Hydrothermal Syntheses and Single-Crystal Structures of Some Novel Guanidinium−Zinc−Phosphates

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The mild-condition hydrothermal syntheses and single-crystal structures of three new guanidinium zinc phosphates are reported. $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ are built up from three-dimensional Zn/P/O frameworks encapsulating guanidinium cations in 12-ring channel systems. The latter material has the lowest nodal-framework-atom density per unit volume of any open-framework phase characterized so far. $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ is a one-dimensional phase with respect to Zn/P/O connectivity and has a unique triply bridged tetrahedral chain connectivity for simple phosphates. Crystal data: $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, $M_r = 478.78$, monoclinic, space group $P2_1$ (No. 4), $a = 5.1318(4)$ Å, $b = 7.8411(7)$ Å, $c = 16.510(1)$ Å, $\beta = 90.110(7)°$, $V = 664.36(8)$ Å^3, $Z = 2$, $R = 2.43\%$, $R_w = 2.67\%$ [2608 observed reflections with $I > 3\sigma(I)$]. $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, $M_r = 377.50$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 10.447(2)$ Å, $b = 12.349(2)$ Å, $c = 10.225(2)$ Å, $V = 1319.2(5)$ Å^3, $Z = 4$, $R = 3.26\%$, $R_w = 3.32\%$ [2252 observed reflections with $I > 3\sigma(I)$]. $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, $M_r = 811.17$, trigonal, space group $R\bar{3}$ (No. 148), $a = 20.016(7)$ Å, $c = 13.955(6)$ Å, $V = 4842(4)$ Å^3, $Z = 6$, $R = 5.31\%$, $R_w = 5.52\%$ [630 observed reflections with $I > 3\sigma(I)$].

Introduction

Over the past few years, it has become apparent that non-aluminosilicate open-framework phases—inorganic materials that contain voids and channels of appreciable size occupied by "guest" species—have an astonishingly diverse structural chemistry.[1−8] Our own work, largely focused on the tetrahedral-building-unit zincophosphate/arsenate (ZnPO/ZnAsO) system, has revealed direct analogues of aluminosilicate zeolites,[9] complex organically templated networks,[10] and a family of robust, thermally stable phases based on a completely new type of topology involving ZnO_4, PO_4, and novel OZn_4 tetrahedral units.[11]

One persistent problem in this area of materials chemistry is a fundamental lack of control in directing a reaction toward a desired framework configuration. A major reason for this difficulty is that in general, the mechanisms of mild-condition kinetically controlled reactions are poorly understood.[12] Predictive crystal packing models based on "common sense" or symmetry arguments[13] are of little assistance in this field. Following the methodology of classical aluminosilicate zeolite preparations,[14] exploratory synthesis retains a vital role in this area at present. An especially important concept involves *templating*—the tendency of a particular component of the reaction, usually a cation, to direct the reaction to a particular structure, or at least a structure containing a distinct feature. A simple example for non-aluminosilicate materials appears to be the predilection for Li^+ to template tetrahedral 6-rings in beryllophosphate networks,[15] based on size considerations in terms of optimizing Li−O tetrahedral bond lengths. Small organic molecules, particularly those containing amino groups, have played an outstanding role in templating novel networks.[16,17] In some cases there is a striking and beautiful relationship between the template shape and the surrounding framework topology.[18]

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Table 1. Synthesis Schemes

compound	prepared from: $(C(NH_2)_3)_2CO_3$	H_3PO_4	H_2O	ZnO	ratio[a]	product
$CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$	1.20 g (0.0067 mol)	3.83 g (0.033 mol)	9.32 g	0.814 g (0.01 mol)	4:3:10	transparent blocks/white powder
$(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$	0.72 g (0.004 mol)	1.38 g (0.012 mol)	10.28 g	0.814 g (0.01 mol)	4:5:6	jagged lumps/white powder
$(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$	5.40 g (0.03 mol)	2.29 g (0.02 mol)	9.92 g	0.814 g (0.01 mol)	6:1:2	small rods/white powder

[a] Starting ratio of guanidine:zinc:phosphorus.

Table 2. Crystallographic Parameters

	$CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$	$(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$	$(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$
emp formula	$Zn_2P_3O_{12}N_3C_1H_9$	$Zn_1P_2O_8N_6C_2H_{14}$	$Zn_2P_3O_{14}N_{18}C_6H_{39}$
formula wt	478.78	377.50	811.17
crystal system	Monoclinic	Orthorhombic	Trigonal
a (Å)	5.1318 (4)	10.447 (2)	20.016 (7)
b (Å)	7.8411 (7)	12.349 (2)	20.016 (7)
c (Å)	16.510 (1)	10.225 (2)	13.955 (6)
α (deg)	90	90	90
β (deg)	90.119 (7)	90	90
γ (deg)	90	90	120
V (Å^3)	664.36 (8)	1319.2 (5)	4842 (4)
Z	2	4	6
space group	$P2_1$ (No. 4)	$Pna2_1$ (No. 33)	$R\bar{3}$ (No. 148)
T (°C)	25 (2)	25 (2)	25 (2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
ρ_{calc} (g/cm^3)	2.39	1.90	1.67
μ (cm^{-1})	41.2	21.9	17.5
total data	3639	3475	1329
obsd data[a]	2608	2252	630
parameters	211	179	137
$R(F)$[b]	2.43	3.26	5.31
$R_w(F)$[c]	2.67	3.32	5.52

[a] $I > 3\sigma(I)$ after data merging. [b] $R = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

An interesting candidate for templating inorganic frameworks that has not received much attention so far is the nitrogen-rich guanidinium cation $[C(NH_2)_3^+$ or $CN_3H_6^+]$. The assumption of delocalization of its positive charge over its three "arms" and the resulting symmetrical, rigid "propeller" shape of this cation[19] suggested to us that in a designer synthesis,[20] this species might act to template medium-sized rings in side-on orientation (i.e., the C and N atoms of the guanidinium cation are approximately aligned in the plane of the ring), with the involvement of N−H···O hydrogen bonds to framework oxygen atoms. The guanidinium cation is known to show a similar mode of bonding in adopting a side-on orientation when occupying molecular crown ether rings.[21]

In this paper, we describe our investigations into zincophosphate networks templated by the guanidinium cation. Three new phases have been prepared as single crystals by variations on a simple solution-phase reaction. $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ and $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ are three-dimensional open-framework structures incorporating extraframework guanidinium cations, whereas $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ is one-dimensional (or "polymeric") with respect to Zn/P/O connectivity and contains a triply bridged tetrahedral chain structure which is unprecedented for simple phosphate materials.

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Experimental Section

Synthesis and Initial Characterization. The three title compounds were prepared from guanidinium carbonate [$(C(NH_2)_3)_2CO_3$, Kodak], phosphoric acid (85% H_3PO_4, Fisher) deionized water and zinc oxide (ZnO, St. Joseph's), as shown in Table 1. In each case, the ZnO was added to an aqueous solution of $(C(NH_2)_3)_2CO_3$ and H_3PO_4, and the resulting mixture was shaken well and aged for 1 day at room temperature. The mixture, enclosed in a 100 mL PTFE bottle, was then placed in a 100 °C oven for 5 days. The solid product was recovered from the supernatant liquors by filtration.

X-ray powder diffraction data (Siemens D500 automated diffractometer, Cu Kα radiation, $\lambda = 1.5418$ Å) were recorded for crushed crystals of each phase and revealed complex patterns, unlike those of the starting materials or known zinc phosphates.

Single-Crystal Structure Determinations. In each case, a suitable crystal (for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, transparent block, dimensions ∼0.4 × 0.2 × 0.2 mm; for $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, irregular "glassy" chunk, ∼0.6 × 0.5 × 0.5 mm; for $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, translucent rod, ∼0.4 × 0.15 × 0.15 mm) was selected and glued to a thin glass fiber with cyanoacrylate adhesive and mounted on a Siemens P4 automated diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å). Room temperature [25(2) °C] data collections were performed after the unit cells were established and optimized by the standard procedures of peak-search, centering, indexing, and least-squares routines. Refined cell parameters for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ (monoclinic), $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ (orthorhombic), and $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ (trigonal−rhombohedral) are presented in Table 2. The unit cell of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ was carefully optimized using high-angle reflections to accurately determine the monoclinic *β* angle. Monoclinic symmetry was confirmed by scanning (would-be) equivalent reflections to check their intensity consistencies in 2/*m* (monoclinic) and *mmm* (orthorhombic) Laue symmetry.

