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$(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, a New Layered Guanidinium Zinc Phosphate Built Up from 3-, 4-, and 8-Ring Units

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The solution-mediated synthesis and single crystal structure of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, a new guanidinium zinc phosphate, are described. The use of high-intensity synchrotron radiation was necessary to determine the correct unit cell for this phase. Unlike the previously described one-dimensional or three-dimensional guanidinium zinc phosphates, this material has a strongly layered nature. Vertex-linked ZnO_4, HPO_4, and H_2PO_4 building units self-assemble into complex sheets containing polyhedral 3-rings, 4-rings, and 8-rings. The intersheet guanidinium cations provide charge compensation and interact with the layers via N–H···O hydrogen bonds. Crystal data: $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, $M_r = 861.57$, monoclinic, space group $I2/a$ (No. 15), $a = 23.770$ (2) Å, $b = 5.1036$ (5) Å, $c = 18.100$ (2) Å, $\beta = 94.491$ (2)°, $V = 2189.0$ (5) Å^3, $Z = 4$, $R(F) = 0.047$, $R_w(F^2) = 0.121$ (2322 reflections, 168 parameters). © 1999 Academic Press

INTRODUCTION

A substantial variety of zincophosphates (ZnPOs) built up from vertex-linked ZnO_4 and PO_4 tetrahedra in combination with organic templating cations have been characterized by diffraction methods (1). The inorganic, Zn/P/O/H components of these crystal structures display interesting features such as tetrahedral 3-rings (2) and infinite chains of –Zn–O–Zn–O– bonds (3). The organic cation has a strong structure-directing effect, but it is difficult to control or even to predict the structural features of the resulting ZnPO phases (4). "Zero-dimensional" (i.e., a discrete cluster), chain, layer, and three-dimensional networks have all been observed for the Zn/P/O component of these phases.

Here, we report the solution-mediated synthesis and synchrotron single-crystal structure of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, a new guanidinium zinc phosphate which has a strongly layered (two-dimensional) nature when Zn/P/O bonding is considered. It complements the one-dimensional phase $(CN_3H_6)_6 \cdot Zn_2(OH)(PO_4)_3 \cdot H_2O$ (5) and the three-dimensional phases $CN_3H_6 \cdot Zn_2(HPO_4)_2(H_2PO_4)$ (5), $(CN_3H_6)_2 \cdot Zn(HPO_4)_2$ (5), and $(CN_3H_6)_3 \cdot Zn_7(H_2O)_4(PO_4)_6 \cdot H_3O$ (6) reported earlier.

EXPERIMENTAL

Synthesis and Characterization

First, 0.90 g (5 mmol) guanidinium carbonate $[(CN_3H_6)_2CO_3]$, 2.29 g (20 mmol) 85% phosphoric acid, and 9.92 g deionized water were mixed in a 100-ml PTFE bottle. Then, 10 mmol St Joseph's zinc oxide (0.814 g) was added, and the mixture was shaken well and allowed to stand at room temperature for 1 day prior to being heated to 100°C for 5 days. Upon cooling, 2.09 g (97% yield based on Zn) of transparent needles (maximum linear dimension ~1 cm) of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ was recovered by vacuum filtration and washing with cold water. Elemental analysis data (Galbraith Laboratories) were as follows: C calc 2.79%, obs 2.40%; N calc 9.75%, obs 8.57%; H calc 1.99%, obs 1.40%. The product appears to be completely stable when stored in dry air. Thermogravimetric analysis (TGA) data for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ were collected on an STA 1500 instrument (ramp at 10°C/min in air).

Laboratory Single Crystal Structure Study

The initial diffraction experiment used a transparent needle ($\sim 0.3 \times 0.02 \times 0.02$ mm) of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ which was mounted on a thin glass fiber with cyanoacrylate adhesive. Many crystals displaying split/composite peaks were rejected before a satisfactory crystal was found. Room-temperature [25 ± 2°C] intensity data were collected on a Siemens P4 automated four-circle diffractometer (graphite-monochromated Mo*Kα* radiation, $\lambda = 0.71073$ Å). The routine application of peak-search, centering, indexing, and least-squares refinement routines led to a *C*-centered

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monoclinic unit cell with $a = 18.217\,(4)$ Å, $b = 5.1361\,(9)$ Å, $c = 11.972\,(3)$ Å, and $\beta = 94.84\,(2)^\circ$ [$V = 1116.2\,(5)$ Å^3]. Intensity data were collected based on this cell using protocols described earlier (7). After data reduction and merging, approximate positional parameters for the Zn, P, and some O atoms were located by direct methods in space group *Cc* (No. 9). A chemically plausible structure was established after further atoms were located from difference maps. However, residuals were high ($R > 0.1$), geometrical parameters were unrealistic, and anisotropic thermal factors could not be successfully refined.

