Synthesis and Characterization of a New Three-Dimensional Organically Templated Zinc Phosphate, $Zn_6(PO_4)_4(HPO_4)(H_2O)(H_3NCH_2CH_2NH_3)$, with a Chain of Corner-Linked ZnO_4 Tetrahedra

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The title compound, $Zn_6(PO_4)_4(HPO_4)(H_2O)(H_3NCH_2CH_2NH_3)$, was synthesized at room temperature under acidic conditions. Large crystals for structure determination were grown hydrothermally at 170 °C. The compound crystallizes in the monoclinic space group *C*2/*c* (no. 15) with $a = 19.129(6)$, $b = 5.0304(7)$, $c = 21.148(6)$ Å, and $\beta = 103.27(1)°$. The structure is an open framework of PO_4 and ZnO_4 tetrahedra with two types of one-dimensional channels along *b* (the larger are occupied by the ethylenediamine dication whereas the smaller contain water and hydroxyl groups). There is extensive Zn−O−Zn bonding in the structure in the form of dimers and infinite chains of corner-sharing ZnO_4 tetrahedra. The compound can be fully dehydrated at 380 °C and is stable up to 450 °C.

Introduction

Since the first microporous zinc phosphates with zeolite-like topologies were reported by Stucky et al.,[1] a great deal of effort has been devoted to the pursuit of novel open framework structures within this system. Such new materials may have potential in catalysis and in other applications that can take advantage of microporosity in combination with thermal stability, appropriate acidity, and sturdiness with respect to solvents. The number of such compounds and the diversity of their structural features have been growing rapidly in recent years, and today there are >20 different zinc phosphates with open-framework or low-dimensional structures.[2−5] This variety has been achieved by varying a number of factors that can influence the structure, such as template, pH, solvent, reaction temperature, and, to a lesser extent, zinc source, additives, pressure, and others. The structures of these compounds contain primarily tetrahedrally coordinated zinc but examples of higher coordination are also known.[2j] Some of the compounds are organically templated[3] and some contain either water or alkali-metal cations in their cavities.[2] None contain corner-sharing PO_4 tetrahedra, but a few exhibit such connectivity between two or more ZnO_4 tetrahedra.[2k−l,3e−f] We have been interested in the synthesis of transition-metal borophosphates (MBPOs) similar to the well-known transition-metal alumophosphates. In the case of M = Zn, we obtained instead a new ethylenediamine-templated zinc phosphate, $Zn_6(PO_4)_4(HPO_4)(H_2O)(H_3NCH_2CH_2NH_3)$. We report here its synthesis and characterization.

Experimental Section

Synthesis and Preliminary Characterization. Initially, the title compound (abbreviated as ZnEnPO), was synthesized in an attempt to make ethylenediamine-templated zinc borophosphate isostructural with $MB_2P_3O_{12}(OH)(H_3NCH_2CH_2NH_3)$, where M = Co(II), Fe(II), Mn(II), or Mg.[6] Thus, $Zn(NO_3)_2{\cdot}6H_2O$, H_3PO_4 (85 wt %), H_3BO_3 (all from Aldrich), and ethylenediamine (Acros) were dissolved in water in a molar ratio $ZnO:P_2O_5:B_2O_3$:en:H_2O = 1:1:1:1:250, yielding pH of ∼4 (pH as low as 1 works as well). The synthesis was carried out hydrothermally at 170 °C in Teflon-lined autoclaves for 5 days. The product, white semitransparent needlelike crystals, was washed with water, ethanol, and acetone, and then dried under vacuum filtration.