Data were collected using the $\omega/2\theta$ scan mode to a maximum 2θ of 65° for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$. The $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ crystal was a very weak scatterer, and data were collected to a maximum 2θ of 40° for this material. Intensity standards, remeasured every 100 observations, showed only statistical fluctuations over the course of the three data collections. Absorption was monitored by ψ scans and corrected for at the data reduction stage[22] (ranges of equivalent transmission factors: $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$: 0.57−0.63; $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$: 0.55−0.57; $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$: 0.88−0.99). The raw intensities were reduced to F and $\sigma(F)$ values by means of a profile-fitting routine,[23] the normal corrections for Lorentz and polarization factors were made, and the equivalent data merged, applying the observability criterion $I > 3\sigma(I)$: for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, 3639 reflections merged to 2608 observed reflections with $R_{Int} = 0.032$; for $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, 3475 reflections merged to 2252 observed reflections with $R_{Int} = 0.030$; for $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, 1329 reflections merged to 630 observed reflections with $R_{Int} = 0.079$.

For $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, the systematic absences in the reduced data ($0k0$, $k \neq 2n$) indicated space groups $P2_1$ or $P2_1/m$. For $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, the absence conditions $0kl$, $k + l \neq 2n$; $h0l$, $h \neq 2n$; and $00l$, $l \neq 2n$, indicated space groups $Pna2_1$ or $Pnam$. For $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, the systematic absences $h\bar{h}0l$, $h + l \neq 3n$ and $000l$, $l \neq 3n$ indicated space groups $R3$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$. Trial reflection merges indicated that Laue class $\bar{3}$, as opposed to $\bar{3}m$, was probably applicable to this phase.

The structures of these phases were solved by direct methods using SHELXS86.[24] In each case, a sufficient fragment of the structure was revealed (Zn, P, some O) to enable the remainder of the non-hydrogen atoms to be located from Fourier difference maps, and the refinements to proceed straightforwardly to the $R < 10\%$ stage (isotropic thermal parameters). For $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, only the noncentrosymmetric space groups [$P2_1$ (No. 4) and $Pna2_1$ (No. 33), respectively] revealed a reasonable starting configuration. For $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, the best model was established in the centrosymmetric space group $R\bar{3}$ (No. 148). In each refinement, a Larson-type secondary extinction correction[25] was optimized at the latter stages of the refinement to improve the fit of strong, low-angle reflections which showed a systematic $F_{obs} < F_{calc}$ trend. Full-matrix least-squares refinements and all subsidiary calculations were performed with the Oxford CRYSTALS[26] system.

For $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, several difference-map features corresponding to probable "framework" proton sites were located. The resulting H atom positions were refined using O−H and N−H bond length and P−O−H and C−N−H bond angle restraints to ensure a stable refinement. Hydrogen atoms associated with the guanidinium cation were located geometrically by assuming planar sp^2 hybridization about each N atom and an N−H bond length of 0.95 Å. The Flack polarity parameter[27] was optimized to establish the absolute structure of the individual crystal of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ studied in the diffraction experiment. A refined value of 0.00(2) indicated that the absolute structure is as given in the Results. Final residuals of $R = 2.43\%$ and $R_w = 2.67\%$ ($w_i = 1/\sigma^2$) were obtained for refinements varying positional and anisotropic thermal parameters for all non-hydrogen atoms and an atom-type isotropic thermal factor for H. Setting the Flack parameter to 1.00 (opposite absolute structure) and repeating the refinement resulted in residuals of $R = 3.34\%$ and $R_w = 3.89\%$. Because no chiral reagents were used in the synthesis, there is no reason to suspect that the *bulk* sample of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ consists of anything other than a random 50:50 mixture of crystals of both absolute structures.

Table 3. Final Atomic Coordinates/Thermal Factors for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$

atom	x	y	z	U_{eq}[a]
Zn(1)	0.19821(8)	0.1421(1)	0.58625(2)	0.0131
Zn(2)	0.19570(8)	0.3706(1)	0.92089(2)	0.0137
P(1)	−0.2965(2)	0.2656(2)	0.49857(5)	0.0121
P(2)	0.3056(2)	0.7555(2)	0.98746(5)	0.0124
P(3)	0.4539(2)	0.2507(2)	0.75346(5)	0.0157
O(1)	−0.1497(5)	0.2392(4)	0.5785(1)	0.0161
O(2)	0.3285(5)	0.1284(5)	0.6950(2)	0.0217
O(3)	0.1885(5)	−0.0917(4)	0.5515(2)	0.0183
O(4)	0.4131(5)	0.2896(4)	0.5166(2)	0.0168
O(5)	0.1951(5)	0.6122(4)	0.9369(2)	0.0192
O(6)	−0.1563(5)	0.2855(4)	0.9339(2)	0.0184
O(7)	0.4065(5)	0.2263(4)	0.9915(2)	0.0181
O(8)	0.2751(5)	0.3486(5)	0.8079(2)	0.0227
O(9)	−0.2550(6)	0.1035(4)	0.4436(2)	0.0198
O(10)	0.2773(7)	0.9160(4)	0.9319(2)	0.0236
O(11)	0.6143(6)	0.3889(5)	0.7067(2)	0.0270
O(12)	0.6460(6)	0.1375(5)	0.8040(2)	0.0233
C(1)	−0.1181(8)	−0.2448(7)	0.7414(2)	0.0246
N(1)	−0.2211(8)	−0.2397(7)	0.8157(2)	0.0327
N(2)	0.0985(8)	−0.3280(6)	0.7274(2)	0.0323
N(3)	−0.2394(8)	−0.1643(6)	0.6815(2)	0.0313

[a] U_{eq} (Å^2) = $^1/_3[U_1 + U_2 + U_3]$.

For $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, the refinement proceeded straightforwardly in space group $Pna2_1$. Guanidinium-cation hydrogen atoms were located geometrically, as above. Refinement of the Flack parameter to ∼1.0 indicated that the incorrect absolute structure had been established in the initial model. The polarity of the model was reversed by changing the sign of the polar-axis z coordinate for all the atoms and re-refining the model, which resulted in a final value for the Flack parameter of −0.01(2) and residuals of $R = 3.26\%$ and $R_w = 3.32\%$ ($w_i = 1/\sigma^2$). Re-refinement of this transformed coordinate set with the Flack parameter set to 1.00 led to residuals of $R = 4.17\%$ and $R_w = 4.50\%$. Once again, we assume the bulk sample of $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ contains 50% of each absolute structure.

For $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ no proton positions could be located in difference maps. Guanidinium cation hydrogen atoms were located geometrically, as above. Anisotropic thermal parameter refinement of the bridging Zn−O−Zn oxygen atoms O(5) and O(6) (vide infra) resulted in "pancaked" thermal ellipsoids perpendicular to [0001] which converged to nonpositive-definite values. These were reset to isotropic for the final refinement cycles, which resulted in final residuals of $R = 5.31\%$ and $R_w = 5.52\%$ ($w_i = 1/\sigma^2$).

Results

Crystal Structure of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$. This material forms a new anionic open-framework phase built up from tetrahedral ZnO_4 and PO_4 building blocks, connected via Zn−O−P bonds, surrounding channels occupied by extraframework guanidinium cations. Final atomic coordinates and thermal parameters for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ are presented in Table 3, with selected geometrical data in Table 4. The building unit of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ is shown in Figure 1 using CAMERON,[28] and the complete crystal structure is illustrated in Figure 2.