Synchrotron Single Crystal Study

A second crystal of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ (transparent needle, $0.20 \times 0.05 \times 0.03$ mm) was examined by synchrotron X-ray diffraction methods ($\lambda = 0.6874$ Å as selected by a Si(111) monochromator, $T = 160\,(2)$ K, Siemens SMART CCD area detector diffractometer) at SRS beam-line station 9.8 at Daresbury Laboratory, UK (8, 9). Preliminary scans clearly indicated a body-centered monoclinic unit cell (Table 1) with twice the volume of the cell determined in the laboratory experiment. Data were collected in narrow-slice ω-scan mode (10), resulting in 5333 measured intensities ($-31 \le h \le 12, -6 \le k \le 6, -22 \le l \le 22$) for $3.3^\circ \le 2\theta \le 53.5^\circ$. Data merging resulted in 2322 unique reflections ($R_{\text{Int}} = 0.044$) of which 2112 were considered observed according to the criterion $F > 4\sigma(F)$. Absorption and incident beam decay corrections were applied on the basis of multiple and symmetry-equivalent reflections (11), with a resulting correction factor range of 0.447–0.869. X-ray scattering factors appropriate to the incident wavelength used were taken from Ref. (12). The systematic absences ($hkl, h + k + l$; $h0l, h, l$; $0k0, k$) were consistent with space groups *Ia* and *I*2/*a*, with intensity statistics favoring the latter choice. The initial atomic model was established by direct methods (13) in space group *I*2/*a* (nonstandard setting of *C*2/*c* No. 15), which was assumed for the remainder of the crystal structure analysis. The remaining non-hydrogen atoms were located from difference maps. H atoms associated with the guanidinium cation were located geometrically (d(N–H) = 0.88 Å) and refined (14) by riding on their appropriate N atoms. Framework protons associated with the Zn/P/O component of the structure were not located (*vide infra*). Crystallographic data are summarized in Table 1. Supplementary tables of hydrogen atom coordinates, anisotropic thermal factors, and observed and calculated structure factors are available from the authors.

TABLE 1
Crystallographic Parameters for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$

Empirical formula	$Zn_4P_5O_{20}N_6C_2H_{17}$
Formula weight	861.57
Crystal system	monoclinic
a (Å)	23.770(2)
b (Å)	5.1036(5)
c (Å)	18.100(2)
β (°)	94.491(2)
V (Å^3)	2189.0(5)
Z	4
Space group	*I*2/*a* (No. 15)
T (K)	160(2)
Radiation	synchrotron X-rays
λ (Å)	0.6874
ρ_{calc} (g/cm^3)	2.614
μ (cm^{-1})	49.1
Total data	5333
Merged data	2322
Parameters	168
min., max. $\Delta\rho$ (e/Å^3)	-1.55, $+1.53$
$R(F)$	0.045^a, 0.046^b
$wR(F^2)$	0.121^{b,c}
S (goodness of fit)	1.03

[a] 2113 reflections with $F > 4\sigma\,(F)$.
[b] All data.
[c] $w_i = 1/[\sigma^2(F_o^2) + (0.0884P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

RESULTS

Crystal Structure

Final atomic positional and thermal parameters for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ are listed in Table 2, and selected bond distance/angle data in Table 3. This phase is a new guanidinium zincophosphate with strong two-dimensional character based on sheets of ZnO_4, HPO_4, and H_2PO_4 tetrahedra fused together via Zn–O–P bonds. An ORTEP-3 (15) view of the asymmetric unit of $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ is shown in Fig. 1, and the complete crystal structure in Fig. 2.

