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Pseudopyramidal Building Units in Mixed Inorganic/Organic Network Solids: Syntheses, Structures, and Properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$

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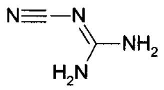
The syntheses, crystal structures, and some properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$ are reported. These polymorphic phases are the first organically templated hydrogen phosphites. They are built up from vertex-sharing HPO_3 pseudopyramids and ZnO_3N tetrahedra, where the Zn−N bond represents a direct link between zinc and the neutral 2-cyanoguanidine template. α-$ZnHPO_3 \cdot N_4C_2H_4$ is built up from infinite layers of vertex-sharing ZnO_3N and HPO_3 groups forming 4-rings and 8-rings. β-$ZnHPO_3 \cdot N_4C_2H_4$ has strong one-dimensional character, with the polyhedral building units forming 4-ring ladders. Similarities and differences to related zinc phosphates are discussed. Crystal data: α-$ZnHPO_3 \cdot N_4C_2H_4$, monoclinic, $P2_1/c$, $a = 9.7718$ (5) Å, $b = 8.2503$ (4) Å, $c = 9.2491$ (5) Å, $\beta = 104.146$ (1)°, $Z = 4$. β-$ZnHPO_3 \cdot N_4C_2H_4$, monoclinic, $C2/c$, $a = 14.5092$ (9) Å, $b = 10.5464$ (6) Å, $c = 10.3342$ (6) Å, $\beta = 114.290$ (1)°, $Z = 8$.

Introduction

Organically templated inorganic networks now cover a remarkable range of compositions and structures.[1] Conceptually, these phases are often considered to be built up from three components: the templating organic cation, the metallic cation, and an oxo anion, with the latter two moieties forming the inorganic framework. A great deal of attention has been paid to the structure-directing role of the organic species[2] and the structural effect of variously coordinated cations, such as distorted octahedral vanadium[3] and pyramidal tin(II).[4] Much less exploratory work has been carried out on the oxo-anion part of the inorganic network, and most groups reported so far invariably adopt tetrahedral coordination. In particular, the $[PO_4]^{3-}$ phosphate anion is ubiquitous in these materials.[5] The possibilities of incorporating the phosphorus(III)-containing pseudopyramidal $[HPO_3]^{2-}$ hydrogen phosphite group into extended structures templated by inorganic, alkaline earth cations was demonstrated several years ago.[6] In this paper we report the syntheses, crystal structures, and some properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$, two polymorphs of 2-cyanoguanidine (**1**) zinc hydrogen phosphite. Their similarities and differences to related organically templated zinc phosphates[7] are briefly noted.



Experimental Section

Synthesis. A total of 2.52 g (30 mmol) of $C_2N_4H_4$ (2-cyanoguanidine or dicyandiamide, Aldrich), 0.81 g (10 mmol) of ZnO (Spectrum), 1.70 g (20 mmol) of H_3PO_3, 97% (Aesar), and 18.0 g (1 mol) of deionized water were combined in a HDPE bottle. This was shaken well and placed in a 70 °C oven for 3 days, after which the contents were filtered hot. The pH of the mother liquors was 5. The solid product was washed with water and then methanol and dried at 70 °C. The yield was 1.86 g of clumped, intergrown, platy crystals of β-$ZnHPO_3 \cdot N_4C_2H_4$ accompanied by one or two gemlike chunks of α-$ZnHPO_3 \cdot N_4C_2H_4$ and a small amount of ZnO powder. A reflux reaction (∼90 °C for 4 h) of the same starting mixture led to a different, as-yet unidentified, product on the basis of powder diffraction.

The addition of 2.12 g (10 mmol) of $Sr(NO_3)_2$ (Spectrum) to the above reaction mixture consequently treated by the same hydrothermal reaction conditions (final pH 4.0) and workup appeared to completely suppress the formation of β-$ZnHPO_3 \cdot N_4C_2H_4$ and led to 2.60 g of a mixture of large (to 1 mm), faceted, gemlike chunks of α-$ZnHPO_3 \cdot N_4C_2H_4$ and plates of the known strontium zinc hydrogen phosphite phase $SrZn(HPO_3)_2 \cdot 2H_2O$ [6] in roughly 50:50 ratio, based on visual estimation. The distinctive morphologies of the two components allowed for hand sorting of α-$ZnHPO_3 \cdot N_4C_2H_4$ crystals for physical measurements.