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After the structure and, therefore, the stoichiometry of the compound were determined, the compound was synthesized without the use of a boron source. Large crystals can be synthesized at temperatures as high as 190 °C, but the compound forms at room temperature as well. A fine powder of ZnEnPO is instantly made by adding ethylenediamine to a clear solution of zinc nitrate and phosphoric acid. Also, we attempted to repeat the synthesis of a reported ethylenediamine-templated zinc phosphate with a different structure, $Zn_2(HPO_4)_3 \cdot (en^{2+})$.[4] Following the reported recipe (140 °C for 20 days), we used zinc acetate and ethylene glycol in the place of zinc nitrate and water, respectively. The major phase in the product (>95%) was fine powder with a diffraction pattern that did not match either that of the reported compound or that of ZnEnPO. The pattern matched that of a third ethylenediamine-templated zinc phosphate, $Zn_2(PO_4)_2 \cdot (en^{2+})$,[5] with a structure that has been determined from powder diffraction (with quite high residual factors). The powder pattern was indexed satisfactory with unit cell parameters very close to the reported ones for that compound.[7] Later, we found that $Zn_2(PO_4)_2 \cdot (en^{2+})$ also forms instantly at room temperature by adding ethylenediamine to an aqueous solution of zinc acetate and phosphoric acid. On the other hand, when heated in an autoclave at 140 °C for 2−3 days, the same mixture produces ZnEnPO as a minor phase (∼ 20%). ZnEnPO can be made as a single phase also from a reaction in ethylene glycol at 140 °C but using zinc nitrate instead of the acetate. In summary, it seems that the zinc source or byproducts can dramatically influence the stability of the compounds and therefore the outcome of the corresponding reaction.

X-ray powder diffraction on a Guinier camera with Cu Kα1 radiation was used for phase identification. Perkin-Elmer Fourier transform infrared (FTIR) spectroscopy was utilized for monitoring the presence or lack of ethylenediamine in the compound before and after heat treatments. The latter were carried out on a CAHN TG-131 under different gases, flow and heating rates, and temperatures.

Structure Determination. A needlelike single crystal, 0.3 × 0.01 × 0.01 mm, glued to a fiber was mounted on a CAD4 diffractometer, and 25 reflections from a random search were indexed with a C-centered monoclinic cell. A hemisphere of data ($2\theta \leq 50°$) was collected at room temperature with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). After corrections for Lorentz and polarization effects, the data were consistent with two space groups, *Cc* and *C*2/*c*. The Wilson plot statistics strongly suggested a centrosymmetric space group, and *C*2/*c* was selected. The structure was solved by direct methods and refined on F^2 with the aid of the SHELXTL-V5.0 software package. The three zinc atoms, two of the phosphorus atoms (P1, P2), and most of the oxygen atoms (O1 to O10) were initially found and refined. The positions for the nitrogen, carbon, the third phosphorus atom, P3, and the two remaining oxygens, O11 and O12, were located from a difference Fourier map, but the P3−P3 and O11−O12 distances were unrealistically short. Next, the occupancies of P3, O11, and O12 were freed to vary. These refined to half occupancies within maximum of 2σ for all three atoms [49.3(5), 46(2), and 52(2)% for P3, O11, and O12, respectively]. The symmetry element that generates these "extra" positions is clearly the 2-fold axis at $x = 0$ and $z = 1/4$. To avoid this axis, the refinement was attempted in *Cc*, which does not have rotations but retains the *c*-glide. This procedure led to essentially the same result with two independent positions for P3 and P3′, and for O11 and O12, both pairs at very close distances. This result clearly indicated a true statistical disorder of the P3 atoms among the two positions. One of the two problematic oxygen atoms, O12, is at a bonding distance from one of the P3 positions, at 1.558(6) Å, whereas the other one, O11, is quite farther from it. This factor, combined with the 50% occupancy in *C*2/*c* for all of these positions and the fact that there are two pairs of O11−O12 positions per a pair of P3 position, clearly suggests that P3 is always bonded to O12 of one pair whereas O11 is occupied in the second pair. This suggestion, in turn, indicates that O11 is a water molecule and O12 is a hydroxyl group, and these were refined as such. It is possible that these alternate perfectly along the *b*-axis throughout the structure, which would lead to doubling (or multiplying, in general) of that axis. A long-exposure oscillation photograph (50 min, 20° oscillation angle) along *b* was taken to check this possibility. The photograph showed no additional reflections, thus confirming that P3, O11, and O12 are indeed randomly distributed at their sites. The final refinement of the structure with all non-hydrogen atoms with anisotropic thermal parameters, and with the occupancies of P3, O11, and O12 fixed at 50%, converged at $R1/wR2 = 2.63/6.15\%$ for 1467 reflections with $I > 2\sigma I$ and 206 variables. Further details of the data collection and refinement are listed in Table 1. Positional and isotropic thermal parameters and essential distances and angles are listed in Tables 2 and 3, respectively.

