3-ring-containing zincosilicates reported include some 3D nonmicroporous minerals (*4*). Two nonzeolitic materials also have been recently synthesized that contain one-dimensional chains of three-member rings, a synthetic bearsite, (Be,As)–O, and a novel (Zn,P)–O chain (*5*). An aluminosilicate was synthesized at high temperature, ZSM-18, and is a zeolite which contains 3-rings of oxygen in an (Al,Si)–O species (*6*). Two nonzeolitic layered materials, similar in structure to that reported here, have also been synthesized: a $NaZn_2(PO_4)(PO_3(OH))$ has been prepared at high temperature and pressure (300°C and 1000 atm) (*7*), the crystallographic study of which does not indicate the presence of 3-rings or hydrogen bonding; and a similar layered potassium zincophosphate has been synthesized at low temperature and ambient pressure, the structure of which has been solved by X-ray diffraction (*8*).

In this paper, we report the syntheses and characterization, by X-ray, TGA, and ^{31}P MAS NMR, of two two-dimensional zinc phosphates prepared at low temperatures: sodium zinc orthophosphate ($NaH(ZnPO_4)_2$) and cesium zinc orthophosphate ($CsH(ZnPO_4)_2$). The similarities in these systems include the negative charge on the zinc phosphate layer which is compensated for by protons found in the layers on the "terminal" –OH groups and the interlayer cations, sodium and cesium, respectively. However, the difference in these materials is due to the templating cations, which directly affect both the nature of the hydrogen bonding from the hydroxide group and the topology of the two layers, as described below.

Experimental

Both phases were prepared hydrothermally. Sodium zinc orthophosphate (Na/Zn/P/O) was prepared from 2.25 g of 4 *M* NaOH, 1.65 g of 4 *M* H_3PO_4, and 6.0 g of $Zn(NO_3)_2$. Addition of the reactants to a Teflon bottle formed a thixotropic gel, which upon shaking turned milky. The pH at this point was approximately 3. The mixture was heated to 70°C for 96 hr. A mass of transparent crystals in aqueous solution were recovered by vacuum filtration and washed with H_2O. The crystals ranged in size from the predominant 0.3 mm to a maximum of 5.0 mm, with plenty suitable for single-crystal X-ray diffraction. Cesium zinc orthophosphate (Cs/Zn/P/O) was prepared from 5.24 g of 50% CsOH, 1 g of 85% H_3PO_4, 1.2 g of 2 *M* $ZnCl_2$, and 6.55 g of H_2O. Upon mixing in a Teflon bottle, the solution had the appearance of milk. The pH at this point was approximately 2. The mixture was heated to 100°C for 72 hr. A mass of transparent crystals in aqueous solution were recovered by vacuum filtration and washed with H_2O. The crystals had the similar range of sizes that were observed in the Na/Zn/P/O system.

Structure Determination

Suitable single crystals for structure determination were selected for each of the two phases and mounted on thin glass fibers, using cyano-acrylate glue. Room-temperature (25°C) intensity data was collected for the phases on a Huber automated four-circle diffractometer (graphite-monochromated Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) as outlined in Table I; 25 reflections for Na/Zn/P/O and 42 reflections for Cs/Zn/P/O were located and centered by searching reciprocal space and indexed to obtain a unit cell and orienta-

TABLE I

CRYSTALLOGRAPHIC PARAMETERS

	$NaH(ZnPO_4)_2$	$CsH(ZnPO_4)_2$
Emp. formula	$Zn_2P_2NaO_8H$	$CsZn_2P_2O_8H$
mol. wt.	345.3	454.6
Habit	Colorless cuboid	Colorless cuboid
Crystal size	0.3 × 0.3 × 0.3 mm	0.1 × 0.1 × 0.1 mm
Crystal system	Triclinic	Orthorhombic
a (Å)	8.640 (2)	7.739 (8)
b (Å)	8.817 (3)	6.594 (7)
c (Å)	5.126 (9)	15.94 (2)
α (°)	100.401 (8)	90
β (°)	105.684 (8)	90
γ (°)	96.924 (9)	90
V (Å^3)	363.90 (1)	813.56 (5)
Z	2	4
Space group	$P\bar{1}$ (no. 2)	*Abma* (no. 64)
T (°C)	25 (1)	25 (1)
λ (Mo $K\alpha$) (Å)	0.71073	0.71073
ρ_{calc} (g/cm^3)	2.927	3.711
μ (cm^{-1})	71.961	108.250
Absorption correction	ψ-scan	ψ-scan
hkl limits	−12 to +11,±12,+7	+11,+9,+24
Observed data[a]	1873	762
$R(F_o)$[b] (%)	5.21	4.56
$R_w(F_o)$[c] (%)	4.96	5.23