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Table 1. Crystallographic Parameters

	α-$ZnHPO_3 \cdot N_4C_2H_4$	β-$ZnHPO_3 \cdot N_4C_2H_4$
empirical formula	$ZnPO_3N_4C_2H_5$	$ZnPO_3N_4C_2H_5$
fw	229.44	229.44
a (Å)	9.7718(5)	14.5092(9)
b (Å)	8.2503(4)	10.5464(6)
c (Å)	9.2491(5)	10.3342(6)
β(°)	104.146(1)	114.290(1)
V (Å^3)	723.1(1)	1441.4(3)
Z	4	8
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
temp (°C)	25 ± 2	25 ± 2
λ(Mo Kα) (Å)	0.710 73	0.710 73
ρ_{calc} (g/cm^3)	2.11	2.12
μ (cm^{-1})	36.6	35.9
$R(F)^a$	2.33	3.01
$R_w(F)^b$	2.52	3.40

[a] $R = 100 \times \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = 100 \times [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Parameters for α-$ZnHPO_3 \cdot N_4C_2H_4$

atom	x	y	z	U_{eq}
Zn1	0.324853(17)	0.10419(2)	0.040809(17)	0.0185
P1	0.51909(4)	−0.16770(4)	0.20810(4)	0.0177
O1	0.36827(12)	0.07882(15)	−0.15002(12)	0.0255
O2	0.37932(12)	−0.07812(15)	0.17323(13)	0.0265
O3	0.42903(12)	0.29992(14)	0.12552(11)	0.0244
N1	0.12630(16)	0.1475(2)	0.0332(2)	0.0355
N2	−0.08053(15)	0.2616(2)	0.10006(17)	0.0307
N3	−0.15055(16)	0.4061(2)	−0.12594(16)	0.0299
N4	−0.25873(16)	0.4467(2)	0.06363(17)	0.0315
C1	0.02752(16)	0.2043(2)	0.05978(19)	0.0273
C2	−0.16286(15)	0.37024(18)	0.01049(17)	0.0226
H1	0.498(2)	−0.299(3)	0.144(2)	0.026(5)
H31	−0.213(3)	0.470(3)	−0.186(3)	0.037(6)
H32	−0.104(3)	0.346(4)	−0.170(3)	0.047(7)
H41	−0.321(3)	0.515(3)	0.004(3)	0.039(6)
H42	−0.272(3)	0.419(3)	0.150(3)	0.045(7)

Table 3. Selected Bond Distances[a] (Å) and Angles (deg) for α-$ZnHPO_3 \cdot N_4C_2H_4$

Zn1−O1	1.925(1)	Zn1−O2	1.9305(11)
Zn1−O3	1.9668(11)	Zn1−N1	1.9570(15)
P1−O1	1.5254(11)	P1−O2	1.5167(12)
P1−O3	1.5215(11)	P1−H1	1.23(2)
N1−C1	1.152(2)	N2−C1	1.292(2)
N2−C2	1.346(2)	N3−C2	1.330(2)
N4−C2	1.3198(19)		

O1−Zn1−O2	114.12(5)	O1−Zn1−O3	104.24(5)
O2−Zn1−O3	110.57(5)	O1−Zn1−N1	115.18(6)
O2−Zn1−N1	106.40(6)	O3−Zn1−N1	106.06(6)
O1−P1−O2	112.37(7)	O1−P1−O3	110.48(6)
O2−P1−O3	111.15(6)	O1−P1−H1	107.5(10)
O2−P1−H1	107.1(10)	O3−P1−H1	108.0(10)
Zn1−O1−P1	127.62(7)	Zn1−O2−P1	127.51(7)
Zn1−O3−P1	123.99(7)	Zn1−N1−C1	160.26(16)
C1−N2−C2	118.29(14)	N1−C1−N2	175.24(18)
N2−C2−N3	123.60(14)	N2−C2−N4	117.45(14)
N3−C2−N4	118.94(15)		

N3−H31···O1	0.89(3)	2.07(3)	2.9489(19)	169(2)
N3−H32···N2	0.84(3)	2.37(3)	3.107(2)	147(3)
N4−H41···O3	0.91(3)	2.06(3)	2.963(2)	169(3)
N4−H42···O2	0.87(3)	2.15(3)	2.959(2)	155(3)

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

Physical Measurements. TGA/DTA data for β-$ZnHPO_3 \cdot N_4C_2H_4$ were collected on a Universal V2.5H TA instrument (ramp rate 10 °C/min in flowing air) and showed a near featureless total weight loss of ~36% occurring over the very broad range ~100−900 °C. A strong endothermic event at ~840 °C, possibly a melting transition, was apparent. Powder diffraction showed the residue to be glassy. The calculated weight loss for the loss of all the organic species to result in a nominal residue of $ZnHPO_3$ is 36.6%. For α-$ZnHPO_3 \cdot N_4C_2H_4$, TGA data collected on a Mettler Toledo Star system showed a continuous weight loss of ~34% over the temperature range ~280−850 °C, followed by a distinct weight uptake between ~850 and 1000 °C. This weight increase may correspond to aerial oxidation of phosphite to phosphate. Again, the product was noncrystalline.