Table 1. Data Collection and Refinement Details for ZnEnPO

formula	$Zn_6(PO_4)_4(HPO_4)(H_2O)(H_3NCH_2CH_2NH_3)$
space group, *Z*	*C*2/*c*, 4
unit cell params	
a, Å	19.129(6)
b, Å	5.0304(7)
c, Å	21.148(6)
β, deg	103.27(1)
V, Å^3	1980.7(9)
cryst size, mm	0.30 × 0.01 × 0.01
density (calculated), g·cm^3	3.180
$2\theta_{max}$, deg, radiation	50, Mo Kα, graphite monochromated
absn coeff, cm^{-1}	76.67
octants measd	$\pm h,k,\pm l$
scan method	$\omega-2\theta$
reflns collcd	3568
indt reflns with $I > 2\sigma_I$	1467 ($R_{av} = 2.9\%$)
no. of variables	206
R indices ($I > 2\sigma$)[a]	$R1 = 2.63\%$, $wR2 = 6.15\%$
R indices (all data)[a]	$R1 = 3.49\%$, $wR2 = 6.67\%$

[a] $R1 = ||F_o| - |F_c||/|F_o|$; $wR2 = [[w(F_o^2 - F_c^2)^2/[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2 F_o^2 + (0.0314P)^2 + 0.167P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Positional and Isotropic Equivalent Displacement Parameters for ZnEnPO

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Zn1	0.74002(2)	0.0405(1)	0.42899(2)	0.0124(2)
Zn2	0.49969(2)	0.5217(1)	0.33333(2)	0.0114(2)
Zn3	0.73520(3)	−0.4562(1)	0.32212(2)	0.0148(2)
P1	0.83560(5)	0.0194(2)	0.32832(5)	0.0105(2)
P2	0.65162(5)	0.5138(2)	0.43792(5)	0.0090(2)
P3[b]	0.52742(11)	0.0232(4)	0.2581(1)	0.0105(4)
O1	0.57342(14)	0.4544(6)	0.4094(2)	0.0167(7)
O2	0.69958(14)	0.3902(6)	0.3949(1)	0.0135(6)
O3	0.91231(14)	−0.0491(6)	0.3628(1)	0.0126(6)
O4	0.7844(2)	−0.1344(6)	0.3631(2)	0.0197(7)
O5	0.8198(2)	−0.0816(7)	0.2586(2)	0.0244(8)
O6	0.67437(14)	0.3788(6)	0.5044(1)	0.0160(7)
O7	0.6656(2)	0.8118(6)	0.4442(2)	0.0168(7)
O8	0.82272(14)	0.3159(6)	0.3346(2)	0.0166(7)
O9	0.4989(2)	0.8965(6)	0.3094(1)	0.0175(7)
O10	0.5000	0.3249(8)	0.2500	0.020(1)
O11	0.6473(5)	0.888(2)	0.3011(4)	0.040(2)
O12	0.6108(3)	0.005(1)	0.2795(4)	0.022(2)
N	0.9064(2)	−0.4644(9)	0.4492(2)	0.0168(8)
C	0.9801(2)	0.427(1)	0.4704(2)	0.020(1)

[a] U_{eq} is defined as one-third of the trace of the ortogonalized $\mathbf{U}_{ij}$ tensor. [b] P3, O11, and O12 are with half-occupancies.

(7) Refined lattice parmeters from a Guinier camera for X-ray powder diffraction with internal standard of Si (NBS) and Cu Kα radiation: tetragonal, $a = 14.713(3)$, $b = 8.945(2)$ Å (15 lines); reported lattice parameters: $a = 14.7017(1)$, $c = 8.9417(1)$ Å.[5]

Table 3. Selected Distances and Angles in ZnEnPO

Zn1−O2	1.989(3)	P2−O2	1.561(3)
Zn1−O4	1.996(3)	P2−O6	1.531(3)
Zn1−O6	1.942(3)	P2−O7	1.523(3)
Zn1−O7	1.914(3)	P3−O9	1.468(4)
Zn2−O1	1.910(3)	P3−O9	1.539(4)
Zn2−O3	1.946(3)	P3−O10	1.602(4)
Zn2−O9	1.951(3)	P3−O12	1.558(6)
Zn2−O10	2.023(2)	N−C	1.482(6)
Zn3−O2	1.978(3)	C−C	1.503(10)
Zn3−O4	1.970(3)	O11−H6	1.12(3)
Zn3−O5	1.896(3)	O11−H7	1.11(3)
Zn3−O8	1.996(3)	O12−H6	0.88(3)
P1−O3	1.521(3)	N−H3	0.84(7)
P1−O4	1.558(3)	N−H4	0.92(6)
P1−O5	1.522(3)	N−H5	0.91(6)
P1−O8	1.522(3)	C−H1	0.91(5)
P2−O1	1.509(3)	C−H2	0.88(6)