[a] $I > 3\sigma(I)$.
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

tion matrix. Unit cell constants were optimized by least-squares refinement, resulting in the lattice parameters and e.s.d.'s shown in Table I. Intensity data were collected in the $\Theta - 2\Theta$ scanning mode between 2Θ = 0 and 65°, using a scan speed of 6°/min and scan width parameters of 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. Three standard reflections were monitored for intensity variation throughout the course of each experiment: no significant variation was observed. Crystal absorption was empirically corrected by using psi-scans for three selected reflections. The raw data were reduced using a Lehmann–Larsen profile fitting routine and the normal corrections for Lorentz and polarization effects were made. All the data collection and reduction routines were based on the UCLA/Crystal Logic package (*9*).

The Na/Zn/P/O structure was solved by a combination of direct methods and Fourier syntheses, assuming that the crystal structure was centrosymmetric triclinic $P\bar{1}$ (no. 2), as confirmed by the course of the subsequent refinements. A chemically reasonable direct-methods solution for the structure was obtained from the program SHELX-86, (*10*), and the sodium cation site was located from Fourier maps. No reasonable proton locations could be determined from difference Fourier syntheses, and after anisotropic refinement, the proton position was located geometrically (by prediction of the atom location based upon O–H bond lengths and probable O–H---O bond angles) on its correct oxygen atom. The proton was attached to the oxygen atom that was bound only to one T-atom, and subsequently had a distinctively long O–P bond length (O(8)–P(2) = 1.587 (6) Å). Final agreement factors of $R(F_o)$ = 5.21% and $R_w(F_o)$ = 4.96% were obtained, as defined in Table 1. The least-squares, Fourier, and subsidiary calculations were performed using the Oxford CRYSTALS (*11*) system, running on a DEC μVAX-II computer. Final full-matrix refinements were against F and included anisotropic temperature factors and a secondary extinction correction (*12*). Complex, neutral-atom scattering factors were obtained from "International Tables" (*13*). The final weighting scheme was that of Tukey and Prince, using a three-term modified-Chebychev polynomial fit (*14*). Final Fourier difference maps showed no regions of significant electron density, and analysis of the various trends in F_o versus F_c revealed no unusual effects. Tables of observed and calculated structure factors are available as supplementary material from the authors.

The Cs/Zn/P/O reflection data (absent reflections: $h0l$, l; $0kl$, k, l; $hk0$, h,k), and a measured powder SHG = 0, identified the space group as the centrosymmetric orthorhombic *Abma* (with absences applying to this nonstandard setting of *Cmca*, no. 64). The structure was solved by a combination of direct methods and Fourier syntheses and confirmed by subsequent refinements (cesium, zinc, and phosphorus atoms were determined from SHELX; oxygen atoms were determined from difference Fourier maps).

TABLE II

ATOMIC POSITIONAL PARAMETERS FOR $NaH(ZnPO_4)_2$

Atom	x	y	z	U_{equiv}
Zn(1)	0.6174(1)	0.3931(1)	0.3303(2)	0.0144
Zn(2)	0.8880(1)	0.2405(1)	0.7787(2)	0.0145
P(1)	0.2505(2)	0.4397(2)	0.0912(4)	0.0122
P(2)	0.7556(2)	0.0816(2)	0.1610(4)	0.0132
Na(1)	0.1862(4)	0.1885(4)	0.4091(7)	0.0231
O(1)	0.3843(6)	0.3721(7)	0.275(1)	0.0158
O(2)	1.0890(6)	0.3361(7)	1.058(1)	0.0174
O(3)	0.7261(7)	0.5502(7)	0.190(1)	0.0190
O(4)	0.7411(6)	0.3937(6)	0.729(1)	0.0167
O(5)	0.9042(6)	0.1505(7)	0.412(1)	0.0174
O(6)	0.8053(7)	0.0544(7)	0.895(1)	0.0187
O(7)	0.6206(6)	0.1807(7)	0.140(1)	0.0184
O(8)	0.6857(6)	−0.0833(6)	0.206(1)	0.0185
H(1)[a]	0.549302	−0.126703	0.052063	0.05

[a] Calculated proton positions as discussed in text.