Crystal Structures. Suitable crystals (for α-$ZnHPO_3 \cdot N_4C_2H_4$, transparent faceted gem, ~0.19 mm × 0.31 mm × 0.39 mm; for β-$ZnHPO_3 \cdot N_4C_2H_4$, transparent rod ~0.05 mm × 0.06 mm × 0.43 mm) of each compound were selected and mounted on thin glass fibers with cyanoacrylate adhesive. The β form of $ZnHPO_3 \cdot N_4C_2H_4$ is highly prone to twinning, and many crystals showing split/smeared reflection profiles were screened and rejected before a suitable specimen was found. Intensity data for each phase were collected on a Bruker SMART 1000 CCD diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 25 \pm 2$ °C) with the aid of the SMART and SAINT software packages[8] as summarized in Table 1.

In both cases, a hemisphere of data were collected in narrow (0.3°)-slice ω-scan mode (for α-$ZnHPO_3 \cdot N_4C_2H_4$ $2° \le 2\theta \le 65°$; for β-$ZnHPO_3 \cdot N_4C_2H_4$ $2° \le 2\theta \le 60°$). Absorption corrections were applied using SADABS[9] with resulting correction factor ranges of 0.569−0.802 for α-$ZnHPO_3 \cdot N_4C_2H_4$ [7305 reflections scanned, 2575 unique ($R_{Int} = 0.019$), 2222 observed with $I > \sigma(I)$] and 0.457−0.862 for β-$ZnHPO_3 \cdot N_4C_2H_4$ [6288 reflections scanned, 2112 unique ($R_{Int} = 0.032$), 1728 observed with $I > \sigma(I)$].

The starting positional parameters for the non-hydrogen atoms were located by direct methods[10] in the space groups $P2_1/c$ (No. 14) for α-$ZnHPO_3 \cdot N_4C_2H_4$ and $C2/c$ (No. 15) for β-$ZnHPO_3 \cdot N_4C_2H_4$, which were assumed for the remainder of the crystallographic study. After isotropic refinement, the five hydrogen atom positions for each phase showed up very clearly in difference Fourier maps, and subsequently, their positional and isotropic thermal factors were refined without constraints. The final difference maps were essentially featureless (for α-$ZnHPO_3 \cdot N_4C_2H_4$, min/max $\Delta\rho = -0.32/+0.45$ e Å^{-3}; for β-$ZnHPO_3 \cdot N_4C_2H_4$, min/max $\Delta\rho = -0.44/+0.67$ e Å^{-3}).

The final cycles of full-matrix least-squares refinement with CRYSTALS[11] using complex, neutral-atom scattering factors included positional and anisotropic thermal factors for all the non-hydrogen atoms and a Larson-type[12] secondary extinction correction. A calculated weighting scheme was applied in each case,[13] and satisfactory convergence was achieved, as summarized in Table 1.

Results

Crystal Structure of α-$ZnHPO_3 \cdot N_4C_2H_4$. The final atomic positional and thermal parameters and selected geometrical data are presented in Tables 2 and 3, respectively. The building unit of α-$ZnHPO_3 \cdot N_4C_2H_4$ is shown in Figure 1 and the complete structure in Figure 2.

α-$ZnHPO_3 \cdot N_4C_2H_4$ contains 11 non-hydrogen atoms. The tetrahedrally coordinated zinc atom is surrounded by three O atoms (also bonded to P) and one N atom, the latter being the nitrile nitrogen[14] of the 2-cyanoguanidine species. Because this

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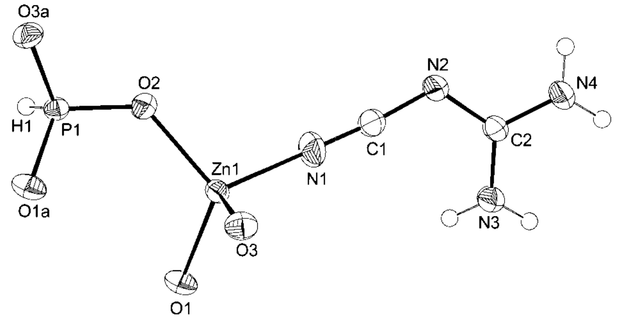

Figure 1. Fragment of the α-$ZnHPO_3{\cdot}N_4C_2H_4$ structure (50% thermal ellipsoids) showing the atom labeling scheme. Symmetry-related atoms are indicated by O1a, etc.