The two zinc atoms in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ are both tetrahedrally coordinated by their O atom neighbors with average zinc−oxygen bond distances of 1.939(2) Å for Zn(1) and 1.930(2) Å for Zn(2). Both zinc atoms make four Zn−O−P bonds to four distinct P-atom

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$

Zn(1)−O(1)	1.945(3)	Zn(1)−O(2)	1.918(3)
Zn(1)−O(3)	1.922(3)	Zn(1)−O(4)	1.970(3)
Zn(2)−O(5)	1.913(3)	Zn(2)−O(6)	1.938(3)
Zn(2)−O(7)	1.950(3)	Zn(2)−O(8)	1.919(3)
P(1)−O(1)	1.532(3)	P(1)−O(3)	1.498(3)
P(1)−O(4)	1.532(2)	P(1)−O(9)	1.576(3)
P(2)−O(5)	1.510(3)	P(2)−O(6)	1.527(3)
P(2)−O(7)	1.534(3)	P(2)−O(10)	1.564(3)
P(3)−O(2)	1.503(3)	P(3)−O(8)	1.497(3)
P(3)−O(11)	1.566(3)	P(3)−O(12)	1.566(3)
C(1)−N(1)	1.337(5)	C(1)−N(2)	1.310(6)
C(1)−N(3)	1.327(6)		
O(1)−Zn(1)−O(2)	113.7(1)	O(1)−Zn(1)−O(3)	109.3(1)
O(2)−Zn(1)−O(3)	103.6(1)	O(1)−Zn(1)−O(4)	104.3(1)
O(2)−Zn(1)−O(4)	112.6(1)	O(3)−Zn(1)−O(4)	113.6(1)
O(5)−Zn(2)−O(6)	108.9(1)	O(5)−Zn(2)−O(7)	119.5(1)
O(6)−Zn(2)−O(7)	104.5(1)	O(5)−Zn(2)−O(8)	102.9(1)
O(6)−Zn(2)−O(8)	106.1(1)	O(7)−Zn(2)−O(8)	114.2(1)
O(1)−P(1)−O(3)	113.2(2)	O(1)−P(1)−O(4)	109.0(1)
O(3)−P(1)−O(4)	112.2(2)	O(1)−P(1)−O(9)	108.6(2)
O(3)−P(1)−O(9)	103.5(2)	O(4)−P(1)−O(9)	110.1(2)
O(5)−P(2)−O(6)	113.3(2)	O(5)−P(2)−O(7)	112.0(2)
O(6)−P(2)−O(7)	108.4(1)	O(5)−P(2)−O(10)	103.9(2)
O(6)−P(2)−O(10)	109.2(2)	O(7)−P(2)−O(10)	109.9(2)
O(2)−P(3)−O(8)	116.7(2)	O(2)−P(3)−O(11)	110.5(2)
O(8)−P(3)−O(11)	105.3(2)	O(2)−P(3)−O(12)	104.4(2)
O(8)−P(3)−O(12)	110.9(2)	O(11)−P(3)−O(12)	108.9(2)
Zn(1)−O(1)−P(1)	124.0(1)	Zn(1)−O(2)−P(3)	135.5(2)
Zn(1)−O(3)−P(1)	150.2(2)	Zn(1)−O(4)−P(1)	126.0(2)
Zn(2)−O(5)−P(2)	144.4(2)	Zn(2)−O(6)−P(2)	128.1(2)
Zn(2)−O(7)−P(2)	125.6(2)	Zn(2)−O(8)−P(3)	139.6(2)

neighbors and an average Zn−O−P bond angle of 134.2° results from a fairly wide spread of angles (Table 4). These geometrical data are in good agreement with the results of previous structure determinations on similar compounds.[10] There are three crystallographically distinct PO_4 tetrahedra in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$: Two of these phosphate entities [P atoms P(1) and P(2)] make three P−O−Zn bonds and possess one terminal P−O bond. P(3) makes two P−O−Zn links and has two uncoordinated oxygen atom neighbors. Average P−O bond distances of 1.535(2), 1.534(2), and 1.533(2) Å result for P(1), P(2), and P(3), respectively. Assuming the usual valences of Zn, P, and O, the framework stoichiometry of $Zn_2P_3O_{12}$ in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ has a charge of −5. We assume that the extraframework guanidine species is present as the singly charged guanidinium cation; thus four "framework" protons are required for charge-balancing purposes, which corresponds to the four proton sites located in Fourier maps, one of which is associated with each terminal P−O moiety, i.e., two HPO_4 groups and one H_2PO_4 group. This assignment is also consistent with the P−O bond lengths of the oxygen atoms involved [O(9)−O(12)] which show characteristic values in the range ∼1.56−1.60 Å.[29] It would be difficult to envisage a structural model that involves five framework protons and a neutral guanidine (as opposed to guanidinium cation) extraframework species. All the (di)hydrogen phosphate protons are involved in intraframework hydrogen bonds as shown in Figure 2: O(9)−H(9)···O(4) (d = 1.76 Å), O(10)−H(10)···O(7) (d = 1.78 Å), O(11)−H(11)···O(1) (d = 1.77 Å), O(12)−H(12)···O(6) (d = 1.72 Å) with the H-bonding distances based on the restrained refinement of the framework H atoms as described above.

(29) Lightfoot, P.; Masson, D. *Acta Crystallogr.* **1996**, *C52*, 1077.

The polyhedral connectivity in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ leads to the open-framework network shown in Figure 2. ZnO_4 and HPO_4 groups are arranged in sheets lying perpendicular to the crystallographic c direction. These sheets (Figure 3) consist of 6-rings of tetrahedra, with the Zn and P species strictly alternating—there are no Zn−O−Zn or P−O−P linkages in this structure. An intrasheet H-bond is apparent in each 6-ring. There are two very similar, but crystallographically distinct sheets; at $z \approx {}^1/_2$ (atoms Zn(1), P(1), etc.) and $z \approx 0$ (atoms Zn(2), P(2), etc.), as indicated in Figure 3. The doubled repeat pattern arises from the "ordering" of the guanidinium cations in the [100] channels (Figure 2). The Zn(1)/P(1) and Zn(2)/P(2) sheets are linked into a three-dimensional framework by the $H_2P(3)O_4$ group, in the c-direction. This polyhedral connectivity of two zinc-centered tetrahedra and three phosphorus-centered tetrahedra results in an extraframework channel system of 12-rings along [100] (approximate atom-to-atom dimensions = 6.8 × 6.1 Å) and squashed 8-rings along [010].

The guanidinium cations occupy the [100] channels (Figure 2). Two of the hydrogen atoms associated with this guanidinium cation were located from Fourier difference maps; the remaining four were located geometrically by assuming planar sp^2 hybridization about the remaining two N atoms. On the basis of this assumption, five hydrogen-bonding links are made by the guanidinium cation's N−H groups, as N(1)−H(1)···O(5) [d = 2.23 Å]; N(2)−H(3)···O(8) [d = 2.27 Å]; N(2)−H(4)···O(9) [d = 2.06 Å]; N(3)−H(5)···O(2) [d = 2.31 Å]; N(3)−H(6)···O(3) [d = 2.31 Å]. On average, these template−framework N−H···O hydrogen bonds are substantially longer that the intraframework O−H···O links noted above.

Crystal Structure of $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$: This phase consists of an anionic zincophosphate framework of unprecedentedly low framework atom density (vide infra), enclosing an intersecting two-dimensional network of channels, occupied by guanidinium cations. Final atomic coordinates and thermal parameters for $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ are presented in Table 5, with selected geometrical data in Table 6. The building unit of $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ is shown in Figure 4.