A few "observable" weak reflections that are prohibited in this space group, but are accountable for in the reduced monoclinic symmetry of $A2$ (no. 5, b-unique, $\beta \approx 90°$), were identified. Attempts to refine a structural model in space group $A2$ led to oscillations and high correlations between parameters, and were unsuccessful. This is an indication that the structure may be near a phase transition. (The following *specific* reflections are forbidden in *Abma* yet are weakly present, with $I < 5\sigma(I)$. $h00$, $h \neq 2n$: 100 and 300; $0kl$, $k \neq 2n$: 013, 015, 033, and 051; $0kl$, $l \neq 2n$: 013, 015 and 033; $hk0$, $h + k \neq 2n$: 100 and 300). The proton was geometrically attached to the oxygen atom that was bound only to one T-atom. Final agreement factors of $R(F_o) = 4.56\%$ and $R_w(F_o) = 5.23\%$ were obtained, and other refinement procedures followed those for the Na/Zn/P/O structure and are summarized in Table I.

Discussion

$NaH(ZnPO_4)_2$ and $CsH(ZnPO_4)_2$ are structures whose negatively charged zinc phosphate layers are charge balanced by protons and interlayer sodium and cesium cations, respectively (see Figs. 1 and 4). Final structural parameters are presented in Tables II–V, with selected bond distance and angle data in Tables VI and VII.

In $NaH(ZnPO_4)_2$, there are two zinc atoms, two phosphorus atoms, eight oxygen atom, one proton and one sodium cation per asymmetric unit (see Fig. 1). Both the zinc and phosphorus atoms are tetrahedrally coordinated to oxygen, as ZnO_4 and PO_4, and bond lengths and angles are considered typical from previous crystal structure determinations. (Zn–O average distance = 1.941 (5) Å, P–O average = 1.5333 (5) Å, and P–OH average = 1.587 (6) Å; and Θ_{ave} (Zn–O–P) = 129.9 (3)° calculated (*15*). Each zinc atom is bound to two different phosphorus atoms, each through three distinct Zn–O–P bonds. However, the two zinc atoms are also bound to the same oxygen atom, forming the Zn(1)–O(4)–Zn(2) bond that is found in the unique 3-ring. This bond indicates that the material differs from previous zinc phosphates reported because it does not maintain a strict alternation of the tetrahedral atoms. Crystallographically, these two zinc atoms are distinguishable in the 3-ring through their bond lengths (Zn(1)–O(4) = 2.034 (4) Å, Zn(2)–O(4) = 1.966 (5) Å) and through

TABLE III

ATOMIC POSITIONAL PARAMETERS FOR $CsH(ZnPO_4)_2$

Atom	x	y	z	U_{iso}
Cs(1)	0	1/2	1/2	0.0313
Zn(1)	1/4	1/4	0.26754(3)	0.0192
P(1)	0.9571(3)	0	0.3572(6)	0.0177
O(1)	0.7980(4)	0	0.2967(2)	0.0200
O(2)	0.0595(3)	0.699(2)	0.3419(2)	0.0253
O(3)	0.8872(4)	0	0.4472(2)	0.0242
H(1)[a]	0	0	1/2	0.0200

[a] Calculated proton positions as discussed in text.

the oxygen bond valences (Zn(1) = 1.97, Zn(2) = 2.07) (*16*).

As for the two phosphorus atoms, each forms three bonds to the two zinc atoms through a "normal" oxygen bridge (see angle information above). However, there are two bonds, each associated with one of the phosphorus atoms, that are different. There is one phosphorus atom that is incorporated in the 3-ring which is bound directly to Zn(1) and Zn(2) through O(4) (see Fig. 2). Crystallographically, this is seen with the elongation of the P(1)–O(4) bond (1.569 (5) Å), the decrease in the bond angles, from the average (see above), in the 3-ring (Zn(1)–O(4)–Zn(2) = 116.2 (3)°, P(1)–O(4)–Zn(1) = 107.0 (3)°), and an increase in the bond valence of the oxygens surrounding P(1) to 5.03 (*16*).