There are 19 distinct nonhydrogen atoms in $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, all of which occupy general positions in the unit cell, except for P3 which has 2-fold symmetry. The two distinct zinc atoms adopt tetrahedral coordination with typical (1, 2) geometrical parameters of d_{av}(Zn1–O) = 1.947 (2) Å and d_{av}(Zn2–O) = 1.929 (2) Å. Both zinc atoms make four Zn–O–P linkages to nearby phosphorus atoms; in addition Zn1 bonds to two of the three-coordinate O5 species, hence forming an infinite –O5–Zn1–O5–Zn1–O5– chain. The three distinct P atoms form the centers of tetrahedral (di)hydrogen phosphate groups with d_{av}(P1–O) = 1.533 (2) Å, d_{av}(P2–O) = 1.533 (2) Å, and d_{av}(P3–O) = 1.529 (3) Å. P1 forms three P–O–Zn links and possesses one terminal P–O bond. P2 forms two P–O–Zn links, one terminal P–O bond, and one bond via O5 to a pair of Zn atoms. P3 forms two P–O–Zn links and two terminal P–O bonds.

The 10 distinct oxygen atoms in $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ divide into six Zn–O–P bridges [$\theta_{\text{av}} = 133.6^\circ$], three terminal P–O or P–OH links, and the three-coordinate (to two

TABLE 2
Atomic Coordinates/Thermal Factors for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$

Atom	x	y	z	U_{eq}
Zn1	0.459041(16)	0.47956(8)	0.21686(2)	0.00790(17)
Zn2	0.336328(16)	0.06733(8)	0.12399(2)	0.00823(17)
P1	0.32616(4)	0.55430(17)	0.21935(5)	0.0077(2)
P2	0.46973(4)	0.00250(17)	0.12440(5)	0.0073(2)
P3	0.25	− 0.1939(3)	0	0.0099(3)
O1	0.38407(11)	0.4687(5)	0.24948(13)	0.0122(5)
O2	0.30569(10)	0.4093(5)	0.14893(13)	0.0116(5)
O3	0.31981(10)	0.8511(5)	0.20801(12)	0.0107(5)
O4	0.28842(11)	0.4768(5)	0.28364(14)	0.0126(6)
O5	0.49358(10)	0.1371(5)	0.19849(12)	0.0095(5)
O6	0.41284(10)	0.1321(5)	0.10385(13)	0.0128(5)
O7	0.50973(11)	0.0683(5)	0.06512(14)	0.0115(5)
O8	0.46550(11)	− 0.2892(5)	0.13597(13)	0.0143(5)
O9	0.29936(12)	− 0.0351(5)	0.03145(14)	0.0154(6)
O10	0.22621(10)	− 0.3692(6)	0.06065(14)	0.0191(6)
C1	0.60653(14)	0.5983(8)	0.08304(19)	0.0131(7)
N1	0.63694(12)	0.8140(7)	0.08380(17)	0.0164(7)
N2	0.60167(15)	0.4693(7)	0.14687(19)	0.0197(7)
N3	0.58099(14)	0.5068(6)	0.02197(18)	0.0182(7)

Zn1 and one P2) O5 species. The Zn–O–P bond angles around this atom are much smaller than those of the simple Zn–O–P bridges. The grouping of O5, P2, and 2 × Zn1 is planar to within 0.1 Å. The "overbonded" situation of O5 is probably responsible for its rather long bonds to Zn and P, although its bond valence, calculated by the Brown formalism (16), of 2.07 (expected 2.00) is satisfied by this geometry. The C–N geometrical parameters of the guanidinium cation are in good accord with those seen in related structures (5).

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$

Zn1–O1	1.922(2)		Zn1–O5	1.970(3)
Zn1–O5	1.998(2)		Zn1–O8	1.896(2)
Zn2–O2	1.957(2)		Zn2–O3	1.944(2)
Zn2–O6	1.911(2)		Zn2–O9	1.903(3)
P1–O1	1.505(3)		P1–O2	1.521(2)
P1–O3	1.534(3)		P1–O4	1.574(3)
P2–O5	1.573(2)		P2–O6	1.525(2)
P2–O7	1.526(3)		P2–O8	1.508(3)
P3–O9	1.501(3)		P3–O10	1.556(3)
C1–N1	1.316(5)		C1–N2	1.343(5)
C1–N3	1.305(5)			
P1–O1–Zn1	136.4(2)		P1–O2–Zn2	121.8(2)
P1–O3–Zn2	129.9(2)		P2–O5–Zn1	113.8(2)
P2–O5–Zn1	128.5(2)		Zn1–O5–Zn1	116.4(2)
P2–O6–Zn2	135.8(2)		P2–O8–Zn1	137.1(2)
P3–O9–Zn2	140.9(2)			
N1–H11 ··· O9[a]	0.88	2.15	2.900(4)	143.60
N1–H12 ··· O4[a]	0.88	2.13	2.988(4)	166.49
N3–H31 ··· O6[a]	0.88	2.08	2.942(4)	165.65
N3–H32 ··· O7[a]	0.88	2.11	2.949(4)	158.84

[a] For the hydrogen bonds, the four values correspond to the N–H, H ··· O, N ··· O separations and the N–H ··· O bond angle, respectively.