The single distinct zinc atom in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ is tetrahedrally coordinated to oxygen with an average Zn−O bond distance of 1.943(2) Å. This zinc atom makes four Zn−O−P bonds to four distinct P atom neighbors resulting in an average Zn−O−P bond angle of 125.7°. There are two crystallographically distinct phosphate tetrahedra in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$: Both of these groups make two bonds to adjacent Zn atoms and possess two terminal P−O bonds. Average P−O bond distances of 1.536(2) Å result for both P(1) and P(2). The resulting ZnP_2O_8 framework stoichiometry has a charge of −4. In this material, there are two extraframework guanidinium cations, thus two "framework" protons are required for charge-balancing purposes. One of these, attached to O(5), was located in Fourier difference maps, and the other [attached to O(8)] may be located on the basis of the uncoordinated P−O bond lengths, as noted above, i.e., there are two HPO_4 groups in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$. The proton attached to O(5) is involved in a strong H-bonding interaction as O(5)−H(1)···O(7) (d = 1.58 Å) based on the restrained refinement of the H

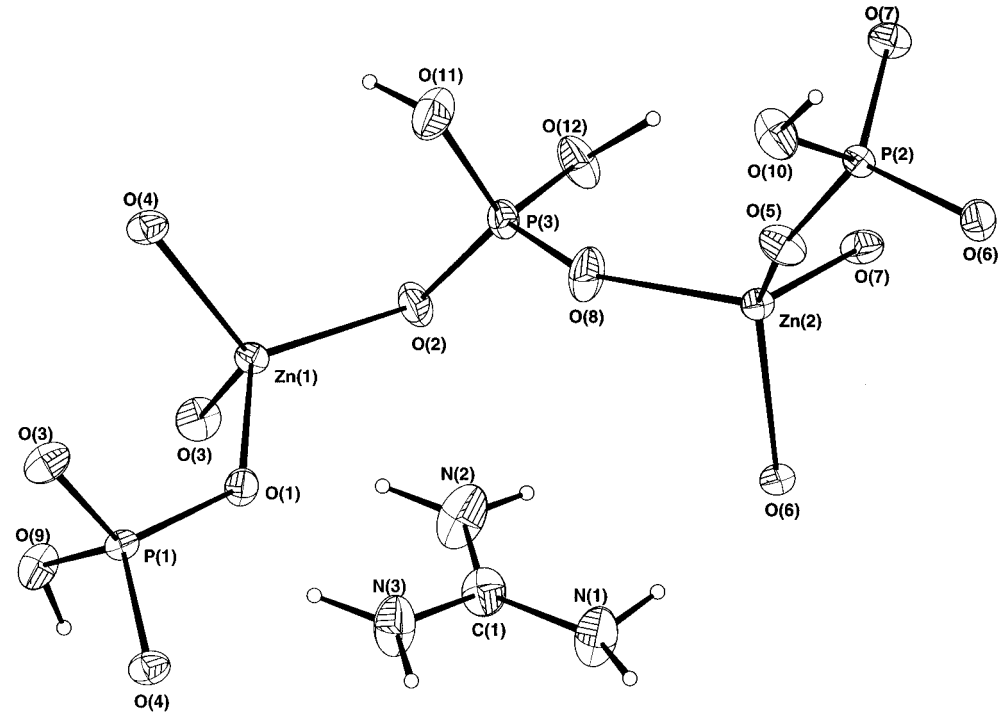

Figure 1. View of a fragment of the crystal structure of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ showing the atom-labeling scheme (50% thermal ellipsoids; protons represented by spheres of arbitrary radius).

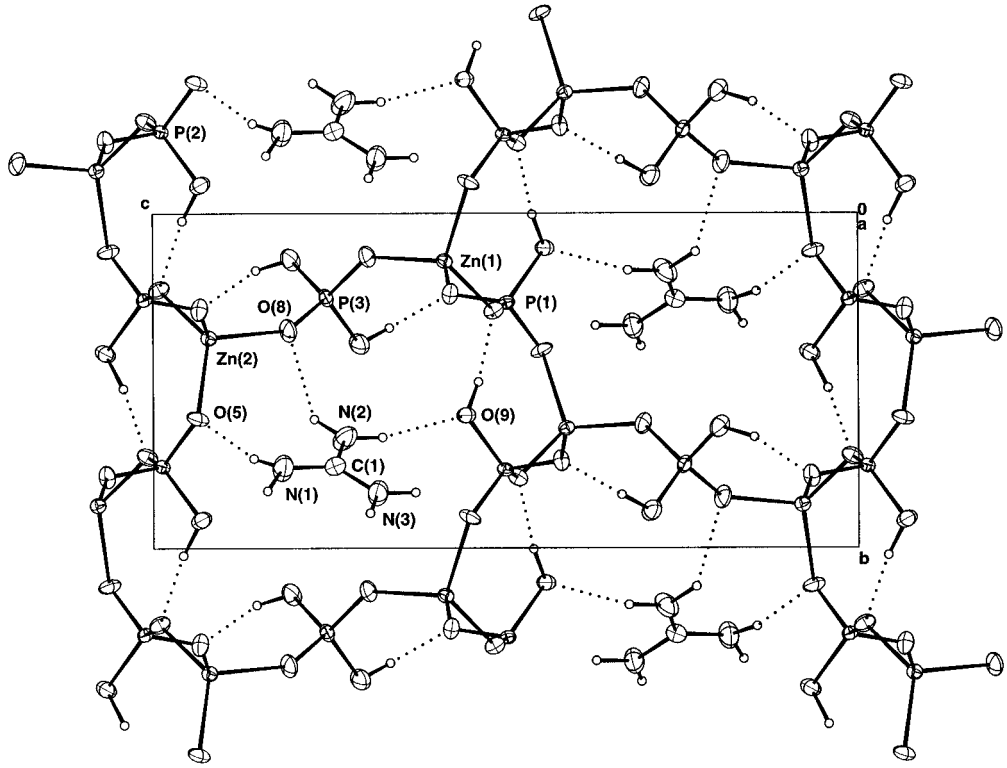

Figure 2. View down [100] of the crystal structure of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ showing the one-dimensional 12-ring channel system occupied by guanidinium cations. Possible hydrogen-bonding links are indicated by dotted lines.

atoms as described above; O(8) has several suitable nonbonded contacts to nearby oxygen atoms to accommodate a possible O(8)−H···O hydrogen bond.

The polyhedral connectivity in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ leads to a new open-framework topology. Vertex-sharing helical chains of $Zn(1)O_4$ and $HP(1)O_4$ groups propagate in the polar *c* unit-cell direction. The zinc nodes of these chains are cross-linked by the $HP(2)O_4$ moieties in the *a* direction. As with $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, there are no Zn−O−Zn or P−O−P links in this structure. This polyhedral connectivity of one zinc-centered tetrahedron and two phosphorus-centered tetrahedra results in a striking channel system of intersecting 12-rings which propagate in the [100] and [001] directions (Figures 5 and 6). Conversely, no channels are apparent in this structure when viewed down [010]. The smallest identifiable ring system in this topology is a *12-ring* for both Zn and P.

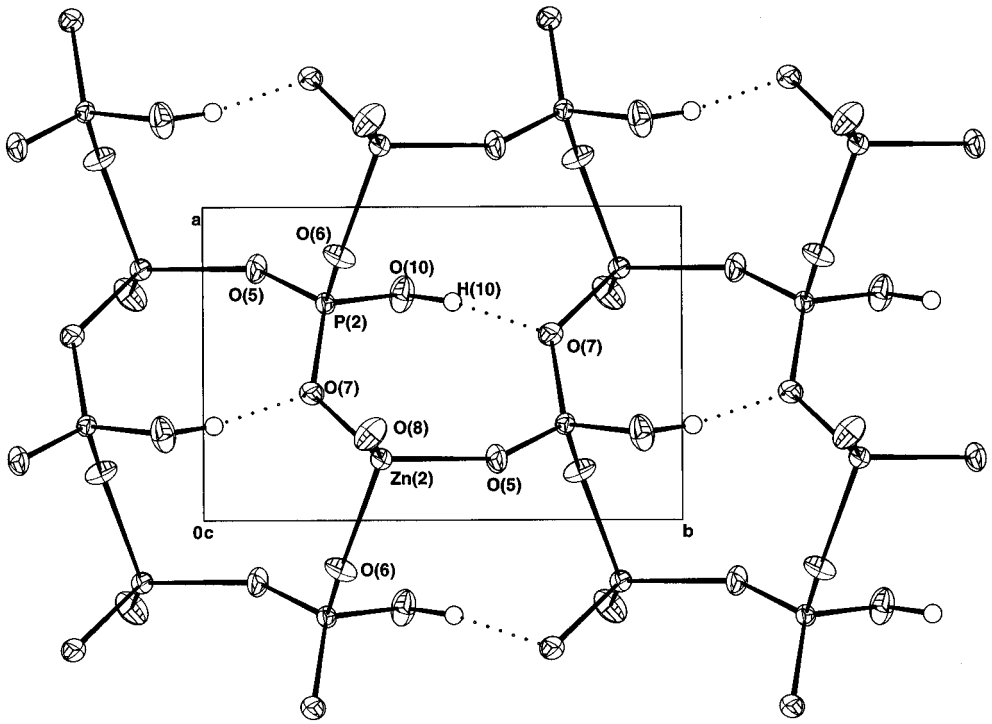

Figure 3. View down [001] of part of a $Zn(HPO_4)$ sheet in the $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ structure. Note the in-sheet H-bonding linkage.