There is also the unusual, though not unique to these layered zinc phosphates, "terminal" P–OH bond (*15*). Crystallographically, this is seen with the elongation of the P(2)–O(8) bond to 1.587 (6) Å, a decrease in the bond valence of the oxygens surrounding P(2) to 4.99 (*16*), and the absence of any bonding of the oxygen with other tetrahedral atoms. This can be characterized as a long fourth tetrahedral vertex that is not joined to any other tetrahedral atom. It is important to note that if this were an unsaturated bond (a P=O bond), the

TABLE IV

ANISOTROPIC THERMAL PARAMETERS FOR $NaH(ZnPO_4)_2$

Atom	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Zn(1)	0.0102(4)	0.0206(4)	0.0145(4)	0.0037(3)	0.0043(3)	0.0018(3)
Zn(2)	0.0109(4)	0.0209(4)	0.0132(4)	0.0023(3)	0.0040(3)	0.0016(3)
P(1)	0.0089(7)	0.0175(8)	0.0123(7)	0.0022(6)	0.0043(6)	0.0004(6)
P(2)	0.0109(7)	0.0173(8)	0.0128(7)	0.0017(6)	0.0050(6)	0.0006(6)
Na(1)	0.020(1)	0.032(2)	0.023(2)	0.010(1)	0.009(1)	0.004(1)
O(1)	0.008(2)	0.027(3)	0.019(2)	0.006(2)	0.003(2)	0.003(2)
O(2)	0.010(2)	0.031(3)	0.017(2)	0.006(2)	0.002(2)	−0.003(2)
O(3)	0.029(3)	0.024(3)	0.013(2)	0.003(2)	0.011(2)	−0.002(2)
O(4)	0.015(2)	0.022(3)	0.013(2)	0.003(2)	0.003(2)	0.004(2)
O(5)	0.014(2)	0.031(3)	0.013(2)	−0.001(2)	0.007(2)	−0.000(2)
O(6)	0.022(3)	0.024(3)	0.015(2)	0.003(2)	0.009(2)	0.001(2)
O(7)	0.011(2)	0.025(3)	0.023(3)	0.004(2)	0.005(2)	0.005(2)
O(8)	0.017(2)	0.022(3)	0.018(2)	0.006(2)	0.005(2)	−0.000(2)

TABLE V

ANISOTROPIC THERMAL PARAMETERS FOR $CsH(ZnPO_4)_2$

Atom	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Cs(1)	0.0307(3)	0.0290(3)	0.0340(3)	0.0000	−0.0039(1)	0.0000
Zn(1)	0.0200(3)	0.0187(3)	0.0198(3)	0.0000	0.0000	−0.0008(1)
P(1)	0.0159(4)	0.0225(5)	0.0155(4)	0.0000	−0.0000(3)	0.0000
O(1)	0.020(1)	0.020(1)	0.021(1)	0.0000	−0.005(1)	0.0000
O(2)	0.023(1)	0.032(1)	0.025(1)	−0.0040(0)	0.0041(8)	−0.0084(9)
O(3)	0.021(1)	0.042(2)	0.017(1)	0.0000	0.002(1)	0.0000

TABLE VI

BOND DISTANCES (Å) AND ANGLES (°) FOR $NaH(ZnPO_4)_2$

Zn(1)–O(1)	1.938(5)	Zn(1)–O(3)	1.932(5)
Zn(1)–O(4)	2.034(5)	Zn(1)–O(7)	1.956(6)
Zn(2)–O(2)	1.908(5)	Zn(2)–O(4)	1.966(5)
Zn(2)–O(5)	1.952(5)	Zn(2)–O(6)	1.964(6)
P(1)–O(1)	1.537(5)	P(1)–O(2)	1.523(5)
P(1)–O(3)	1.525(5)	P(1)–O(4)	1.569(5)
P(2)–O(5)	1.520(6)	P(2)–O(6)	1.527(5)
P(2)–O(7)	1.532(6)	P(2)–O(8)	1.587(6)
Na(1)–O(1)	2.527(6)	Na(1)–O(2)	2.436(6)
Na(1)–O(3)	2.671(7)	Na(1)–O(5)	2.425(6)
Na(1)–O(6)	2.431(7)	Na(1)–O(8)	2.387(6)
O(3)–Zn(1)–O(1)	119.8(3)	O(4)–Zn(1)–O(1)	111.4(2)
O(7)–Zn(1)–O(1)	98.3(2)	O(4)–Zn(1)–O(3)	111.8(2)
O(7)–Zn(1)–O(3)	111.9(2)	O(7)–Zn(1)–O(4)	101.2(2)
O(4)–Zn(2)–O(2)	110.0(2)	O(5)–Zn(2)–O(2)	116.2(2)
O(6)–Zn(2)–O(2)	105.9(2)	O(5)–Zn(2)–O(4)	107.1(2)
O(6)–Zn(2)–O(4)	115.5(2)	O(6)–Zn(2)–O(5)	102.2(2)
O(2)–P(1)–O(1)	106.2(3)	O(3)–P(1)–O(1)	114.0(3)
O(4)–P(1)–O(1)	103.9(3)	O(3)–P(1)–O(2)	111.4(3)
O(4)–P(1)–O(2)	109.5(3)	O(4)–P(1)–O(3)	111.4(3)
O(6)–P(2)–O(5)	110.6(3)	O(7)–P(2)–O(5)	112.8(3)
O(8)–P(2)–O(5)	105.6(3)	O(7)–P(2)–O(6)	111.4(3)
O(8)–P(2)–O(6)	108.5(3)	O(8)–P(2)–O(7)	107.8(3)
P(1)–O(1)–Zn(1)	132.1(3)		
P(1)–O(2)–Zn(2)	139.9(3)		
P(1)–O(3)–Zn(1)	135.0(4)		
Zn(1)–O(4)–Zn(2)	116.2(3)	P(1)–O(4)–Zn(1)	107.0(3)
P(1)–O(4)–Zn(2)	131.3(3)		
P(2)–O(5)–Zn(2)	123.0(3)		
P(2)–O(6)–Zn(2)	117.2(3)		
P(2)–O(7)–Zn(1)	132.4(3)		
Θ_{ave} (P–O–Zn)	129.9(3)		