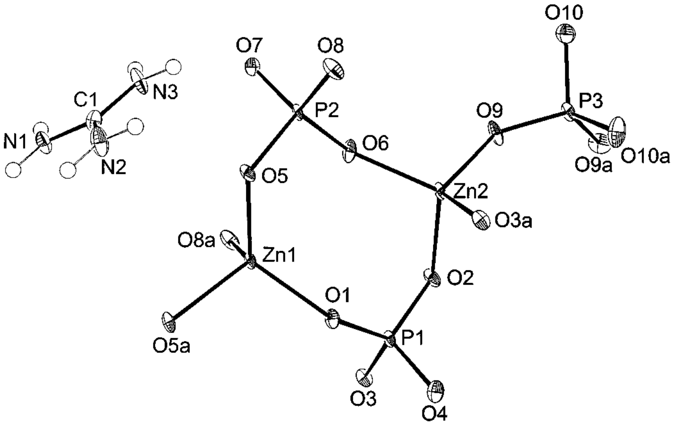

FIG. 1. Fragment of the $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ crystal structure (50% thermal ellipsoids) showing the atom labeling scheme. Symmetry related atoms are indicated by, e.g., O3a.

Assuming that the organic species is present in this phase as the protonated guanidinium cation rather than an unprecedented neutral guanidine molecule, then five "framework" protons (1) are required for charge-balancing purposes. We assume that these atoms are located on some of the terminal P–O vertices, as found for similar phases. Bond length/bond strength considerations (16) suggest that the long P1–O4 and P3–O10 bonds are parts of P–OH groups. This accounts for four protons, i.e., two $HP1O_4$ groups and one H_2P3O_4 group per $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ formula unit. The fifth proton may be associated with the remaining terminal P2–O7 bond. This bond is significantly shorter than the P1–O4 and P3–O10 bonds (Table 3), which might indicate a 50 : 50 random array of protonated (P2–O7H) and unprotonated (P2–O7) bonds. This is exactly consistent with the charge balancing requirement. We note that a possible acceptor atom for a hydrogen bond is another O7 species, i.e., a disordered array of P2–O7–H ··· O7′–P2′ and P2–O7 ··· H–O7′–P2′ bonds or even a symmetrical P2–O7 ··· H ··· O7′–P2′ bond might be present. Based on these proposals, a possible structural formula for the title compound is $(CN_3H_6)_2 \cdot Zn_4(PO_4)(HPO_4)_3(H_2PO_4)$.

The polyhedral connectivity in $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ results in a layered topology based on a complex network of polyhedral 3-rings, 4-rings, and 8-rings (Fig. 3). This network is built up from a backbone of edge-sharing 3-rings (one P2 and two Zn1 nodes), which propagates along [010]. One each side of a 3-ring backbone are 4-rings, formed from Zn1, P2, Zn2, and P1 nodes. The trigonally coordinated O5 is involved in both these rings. Finally, the P3 atoms link the