Table 5. Final Atomic Coordinates/Thermal Factors for$(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$

atom	*x*	*y*	*z*	U_{eq}[a]
Zn(1)	0.01878(4)	0.13320(4)	0.3155(1)	0.0158
P(1)	−0.0022(1)	0.01654(9)	0.0549(2)	0.0178
P(2)	0.2674(1)	0.25549(9)	0.2246(2)	0.0165
O(1)	0.1872(3)	0.1974(2)	0.3270(4)	0.0217
O(2)	−0.0908(3)	0.2525(2)	0.2608(3)	0.0200
O(3)	0.0275(3)	0.0077(2)	0.2009(3)	0.0205
O(4)	−0.0370(3)	0.0886(3)	0.4879(4)	0.0247
O(5)	−0.1522(3)	0.0238(3)	0.0371(4)	0.0294
O(6)	0.0593(4)	0.1161(3)	−0.0027(4)	0.0336
O(7)	0.2259(3)	0.3734(2)	0.2086(4)	0.0249
O(8)	0.2549(3)	0.1976(3)	0.0892(4)	0.0274
C(1)	0.2658(5)	−0.2340(4)	0.2120(6)	0.0305
N(1)	0.2044(5)	−0.1780(4)	0.3019(6)	0.0422
N(2)	0.2360(5)	−0.2217(5)	0.0873(5)	0.0417
N(3)	0.3531(5)	−0.3049(4)	0.2468(5)	0.0475
C(2)	0.4885(5)	0.0184(5)	−0.0475(6)	0.0364
N(4)	0.5130(4)	0.0976(4)	0.0350(6)	0.0415
N(5)	0.5782(5)	−0.0479(4)	−0.0859(6)	0.0444
N(6)	0.3695(5)	0.0053(4)	−0.0931(6)	0.0458

[a] U_{eq} (Å^2) = $^1/_3[U_1 + U_2 + U_3]$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$

Zn(1)−O(1)	1.934(3)	Zn(1)−O(2)	1.948(3)
Zn(1)−O(3)	1.945(3)	Zn(1)−O(4)	1.937(4)
P(1)−O(3)	1.529(4)	P(1)−O(4)	1.524(4)
P(1)−O(5)	1.580(4)	P(1)−O(6)	1.507(4)
P(2)−O(1)	1.520(4)	P(2)−O(2)	1.530(3)
P(2)−O(7)	1.528(3)	P(2)−O(8)	1.564(4)
C(1)−N(1)	1.317(7)	C(1)−N(2)	1.321(7)
C(1)−N(3)	1.313(6)	C(2)−N(4)	1.317(7)
C(2)−N(5)	1.305(7)	C(2)−N(6)	1.338(7)
O(1)−Zn(1)−O(2)	104.0(1)	O(1)−Zn(1)−O(3)	108.7(1)
O(2)−Zn(1)−O(3)	117.2(1)	O(1)−Zn(1)−O(4)	109.6(2)
O(2)−Zn(1)−O(4)	107.4(1)	O(3)−Zn(1)−O(4)	109.6(1)
O(3)−P(1)−O(4)	108.9(2)	O(3)−P(1)−O(5)	108.5(2)
O(4)−P(1)−O(5)	105.2(2)	O(3)−P(1)−O(6)	110.7(2)
O(4)−P(1)−O(6)	113.8(2)	O(5)−P(1)−O(6)	109.4(2)
O(1)−P(2)−O(2)	109.7(2)	O(1)−P(2)−O(7)	111.5(2)
O(2)−P(2)−O(7)	111.2(2)	O(1)−P(2)−O(8)	110.4(2)
O(2)−P(2)−O(8)	105.4(2)	O(7)−P(2)−O(8)	108.5(2)
Zn(1)−O(1)−P(2)	130.8(3)	Zn(1)−O(2)−P(2)	126.1(2)
Zn(1)−O(3)−P(1)	121.5(2)	Zn(1)−O(4)−P(1)	124.8(2)

The guanidinium cations occupy the channels in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, with the C(1)-centered species appearing to occupy the [100] channels, and the C(2)-centered species occupying the [010] channels. Both channels have approximate dimensions of 7.6 × 8.2 Å when measured from O atom to O atom. A more detailed view of the possible hydrogen-bonding configuration of one of the guanidinium species is shown in Figure 7. It appears that the guanidinium cation is acting to template the resulting 12-ring of alternating Zn- and P-centered tetrahedral nodes, with N−H···O hydrogen bonding playing an important role. One of the template−framework hydrogen-bonding links involves an Zn−O−P bridge; the remainder involve terminal P−O (or P−OH) links. The spread of template−framework H-bonding contact distances in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ covers the range ~1.90−2.29 Å, based on geometrical placement and restrained refinement of the hydrogen atoms of the guanidinium cations.

Crystal Structure of $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$. This material adopts a completely different crystal structure to its partners and is built up from one-dimensional chains of vertex-sharing ZnO_4 and PO_4 units (Figure 8). Final atomic positional and thermal parameters are presented in Table 7 with selected geometrical data in Table 8.

The two zinc atoms in $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ are both nominally tetrahedrally coordinated but are significantly distorted and could almost be described as triangular-based pyramidal (Figure 8). Each zinc center makes three Zn−O−P bonds to different P atoms (θ_{av} = 136.4°) and one Zn−OH−Zn link, which is nominally linear. The single phosphate group in $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ is involved in two P−O−Zn linkages

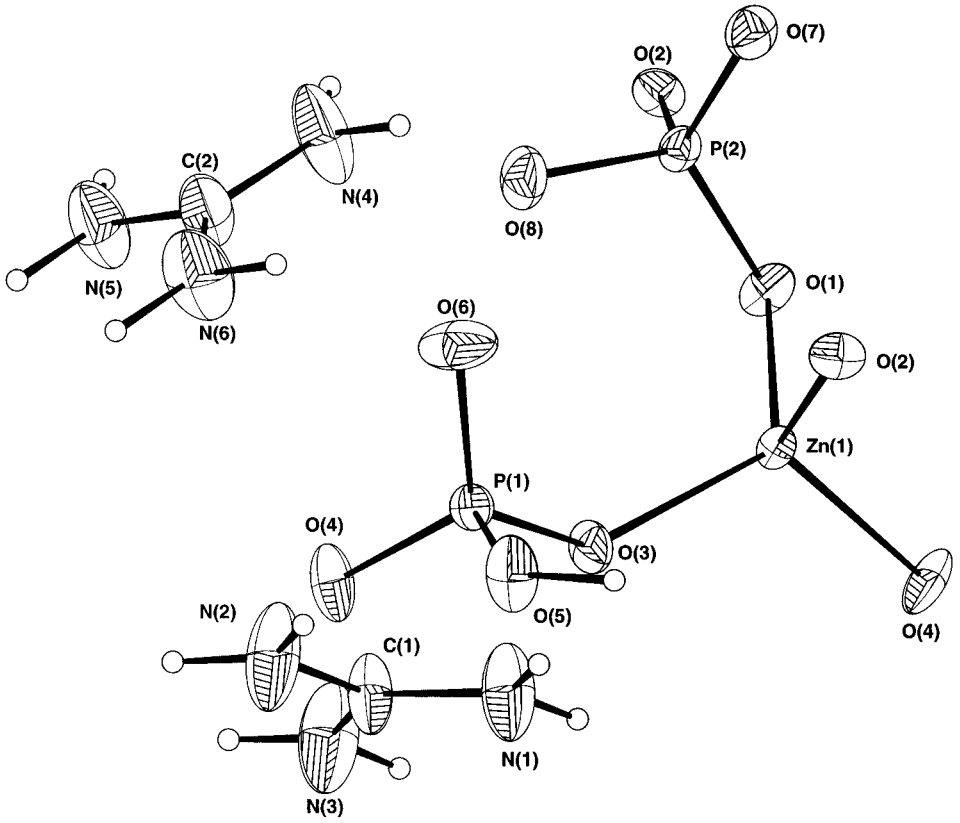

Figure 4. View of a fragment of the $(CN_3H_6)_2 \cdot Zn(HPO_4)_2$ crystal structure showing the atom-labeling scheme (50% thermal ellipsoids; protons represented by spheres of arbitrary radius).