TABLE VII

BOND DISTANCES (Å) AND ANGLES (°) FOR $CsH(ZnPO_4)_2$

Zn(1)–O(1)	1.976(2) ×2	Zn(1)–O(2)	1.928(2) ×2
P(1)–O(1)	1.564(3)	P(1)–O(2) ×2	1.519(3)
P(1)–O(3)	1.536(3)		
Cs(1)–O(2) ×4	3.266(2)	Cs(1)–O(3) ×2	3.106(3)
O(1)–Zn(1)–O(1)′	117.5(2)	O(1)–Zn(1)–O(2)	109.7(2)
O(2)–Zn(1)–O(1)′	107.4(2)		
O(1)–P(1)–O(2)	108.2(2)	O(1)–P(1)–O(3)	107.0(2)
O(2)–P(1)–O(3)	113.8(3)		
Zn(1)–O(1)–Zn(1)′	113.1(2)	Zn(1)–O(1)–P(1)	117.8(1)
Zn(1)–O(2)–P(1)	131.3(2)		
Θ_{ave} (Zn–O–P)	120.6(3)		

length would be shorter, at approximately 1.51 Å. Furthermore, comparison of the bond valences associated with the oxygen atoms surrounding the phosphorus atoms shows that the P(2) atom has a decreased total bond valence, as compared with P(1), due to its bonding to the electron donating –OH group (P(2) = 7.23, P(1) = 7.57) (*16*).

The topology of the Na/Zn/P/O layers are dictated by the connectivity of the phosphorus atoms. The P–OH bond is associated with the P(2) atom while the "bridgehead" phosphorus atom of the 3-ring is the P(1) atom. The resultant "puckered" configuration contains "isolated" 3-rings, which are not directly connected to each other, but are built into the two-dimensional layers by a network of 4-rings (see Fig. 3).

The "puckered" layers (see Fig. 4) of the Na/Zn/P/O crystal are held together through two types of bonds. One type of layer bonding involves the weak hydrogen bonds between the terminal hydroxide and an oxygen in the adjacent layer. By placing

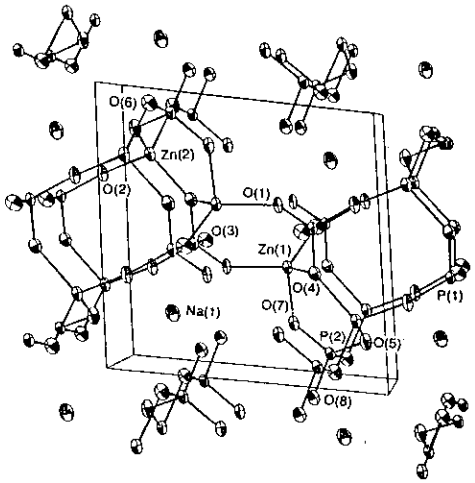

FIG. 1. ORTEP (*19*) view of the framework unit cell of $NaH(ZnPO_4)_2$, showing the atom-labeling scheme.