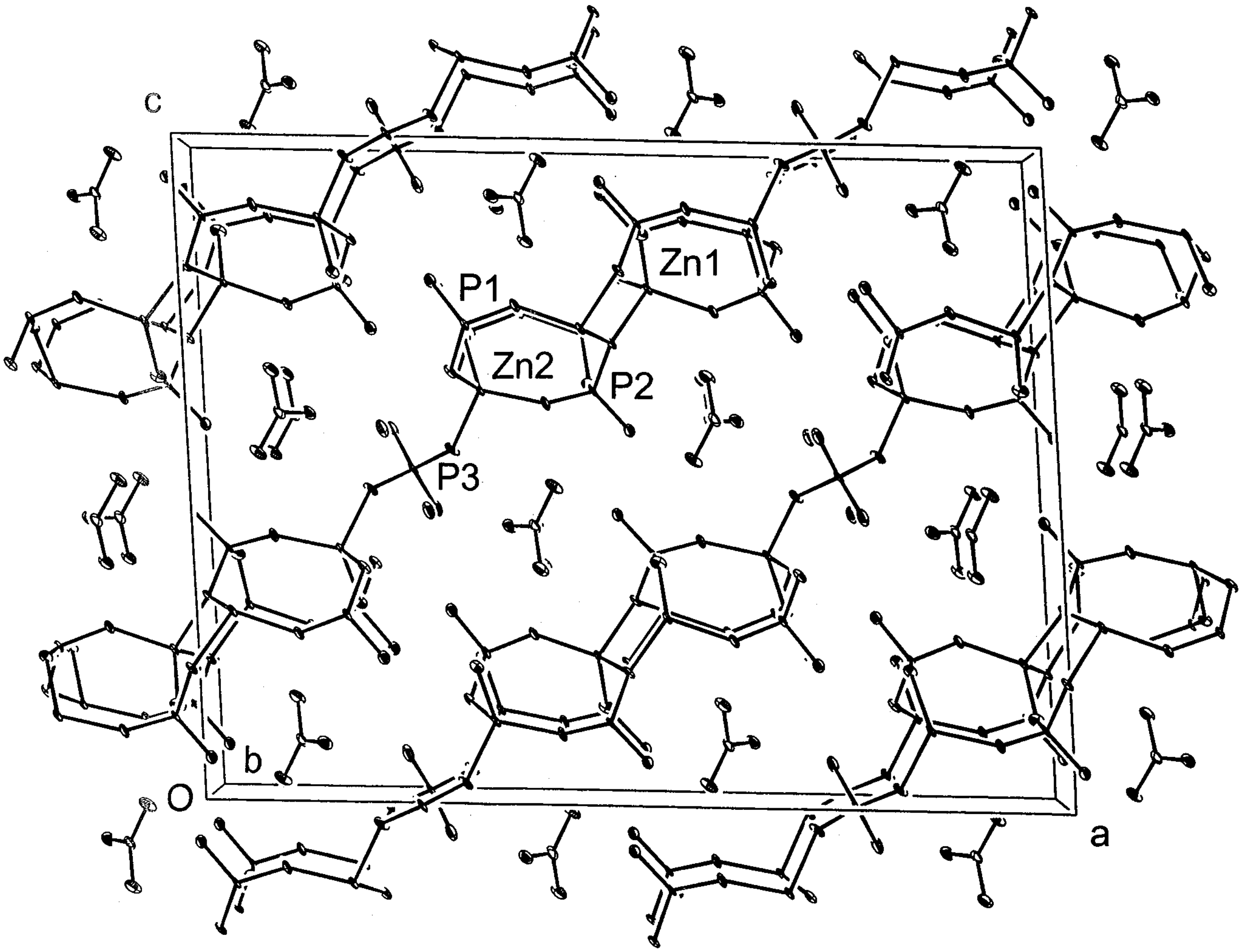

FIG. 2. View down [010] of the $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ crystal structure with hydrogen atoms omitted for clarity.

3-ring/4-ring columns into infinite sheets, by forming 8-ring windows (nodes {Zn2, P1, Zn2, P3} × 2). The pendant P3–O10H groups all point in the same direction in a particular sheet; the orientation of these groups alternates from sheet to sheet. Overall, the anionic $[Zn_4H_5(PO_4)_5]^-$ sheets are aligned normal to $[\bar{1}01]$. There are probably intralayer, and possibly interlayer, hydrogen bonds of the form P–OH ··· O as observed in many other organo-zincophosphates (1).

The guanidinium cations occupy interlayer sites and bond to both of the adjacent zincophosphate layers through N–H ··· O hydrogen bonds (Fig. 4, Table 3). The acceptor O atoms are variously parts of Zn–O–P and P–OH bonds.

Physical Data

TGA for $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ showed a 20.5% weight loss occurring over the broad temperature range 240–650°C. This loss is in good agreement with a scheme involving the loss of all the C, N, and H and $3\frac{1}{2}$ O from $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ to result in a residue of nominal formula "$Zn_4P_5O_{16.5}$" (calculated weight loss = 21%). DTA showed a strong endotherm at ~350°C and an exotherm at ~600°C.