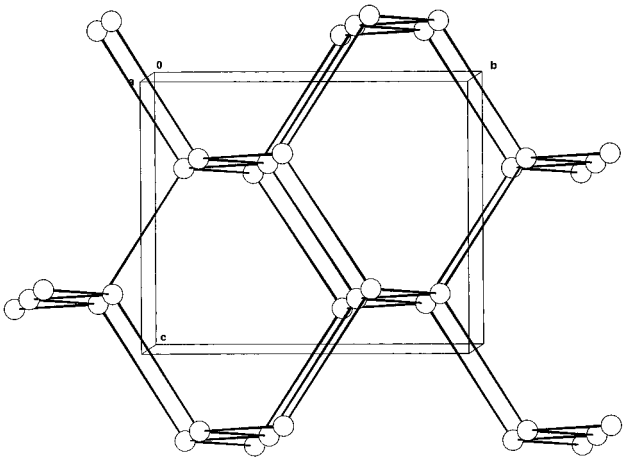

Figure 5. Skeletal representation, viewed approximately down [100], of the ZnPO framework connectivity in $(CN_3H_6)_2 \cdot Zn(HPO_4)_2$, showing the 12-ring channels (see text). In this diagram, plain spheres represent Zn atoms, with lines showing their topological connectivity. Note that these lines represent intervening HPO_4 groups and not simply intervening O atoms. Thus, a "six-ring"of Zn atoms corresponds to a 12-ring of tetrahedral nodes (6 Zn and 6 P), or 24 atoms (6 Zn, 6 P, 12 O) in total.

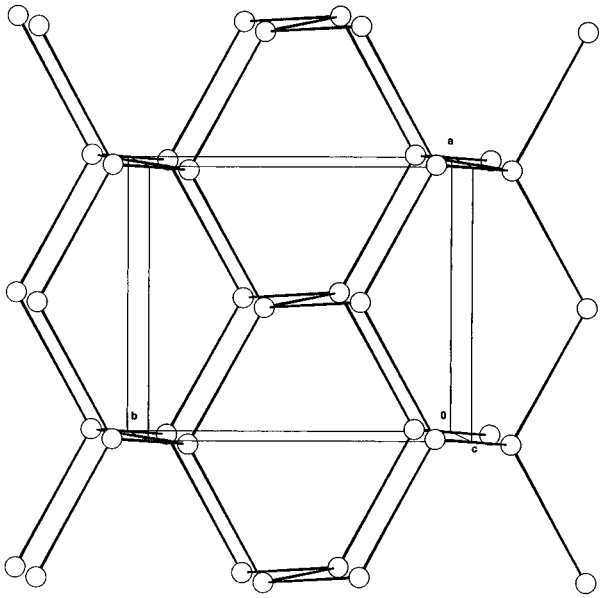

Figure 6. Skeletal view approximately down [001] of the second 12-ring channel system in $(CN_3H_6)_2 \cdot Zn(HPO_4)_2$ (compare Figure 5).

[via O(1) and O(2)] and two terminal P−O bonds. These short (d < 1.52 Å) terminal bonds to O(3) and O(4) indicate that they are not protonated, i.e., this is a simple phosphate group. There are no P−O−P bonds in this structure. The skeletal stoichiometry of $Zn_2P_3O_{13}$ in $(CN_3H_6)_6 \cdot Zn_2(OH)(PO_4)_3 \cdot H_2O$ has a charge of −7; six guanidinium cations are present, thus one skeletal proton is required, which we suggest is located on the inter-zinc bridging oxygen atom, i.e., a bridging hydroxide group. Crystal symmetry dictates the presence of two of these OH groups per asymmetric unit.

The Zn/P/O connectivity in $(CN_3H_6)_6 \cdot Zn_2(OH)(PO_4)_3 \cdot H_2O$ results in infinite chains propagating along the *c* direction. A structural *motif* in which two zinc-centered tetrahedra are bridged by *three* phosphate groups is apparent (Figure 8), which, so far as we are aware, has not been previously observed in simple "inorganic" phosphate-containing chains constructed from tetrahedral building units. These triply bridged units are linked together via hydroxide groups, resulting

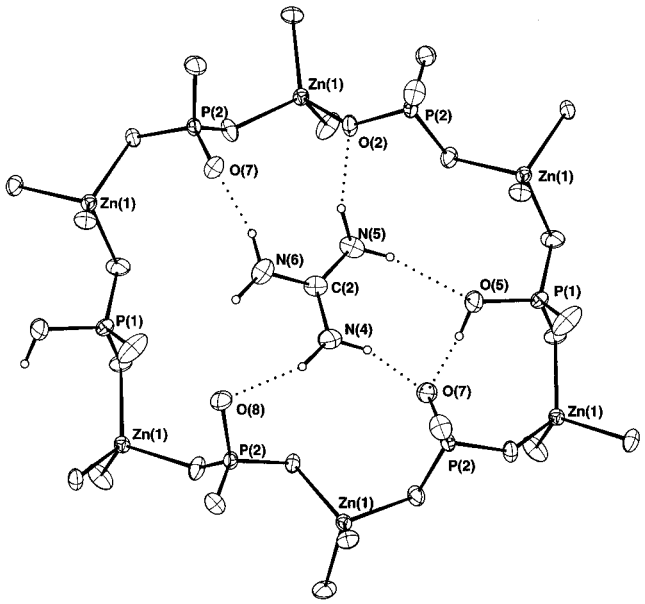

Figure 7. Detail of the $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ structure showing the templating effect of the C(2)-centered guanidinium cation in occupying a framework tetrahedral 12-ring. Possible hydrogen bonding links are indicated by dotted lines. Note the intraframework H bond.

Table 7. Final Atomic Coordinates/Thermal Factors for $(CN_3H_6)_6{\cdot}Zn_2((OH)(PO_4)_3{\cdot}H_2O$

atom	*x*	*y*	*z*	U_{eq}[a]
Zn(1)	0	0	0.3651(2)	0.0175
Zn(2)	0	0	0.1350(2)	0.0180
P(1)	−0.1043(3)	0.0541(3)	0.2499(3)	0.0236
O(1)	0.1060(6)	0.0733(6)	0.1587(8)	0.0359
O(2)	−0.0766(6)	0.0276(6)	0.3377(8)	0.0365
O(3)	−0.1915(6)	0.0097(6)	0.2465(7)	0.0278
O(4)	−0.0725(6)	0.1400(6)	0.2542(7)	0.0311
O(5)	0	0	0	0.09(1)[b]
O(6)	0	0	1/2	0.06(1)[b]
O(10)	0.5153(7)	0.4138(7)	0.1120(8)	0.0505
C(1)	0.252(1)	0.046(1)	0.006(2)	0.0272
N(1)	0.1785(8)	0.0211(9)	0.009(1)	0.0244
N(2)	0.2846(8)	0.0392(8)	−0.075(1)	0.0398
N(3)	0.2967(8)	0.0763(8)	0.084(1)	0.0275
C(2)	0.476(1)	0.086(1)	−0.168(2)	0.0341
N(4)	0.4542(8)	0.0539(8)	−0.079(1)	0.0388
N(5)	0.4645(8)	0.0379(8)	−0.240(1)	0.0346
N(6)	0.5026(8)	0.1599(9)	−0.180(1)	0.0337

[a] U_{eq} (Å^2) = $^1/_3[U_1 + U_2 + U_3]$. [b] U_{iso} (Å^2).