O7−Zn1−O6	122.6(1)	O7−P2−O6	110.4(2)
O7−Zn1−O2	110.5(1)	O1−P2−O2	110.4(2)
O6−Zn1−O2	105.7(1)	O7−P2−O2	109.2(2)
O7−Zn1−O4	107.7(1)	O6−P2−O2	106.1(2)
O6−Zn1−O4	100.2(1)	O9−P3−O9	114.1(2)
O2−Zn1−O4	109.2(1)	O9−P3−O12	106.8(3)
O1−Zn2−O3	102.7(1)	O9−P3−O12	109.9(3)
O1−Zn2−O9	110.5(1)	O9−P3−O10	108.8(2)
O3−Zn2−O9	107.7(1)	O9−P3−O10	105.3(2)
O1−Zn2−O10	119.8(1)	O12−P3−O10	112.0(3)
O3−Zn2−O10	111.3(1)	P2−O1−Zn2	140.7(2)
O9−Zn2−O10	104.4(1)	P2−O2−Zn3	130.6(2)
O5−Zn3−O4	141.2(1)	P2−O2−Zn1	111.9(2)
O5−Zn3−O2	110.6(1)	Zn3−O2−Zn1	116.9(1)
O4−Zn3−O2	101.2(1)	P1−O3−Zn2	127.6(2)
O5−Zn3−O8	101.8(1)	P1−O4−Zn3	119.3(2)
O4−Zn3−O8	96.4(1)	P1−O4−Zn1	121.6(2)
O2−Zn3−O8	95.8(1)	Zn3−O4−Zn1	115.6(1)
O3−P1−O8	109.7(2)	P1−O5−Zn3	134.9(2)
O3−P1−O5	110.1(2)	P2−O6−Zn1	126.0(2)
O8−P1−O5	114.3(2)	P2−O7−Zn1	134.4(2)
O3−P1−O4	107.7(2)	P1−O8−Zn3	134.3(2)
O8−P1−O4	108.3(2)	P3−O9−Zn2	128.5(2)
O5−P1−O4	106.5(2)	P3−O10−Zn2	119.3(1)
O1−P2−O7	111.6(2)	P3−O10−Zn2	116.0(1)
O1−P2−O6	109.0(2)	Zn2−O10−Zn2	121.4(2)

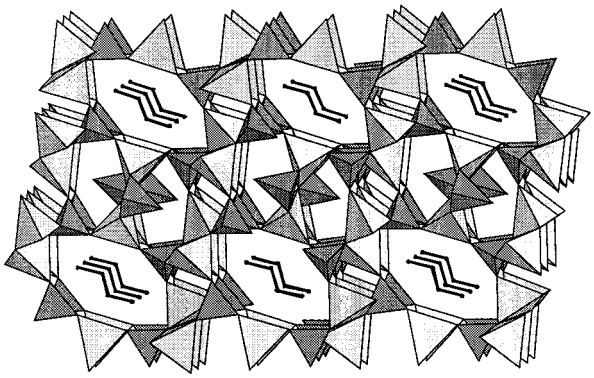

Figure 1. A general polyhedral view of the structure of ZnEnPO along the unique axis (*a* is horizontal). Darker tetrahedra: PO_4; lighter tetrahedra: ZnO_4; isolated molecules: ethylenediamine.

Results and Discussion

The structure of ZnEnPO is an open three-dimensional framework of corner-shared tetrahedra of PO_4 and ZnO_4 (Figure 1). There are two types of one-dimensional openings in the structure, both along the *b*-axis (Figure 2). The larger ones are elliptical in shape and consist of eight alternating P- and Zn-centered tetrahedra involving P1, P2, Zn1, and Zn2. The long and short O−O axes of the ellipse are 9.03 Å between O4 and O4 and 5.27 Å between O1 and O1, respectively. These results compare well with the eight-membered rings of the most common zeolites and AlPOs. For example, the corresponding dimensions for mordenite, stilbite, AlPO−C, and AlPO-D are 8.4 × 5.3, 8.3 × 5.3, 8.4 × 5.6, and 9.0 × 4.8 Å, respectively.[8] The long axis of the channels of ZnEnPO is somewhat longer than these examples because of atom O4 being three-bonded (Figure 2) and thus "pulled" outward from the channel.