DISCUSSION

A new guanidinium zinc phosphate, $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$, has been prepared as single crystals by a typical mild hydrothermal reaction and has been structurally characterized by synchrotron X-ray diffraction methods. We believe that $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ is the first organo-zincophosphate phase to contain Zn and P in a 4:5 ratio. It consists of the expected polyhedral units of ZnO_4 and $(H_2/H)PO_4$ tetrahedra, sharing vertices. The presence of trigonally coordinated oxygen atoms leads to infinite chains of –O–Zn–O–Zn–O– bonds and edge-sharing

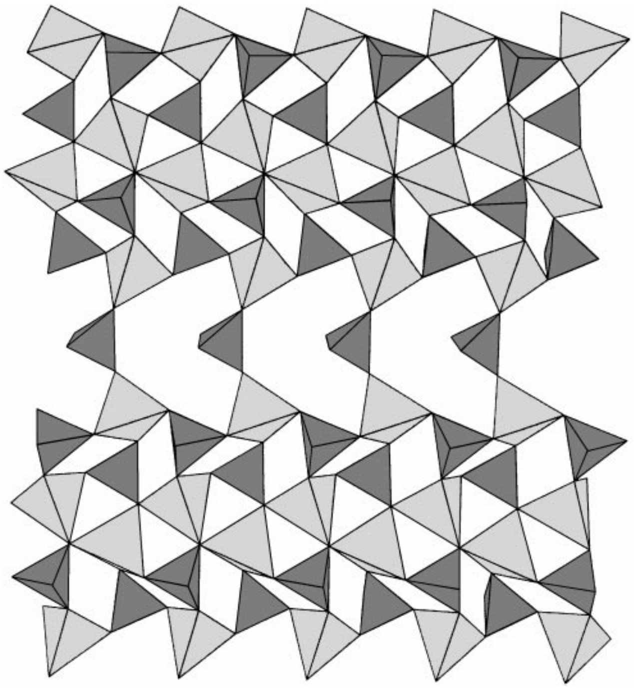

FIG. 3. Polyhedral plot of a zincophosphate layer in $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ showing the connectivity of ZnO_4 (light) and PO_4 (dark) tetrahedra to result in 3-, 4-, and 8-rings, as described in the text.

tetrahedral 3-rings, similar to the situation observed for the three-dimensional phases $NH(CH_3)_3 \cdot Zn_4(H_2O)(PO_4)_3$ and $Zn_4H(PO_4)_3 \cdot H_2O$ (3). The recently described $H_3N(CH_2)_2NH(CH_2)_2NH_3 \cdot [Zn_2(PO_4)(HPO_4)]_2$ (17) also contains –O–Zn–O–Zn–O– chains and tetrahedral 3-rings as part of its layered crystal structure. This type of tetrahedral connectivity is not the sole preserve of zincophosphates: For example, the pseudo-layered phases $Be_3(PO_4)_2 \cdot 2H_2O$ (18) and $Be_3(AsO_4)_2 \cdot 2H_2O$ (19) contain trigonally coordinated O atoms leading to inifinte –O–Be–O–Be–O– chains and 3-ring (2 Be + 1 P/As nodes) groupings.

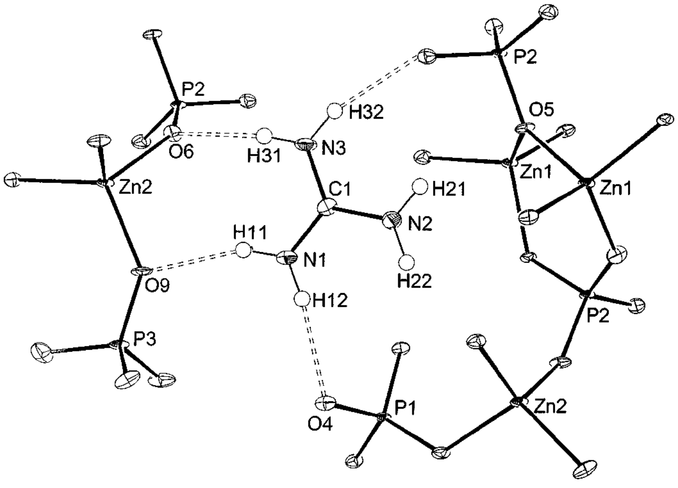

FIG 4. Detail of the $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ structure showing the interaction of a guanidinium cation with adjacent zincophosphate layers by N–H $\cdots$ O hydrogen bonds (dotted lines).

Overall, $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ bears little structural resemblance to the other guanidinium zincophosphate phases reported recently (5, 6). Although the templating effect of the essentially rigid guanidinium cation by way of N–H $\cdots$ O hydrogen bonding is clearly of great importance in stabilizing these types of materials, other features such as the Zn:P ratio and presence of P–OH groups are equally significant in establishing the overall structures. We are still some way from controlling and predicting the synthesis and structures of phases such as $(CN_3H_6)_2 \cdot Zn_4H_5(PO_4)_5$ at the present time.

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