Table 8. Selected Bond Distances (Å) and Angles (deg) for $(CN_3H_6)_6{\cdot}Zn_2((OH)(PO_4)_3{\cdot}H_2O$

Zn(1)−O(2) × 3	1.91(1)	Zn(1)−O(6)	1.883(3)
Zn(2)−O(1) × 3	1.91(1)	Zn(2)−O(5)	1.884(3)
P(1)−O(1)	1.57(1)	P(1)−O(2)	1.54(1)
P(1)−O(3)	1.51(1)	P(1)−O(4)	1.51(1)
C(1)−N(1)	1.30(2)	C(1)−N(2)	1.34(2)
C(1)−N(3)	1.34(2)	C(2)−N(4)	1.36(2)
C(2)−N(5)	1.33(2)	C(2)−N(6)	1.31(2)
O(2)−Zn(1)−O(2)	116.1(2)	O(2)−Zn(1)−O(6)	101.5(3)
O(1)−Zn(2)−O(1)	117.1(2)	O(1)−Zn(2)−O(5)	100.0(3)
O(1)−P(1)−O(2)	106.9(6)	O(1)−P(1)−O(3)	108.2(7)
O(2)−P(1)−O(3)	109.3(6)	O(1)−P(1)−O(4)	110.1(6)
O(2)−P(1)−O(4)	110.0(6)	O(3)−P(1)−O(4)	112.2(6)
Zn(2)−O(1)−P(1)	135.3(7)	Zn(1)−O(2)−P(1)	137.4(7)
Zn(2)−O(5)−Zn(2)	180	Zn(1)−O(6)−Zn(1)	180

in 180° Zn−O−Zn bond angles, as modeled in the crystal structure refinement which is constrained by the 3-fold symmetry of the Zn−O−Zn axis. As with the case of aluminosilicates, this linear intertetrahedral bond configuration is considered to be energetically unfavorable[30] and the real situation almost certainly involves a reduction in the bond angle by the bending of the Zn−O−Zn bond away from the 3-fold axis. This is supported by the fact that anisotropic refinement of the bridging atoms O(5) and O(6) resulted in nonpositive definite thermal factors, indicative of a "smearing" of scattering density around the 3-fold axis. Attempts to model this effect by shifting the bridging O atoms to partially occupied sites around the 3-fold axis led to unstable refinements, perhaps due to the limitations of the data set for this material, as noted above.

The guanidinium cations interact with the $[Zn_2(OH)(PO_4)_3]^{6-}$ chains through a complex network of H-bonds (Figure 9), involving both terminal P−O and bridging Zn−O−P oxygen atom species as acceptors. One of the two crystallographically distinct guanidinium cations [central carbon atom C(1)] serves to cross-link adjacent zincophosphate chains; the other [carbon atom C(2)] makes links to one chain and also interacts with the extraframework water molecule. Both guanidinium cations make five N−H···O hydrogen bonding interactions, with hydrogen−oxygen contact distances ranging from ∼1.90 to 2.20 Å.

Discussion

Three new guanidinium zinc phosphate phases, $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, and $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$, have been prepared as single crystals by a simple synthetic procedure and characterized by single-crystal diffraction methods. They are built up from the expected tetrahedral building blocks of ZnO_4 and PO_4 units, sharing vertexes, but the three new structures that result are quite distinct from each other. As is typical of kinetically controlled solvent-mediated reactions, there is no particular correlation between starting composition and the majority solid-phase product stoichiometry.[31]

$CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ consist of three-dimensional networks; Zn−O−P bonds are strongly favored over possible Zn−O−Zn and P−O−P connections, despite the non-1:1 Zn:P framework ratios in these phases. This results in either one or two terminal P−O bonds for the phosphate moieties, some of which are protonated. A plausible scheme for locating the framework P−OH protons was possible on the basis of charge-balancing and geometrical criteria. One may ask why these framework protons arise, as opposed to possible continuous (all O atoms forming Zn−O−P bridges) networks, which are known to be feasible for several open-framework zincophosphates templated by alkali metals.[9] It is possible that a continuous, fully ordered 1:1 Zn:P framework is difficult to achieve in the organically templated materials because of the difficulty of packing enough bulky *organic cations* into the extraframework pores to achieve charge balance. Unlike many aluminosilicates, in which the Si:Al ratio is variable, and affects the charge-balancing requirement, ZnPOs all appear to have a precisely defined Zn:P ratio for a particular structural topology. We note that inclusion of (di)hydrogen phosphate protons reduces the

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(31) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *J. Solid State Chem.* **1996**, *125*, 234.

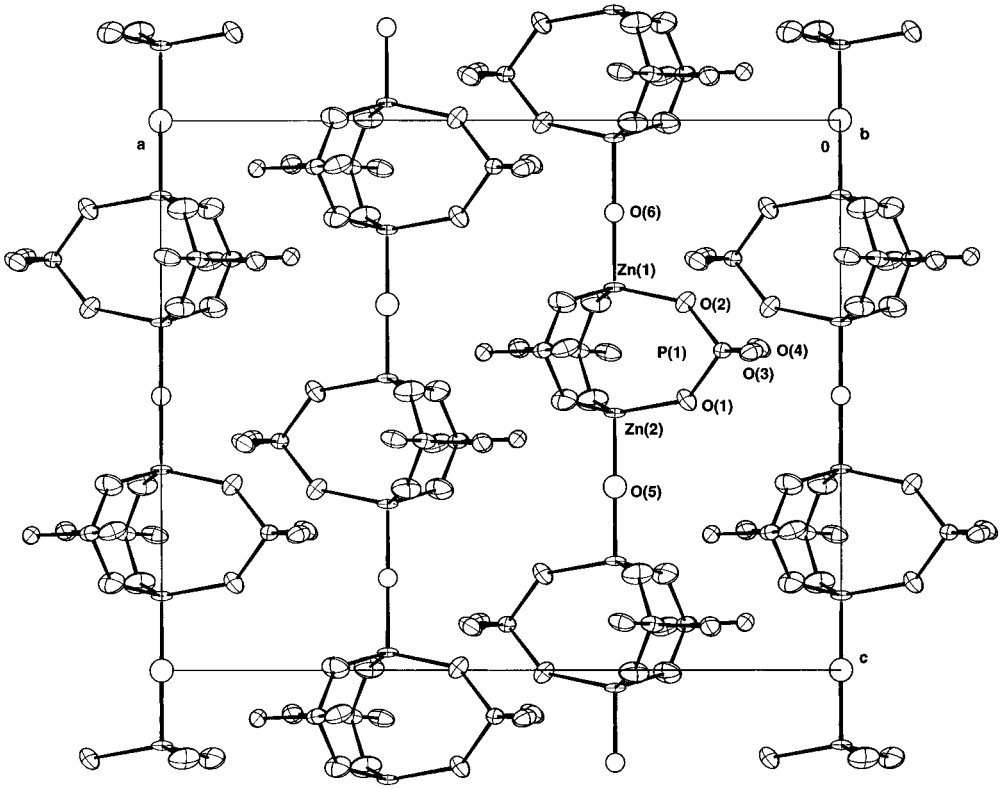

Figure 8. View down [010] of the $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ structure showing isolated, one-dimensional $Zn_2(OH)(PO_4)_3$ columns propagating along [001]. Guanidinuim cations and extraframework water molecules omitted for clarity (50% thermal ellipsoids).