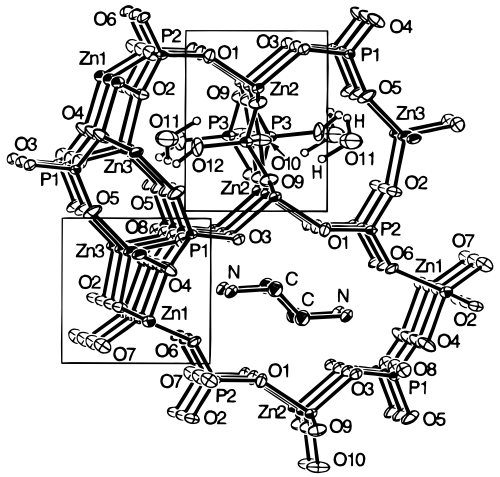

Figure 2. An ORTEP plot of ZnEnPO viewed along the axis *b* (the *a* axis is horizontal). The thermal ellipsoids are shown at 50% probability. The two framed areas are where Zn−O−Zn bonding occurs, and are shown enlarged in Figure 3.

The smaller "channels" are of six tetrahedra centered by P1, P2, P3, Zn2, and Zn3 (Figure 2). These channels are somewhat unusual because of the coordination of P3 (vide supra), which is bonded to three framework oxygens (2 × O9, O10) and an OH group (O12), and because of the statistical disorder of the P3 position. This results in blocking of the channel by some of the P3−OH fragments. The water molecules of the compound are also located in these channels. There is extensive hydrogen bonding involving the hydrogens of the hydroxyl groups and the water (O11, O12) and the oxygen atoms forming the walls of the channels [2.650(9) and 2.815(9) from O11 to O4 and O5, respectively, and 2.688(7) from O12 to O5].

The template, ethylenediamine dication, is positioned in the larger channels (Figures 1 and 2), and its nitrogen atoms are hydrogen bonded to the surrounding oxygens [2.897(5), 2.998, and 2.806 Å to O6, 7, and 8, respectively]. The molecule is in a "trans" conformation, and the C−C and C−N distances are within the normal range (Table 3).

The Zn−O bond lengths in ZnEnPO vary from 1.896(3) to 2.023(2) Å, the longest involving three-coordinated oxygen atoms, O2 and O4 with average Zn−O of 1.983 Å, and O10 with Zn−O distance of 2.023 Å. Each of these three oxygen atoms is bonded to two Zn atoms and one P atom, making the compound one of the rare examples of corner-shared Zn-centered tetrahedra with Zn−O−Zn bonding. These tetrahedra occur in two different parts of the structure (the frames in Figure 2, and their enlargements in Figure 3), and give rise to two different structural motives. One of these motives

(8) Meier, W. M.; Olson, D. H.; Baerlocher, C. *Atlas of Zeolite Structural Types*, 4th Revised ed.; Elsevier Science: New York, 1996.