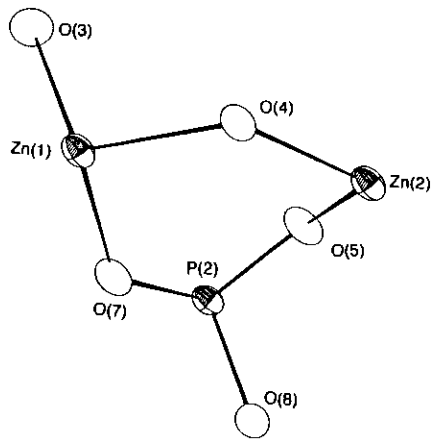

FIG. 2. The 3-ring connectivity in $NaH(ZnPO_4)_2$ and the terminal oxygen (O(8)).

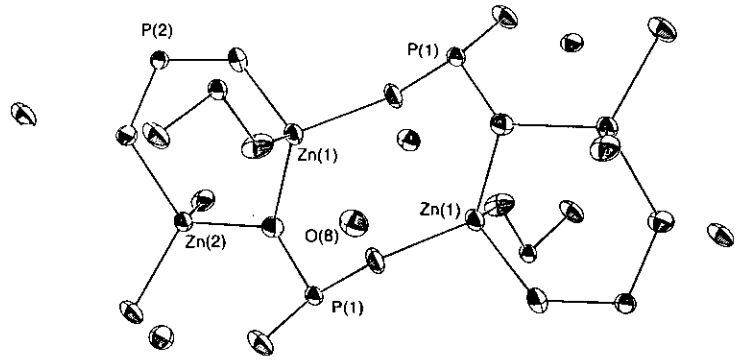

FIG. 3. The "puckered" layer of $NaH(ZnPO_4)_2$, showing the different bonding of the phosphorus atoms.

the proton between O(7) and O(8) (the approximate angle observed between O(7)–O(8)–P(2) is 108.4°), we see crystallographically that this proton is hydrogen bonding with O(7) in the adjacent layer through a hydrogen bond that is approximately 1.69 Å, forming the O(8)–H(1)---O(7) bond. The other type of interlayer bonding is between the sodium cation and the oxygen atoms from both layers. The cation is octahedrally bonded to O(1), O(2), O(3), O(5), O(6), and O(8) with a d_{ave}(Na–O) = 2.48 (2) Å.

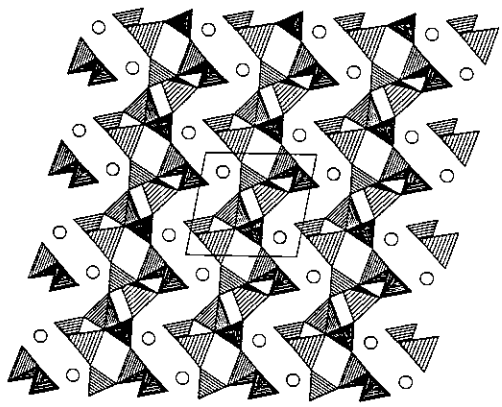

FIG. 4. Polyhedral representation of the framework structure of $NaH(ZnPO_4)_2$, viewed in the c-unit-cell direction.

TGA and MAS NMR data confirm the crystallographic results. The thermogravimetric analyses were run on a DuPont 9900 system, with a heating rate of 10°/min, under flowing N_2 gas. The TGA data shows that the Na/Zn/P/O system loses half a water at approximately 275°C. The final amorphous product can be formulated as $NaZn_2P_2O_{7.5}$ (observed weight loss 3%, calculated 2.6%). The $^{31}P\{^1H\}$ proton-decoupled MAS NMR data for the Na/Zn/P/O sample were collected on a General Electric GN-300 spectrometer system, at 121.65 MHz (field strength 7.05T) with 20 acquisitions and a spinning speed of approximately 4 KHz, and referenced to 85% H_3PO_4. A singlet at 5.49 ppm is evident. These data indicate that this layered material contains only one magnetically distinct phosphorus, at this resolution, though there are two crystallographic sites. This may be rationalized by considering the consistent local environment (an orthophosphate configuration) of the phosphorus atoms throughout the crystals, regardless of the fact that the next nearest neighbors are not equivalent (*17*).