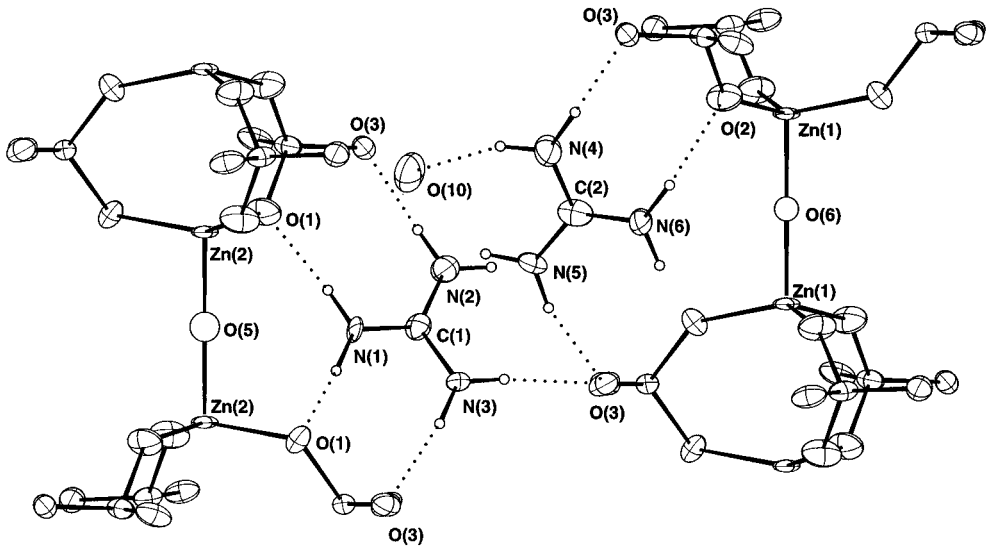

Figure 9. Detail of the $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ structure showing interccolumn hydrogen-bonding connectivity via the guanidinium cations. Note that one guanidinium cation [carbon atom C(2) etc.] also bonds to the extraframework water molecule, O(10).

anionic framework charge density in $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ from −7.52 *e*/1000 Å^3 to −1.51 *e*/1000 Å^3. Continuous-framework zincophosphates templated by metal cations have significantly higher framework charge densities of up to −8 *e*/1000 Å^3, which are essentially the same as those of their aluminosilicate isostructures.

On the basis of the structures of $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ [but not that of $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$], we may tentatively propose a structure-directing effect for the guanidinium cation with respect to zincophosphate networks. This cation appears to preferentially template a tetrahedral 12-ring framework *motif* and adopts a side-on orientation as suggested above and presumably forms longish, but structurally significant N−H···O hydrogen bonding linkages. However, we stress that *intra*framework hydrogen bonds, and the constraints imposed by the fixed Zn:P ratio in terms of preference for Zn−O−P and avoidance of Zn−O−Zn and P−O−P bonds are also clearly important in determining the three-dimensional frameworks of these materials. This distantly relates to Löwenstein's rule for the avoidance of Al−O−Al linkages in aluminosilicates,[32] but the similarity should not be overstressed, because zincophosphates never show any long-range Zn/P site mixing akin to Al/Si

(32) Löwenstein, W. *Am. Miner.* **1954**, *39*, 92.

disorder commonly observed in aluminosilicates. Thus, the *local* templating effect of the guanidinium cation cannot be simply correlated with the resulting overall crystal structures. In the novel phase $(CN_3H_6)_3{\cdot}Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$ the guandinium cations also template 12-rings via structurally important N−H···O hydrogen-bonding linkages, but also show a remarkable "cooperative" effect to result in a group of three $CN_3H_6^+$ cations templating an 18-ring cavity in "side-by-side" configuration.[20]

A useful parameter for quantifying the "openness" of molecular sieve structures is the framework density (FD)—the number of framework tetrahedral (*T*) atoms (here: Zn and P) per unit volume.[33] For $CN_3H_6{\cdot}Zn_2(HPO_4)_2H_2PO_4$, a FD value of 15.1 *T*-atoms/1000 Å^3 results, which is in the middle of the range of FD values observed for aluminosilicate zeolites.[34] Conversely, $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ has a remarkably low FD value of 9.10 *T*-atoms/1000 Å^3, which appears to be the lowest FD value yet observed for a microporous material. Comparable FD values of 12.7 *T*-atoms/1000 Å^3 for aluminosilicate faujasite, and 11.1 *T*-atoms/1000 Å^3 for the interrupted tetrahedral gallofluorophosphate framework in cloverite result.[34] $Cs_3[V_5O_9(PO_4)_2]{\cdot}xH_2O$, which contains a remarkable "diamond"-like 3-dimensional array of spheroidal 32-ring cavities[8] has a FD value of ∼9.3 nodal atoms/1000 Å^3 (square-pyramidal V atoms, tetrahedral P atoms). Another way to quantify the openness of these types of materials is to calculate the fraction of the unit cell volume *not* occupied by the framework (Zn, P, and O) atoms, assuming typical van der Waals' radii for these species. The CALC SOLV option (default settings) of the program PLATON97[35] indicated that 723 Å^3 (55% of the unit-cell volume) could be considered as "solvent accessible" in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$, when the C, N, and H atoms of the guanidinium cations were ignored. However, only 38 Å^3 (3% of the unit-cell volume) remained unoccupied when the guanidinium cations were included in the calculation.

The 1:2 Zn:P ratio found in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ appears to be a fruitful one for construction of ultralow-framework atom density networks. The novel phase $N(CH_3)_4{\cdot}ZnH_3(PO_4)_2$ adopts a different all-12-ring topology to that of $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ and has a resulting FD of ∼10.1.[36] Interestingly, the guanidinium zinc sulfate, $(CN_3H_6)_2{\cdot}Zn(SO_4)_2$,[37] reported a number of years ago, contains an open-framework zincosulfate network (1:2 Zn:S ratio) enclosing 12-ring channels occupied by guanidinium cations.

$(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ adopts a "polymeric" one-dimensional structure involving three PO_4 groups triply bridging pairs of distorted Zn-centered tetrahedra. Various zinc (and other divalent metal) *phosphonates* with bulky/long-chain organic substituents such as $Zn[PO_2(n\text{-}C_4H_9)_2PO_2(n\text{-}C_6H_{13})_2]$ adopt a similar triply bridged tetrahedral chain *motif* and were structurally characterized many years ago.[38] $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ appears to be the first simple *phosphate* to adopt this polymeric configuration, further adding to the variety of novel one-dimensional zincophosphate chain structures.[39] We note that $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ is quite distinct from $Zn[PO_2(n\text{-}C_4H_9)_2PO_2(n\text{-}C_6H_{13})_2]$ in the polymeric linking of the triply bridged tetrahedral units: in $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ the $[OZn(PO_4)_3ZnO]$ units are fused directly together, whereas in $Zn[PO_2(n\text{-}C_4H_9)_2PO_2(n\text{-}C_6H_{13})_2]$, an intermediate phosphonate group joins the nominally equivalent $[OZn(PO_2R_2)_3ZnO]$ units into a contorted polymeric strand. This also results in different Zn:P ratios for the phosphonates (Zn:P = 1:2) and phosphate (Zn:P = 2:3). It is notable that the Zn−(OH)−Zn linkage involves a hydroxide bridge in $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$. In $Na_2ZnPO_4OH{\cdot}7H_2O$, which is built from a unique chain topology of vertex-sharing tetrahedral three-rings, a Zn−(OH)−Zn bridging link is also observed.[39] Any "templating" or structure-directing effect of the guanidinium cation is much harder to quantify in the $(CN_3H_6)_6{\cdot}Zn_2(OH)(PO_4)_3{\cdot}H_2O$ structure although its hydrogen-bonding links, which cross-link adjacent $[Zn_2(OH)(PO_4)_3]^{6-}$ chains are broadly similar in nature to those observed in the other guanidinium zinc phosphates reported here. Conceivably, this phase adopts a one-dimensional structure because its skeletal charge density of −8.67 *e*/1000 Å^3 (protons omitted) is too high to allow the formation of a viable three-dimensional network with sufficient empty space to accommodate the necessary number of guanidinium species for charge balancing.

Supporting Information Available: Tables of calculated atom positions and anisotropic thermal factors (6 pages); observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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