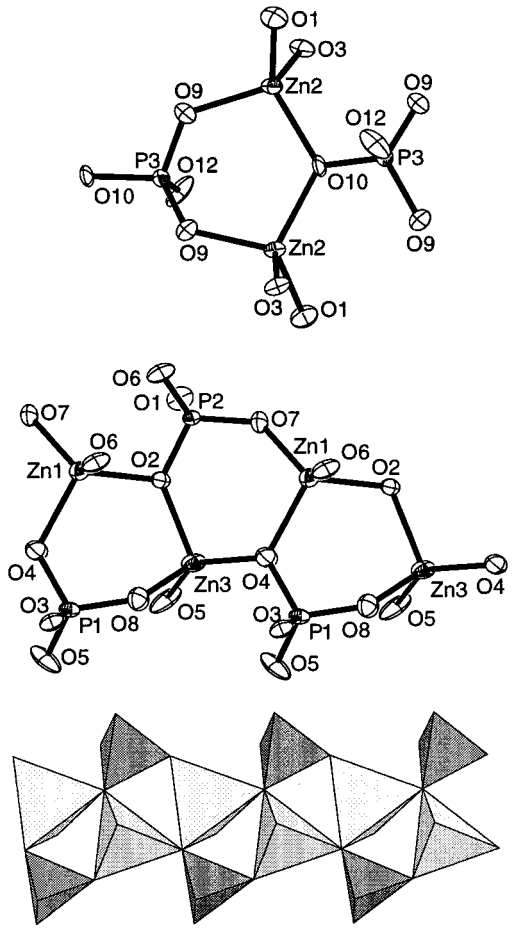

Figure 3. Closer views (along *a* axis) of the framed areas in Figure 2, showing the Zn−O−Zn bonding in ZnEnPO: (a) ORTEP plot of the upper frame in Figure 2 showing the isolated rings of two Zn, one P, and three O atoms; (b) ORTEP plot of the lower frame in Figure 2 showing a Zn−O−Zn chain; and (c) a polyhedral view of the same chain as in (b) with the ZnO_4 tetrahedra shown in light gray and the PO_4 tetrahedra shown in dark gray.

is a ring of two Zn2 atoms and one P3 atom connected through two O9 atoms and the three-bonded O10 (Figure 3a). The third bond to O10 is from another P3 and links the rings to each other along the *b* axis. Similar rings connected in a similar way have been observed in other zinc phosphates.[2k,3f]

The second Zn−O−Zn bonding also occurs in rings of two Zn atoms and one P atom, but two of the three oxygens of the ring, O2 and O4, are three-bonded (Figure 3b). Also, the rings are of two types, both containing Zn1, Zn3, O2, and O4, but one of them has also P1 and O8, whereas the other type has P2 and O7 instead. The rings share common edges, Zn3−O2 and Zn1−O4 as shown in Figure 3b, and form an infinite chain of fused rings along the *b* axis. The motif (Figure 3c) can be described as an infinite −O−Zn−O−Zn−O− chain of ZnO_4 tetrahedra (Zn1, Zn3, O2, and O4) that are bridged and "held" together by PO_4 tetrahedra (P1 and P2). The latter share oxygens O2 and O4 of the chain as well as an additional oxygen from each ZnO_4 tetrahedron, O7 or O8 (Figure 3c). This example is only the second one of such extensive Zn−O−Zn bonding of tetrahedra in a zinc phosphate. The other example occurs in $Na_2ZnPO_4OH{\cdot}7H_2O$, where Zn tetrahedra are linked by OH groups, and the PO_4 tetrahedra share the remaining two oxygens.[2l]

Initial thermogravimetric analysis (TGA) of ZnEnPO were run in a flow of dry air (150 mL/min) at a heating rate of 10°/min to a maximum temperature of 600 °C. Two barely distinguishable weight-loss steps between 340 and 550 °C amounted to ∼8%. To clarify the weight-loss curve, another sample was heated at a slower rate of 5°/min to 380 °C and isothermed for 12 h, then heated at the same rate to 430 °C, and kept at that temperature for 18 h. Constant weight was achieved at both temperatures, but the process is apparently very slow and requires such long times for equilibration. At 380 °C, the weight loss was 1.97%, which corresponds to the loss of one water molecule (calculated as 1.90%). The step at 430 °C amounted to another 6.10%, which is clearly the loss of one ethylenediamine molecule (calculated as 6.18%). Another sample was kept at 380 °C until constant weight was achieved and then was checked for crystallinity by X-ray powder diffraction. This sample showed the same pattern as the parent sample, indicating that the structure remained unchanged after the removal of the water. A sample kept at 430 °C until constant weight, on the other hand, showed complete loss of crystallinity, indicating that the structure "collapses" without the ethylenediamine. The same results were obtained in a flow of nitrogen as well.

The infrared (IR) spectrum of the compound shows the typical sharp peaks for ethylenediamine in the region 1400−1600 cm^{-1}, and the broad absorption at 1000 cm^{-1} due to the phosphate. Clearly distinguishable are also two broad peaks at ∼3500 and 3000 cm^{-1}, corresponding to heavily hydrogen-bonded OH and H_2O, respectively. The IR spectrum of the sample heated at 380 °C for 12 h showed all peaks but the one at 3500 cm^{-1}. This result indicates that the sample is dehydrated but the OH is still present, thus supporting the TGA results. The sample heated at 430 °C for 18 h shows only the broad phosphate peak, which is consistent with the complete removal of the ethylenediamine, water, and OH. This result also confirms the results from the TGA measurements as well as the X-ray diffraction results.

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Supporting Information Available: Tables of anisotropic displacement parameters for all non-hydrogen atoms and positional and isotropic displacement parameters for the hydrogen atoms (1 page). Ordering information is given on any current masthead page.

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