In $CsH(ZnPO_4)_2$, there are one zinc atom, one phosphorus atom, three oxygen atoms, one proton, and one cesium cation per asymmetric unit (see Fig. 5). Both the zinc and the phosphorus atoms are tetrahedrally coordinated to oxygen atoms, as ZnO_4 and PO_4, and bond lengths and angles are typi-

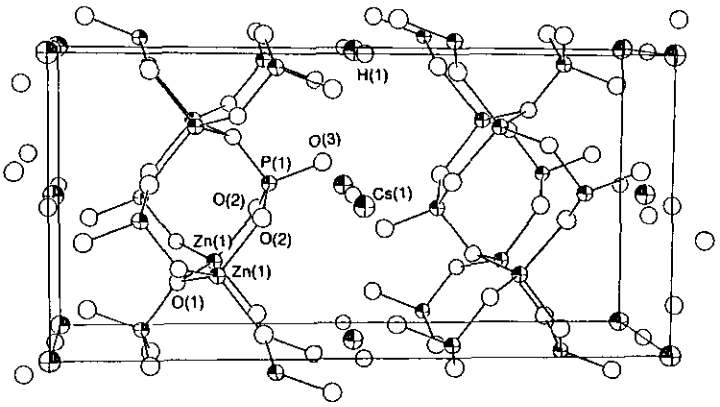

FIG. 5. Framework unit cell of $CsH(ZnPO_4)_2$, showing the atom-labeling scheme.

cal: Zn–O average distance = 1.95 (2) Å, P–O average = 1.534 (5) Å, and P–OH average = 1.534 (3) Å; and Θ_{ave} (Zn–O–P = 120.6 (3)° (*15*). The zinc atom is bound to only two of the three oxygen atoms uniquely, and is bound to another Zn(1) through an O(1) atom (bond valence = 2.05) in a "bridge-head" configuration. This configuration is the basis for the 3-ring of the layered structure.

The phosphorus atom is tetrahedrally coordinated to three different oxygen atoms, and is incorporated into the 3-ring by two P(1)–O(2) bonds. Crystallographically, the oxygen atoms surrounding the phosphorus atom have a small total bond valence sum of 6.65 (*16*). The bond to O(2) is slightly shortened from the average (P–O(2) distance = 1.519(3) Å) and is incorporated in a larger than average bond angle (Zn(1)–O(2)–P(1) = 131(2)°). In comparison, the bond to O(1) is longer (P–O(1) distance = 1.564(3) Å), yet has a slightly smaller angle than average (Zn(1)–O(1)–P(1) = 117.8(1)°). The shape of the resulting ring can be described either as a distorted triangle (with respect to only the T-atoms), or as a distorted hexagon in a boat configuration (including both T-atoms and

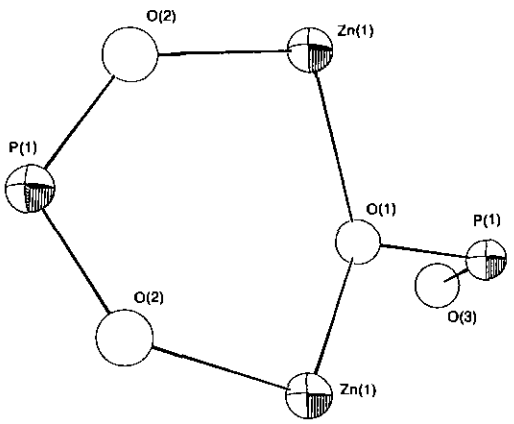

FIG. 6. The 3-ring connectivity in $CsH(ZnPO_4)_2$ and the terminal oxygen (O(3)).

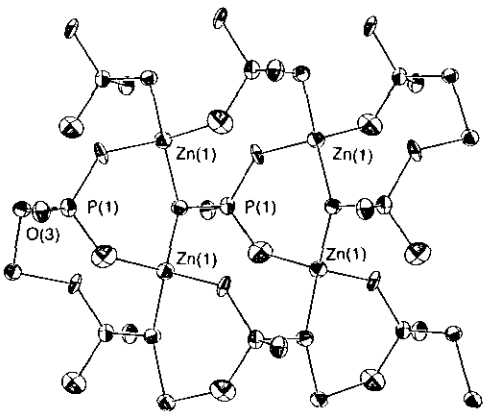

FIG. 7. The "flat" layer of $CsH(ZnPO_4)_2$, showing the connectivity of the 3- and 4-rings through the phosphorous atom.

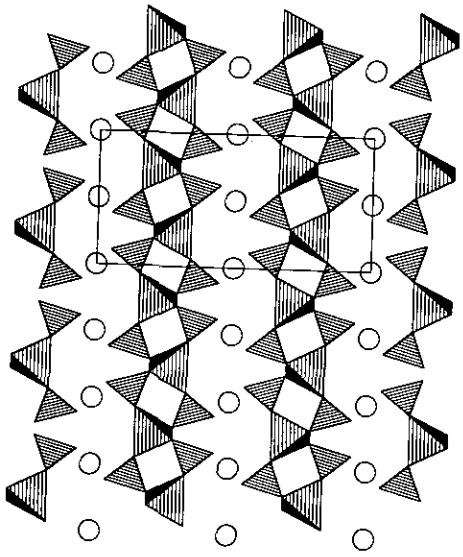

FIG. 8. Polyhedral representation of the framework structure of $CsH(ZnPO_4)_2$, viewed in the *a*-unit-cell direction.

oxygen atoms). This phosphorus atom is also bonded to O(3) with a bond distance of 1.536(3) Å, which is not coordinated to any other framework atom and must therefore be part of the "terminal" P–OH as described in the similar $NaH(ZnPO_4)_2$ layered material. The result is that the total bond valence of the oxygens surrounding this one phosphorus atom (P(1) = 7.86 (2)) is larger than that found in the sodium analog, because even though P(1) is involved in the elongated unsaturated bond, with the small valence, it is also in the tight 3-ring configuration (see Fig. 6), with an enhanced bond valence sum of 2.64 around the oxygen atom (*16*).

The topology of the Cs/Zn/P/O layers are dictated by the connectivity of the phosphorus atoms (as with the Na/Zn/P/O) however, the difference in the topology is due to the connectivity of the 3-ring groups. The P(1) atom is both the "bridgehead" phosphorus atom of the 3-ring, and is also bonded to the "terminal" –OH group. The resultant flat layered configuration contains "fused" 3- and 4-rings, in which the 3-rings are joined head to tail (see Fig. 7).

The flat layers of the Cs/Zn/P/O crystal are held together loosely through interlayer bonding between the cesium cation and the oxygen atoms from both layers (see Fig. 8). The cation is octahedrally bonded to O(2) and O(3) atoms, with a d_{ave}(Cs–O) = 3.18 (2). Close crystallographic inspection shows that no interlayer hydrogen bonding between the terminal hydroxide and an oxygen atom in the adjacent layer exists. By placing the proton with a bond angle of approximately 113° to the O(3) (the only reasonable angle between O(3) and the other oxygen atoms to which it is distantly bound, and not interfering with the cesium cation), we see crystallographically that this proton is hydrogen bonding with O(3) in the same layer through a bond that is approximately 2.45 Å, forming the O(3)–H(1)---O(3) *intralayer* H-bonds.

The structural data are supported analytically by both TGA and MAS NMR. The thermogravimetric analysis was run on a DuPont 9900-system, with a heating rate of 10°/min, under flowing N_2 gas. The TGA data shows that the Cs/Zn/P/O system loses half a water at approximately 290°C. The final amorphous product can be formulated as $CsZn_2P_2O_{7.5}$ (observed weight loss 2.0%, calculated 2.0%). The $^{31}P\{^1H\}$ proton-decoupled MAS NMR data for the Cs/Zn/P/O sample were collected on a General Electric GN-300 spectrometer system, at 121.65 MHz (field strength 7.05T) with 24 acquisitions and a spinning speed of approximately 5 KHz, and referenced to 85% H_3PO_4. A broad singlet at −3.24 ppm is evident. The broadness of the peak indicates that there is quadrupolar coupling between the phosphorus and the cesium, which has spin = 7/2 with 100% abundance. The data show that the layered structure contains only one crystallographic and magnetic phosphorus atom. This is expected due to the consistent local environment of the phosphorus atoms throughout the crystals, as found with the sodium analog (*17*). However, the chemical shift of the Cs/Zn/P/O is shifted downfield from that of the Na/Zn/P/O and can be ex-

plained as resulting from the increased bond valence (see above) of the phosphorus atom in the former material, as compared to the phosphorus atoms in the latter (*18*).

Conclusion

This study, combined with other works, has shown that a wide range of 3-ring containing nonaluminosilicate crystalline materials can be synthesized under very mild conditions (*2*, *4*). This is of great interest because of the indication that synthesizing a 3-ring-containing molecular sieve in the zinc phosphate phase space under the mild conditions exhibited for many zeolitic analogs is possible (*1*). Comparison of this layered material and a recently synthesized nonzeolitic three-dimensional Na/Zn/P/O material, shows that it is possible to produce these different materials by simply varying the ratios of the reactants while using the same reaction conditions (*4*). The sensitivity of the zinc phosphate framework topology to templating is clearly demonstrated in this study. With further investigation of reaction ratios, temperatures and templates, a 3-ring-containing molecular sieve could be synthesized in this phase space.

Acknowledgments

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