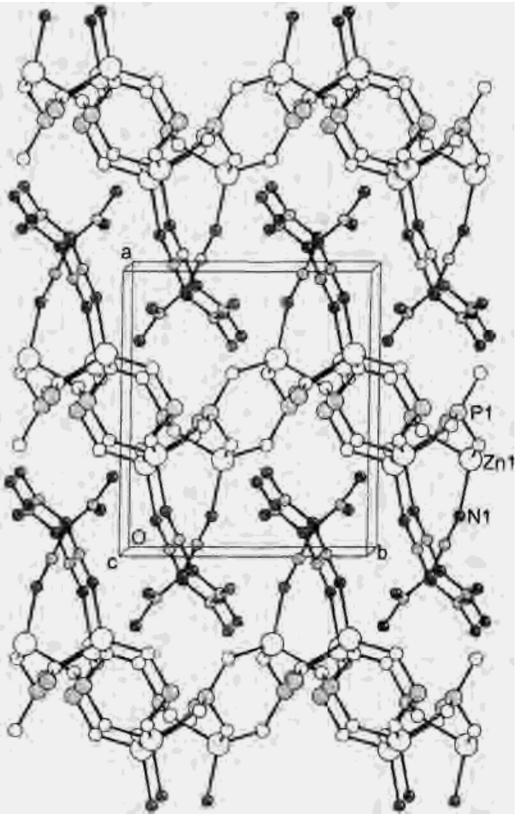

Figure 2. Structure of α-$ZnHPO_3{\cdot}N_4C_2H_4$ viewed approximately down [001] with H atoms omitted for clarity. The infinite sheets propagate in the (011) plane. The 2-cyanoguanidine species on the outer layers have been truncated at their nitrile nitrogen atoms.

molecule is directly bonded to Zn, it could equally well be described as a ligand rather than a template. The P atom makes three O atom bridges to Zn near neighbors and bonds to one H atom. This tetrahedral, or pseudopyramidal, geometry is characteristic of phosphorus(III), as seen previously.[15] The three O atoms form Zn−O−P bridges, with $\theta_{av} = 126.37°$. The geometrical parameters for the 2-cyanoguanidnie component of the structure are in good agreement with structural data for molecular complexes involving the same ligand.[14] To a first approximation the molecule is planar. The refinement makes clear that both guanidine-like[16] terminal nitrogen atoms (N3 and N4) are doubly protonated. Thus, overall, the ligand is neutral, in accordance with the charge-balancing requirement.

Hydrogen bonding appears to be significant in stabilizing this structure. The $N4H_2$ moiety makes two N−H···O bond and templates across an 8-ring in an adjacent zincophosphite layer. The $N3H_2$ group is involved in one N−H···O bond to an adjacent layer and one N−H···N bond, where the acceptor N atom is the imino (N2) nitrogen species on an adjacent pendant 2-cyanoguandine entity associated with the *same* sheet but displaced in the *c* direction. This type of interfragment $N_g{-}H{\cdots}N_i$ (g = guanidine, i = imino) bond has also been observed in molecular complexes.[14] There are no hydrogen-bonding interactions involving the P−H bond, which is expected, because this H atom does not show acidic behavior.[17]

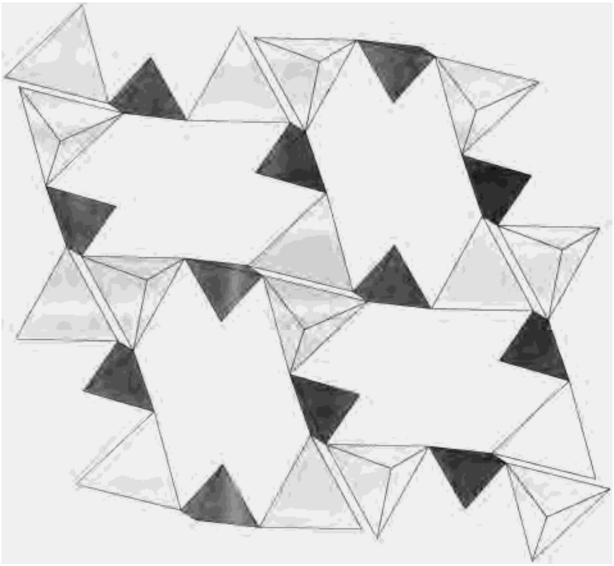

Figure 3. Polyhedral view approximately normal to (011) of part of the α-$ZnHPO_3{\cdot}N_4C_2H_4$ structure showing the connectivity of the ZnO_3N (light shading) and HPO_3 (dark shading) polyhedra to 4-ring and 8-ring loops.

The ZnO_3N and HPO_3 building blocks in α-$ZnHPO_3{\cdot}N_4C_2H_4$ combine to yield a structure with strong two-dimensional character (Figure 3) built up from 4-ring and 8-ring loops (i.e., four or eight polyhedral centers, respectively). The three O atoms form the interpolyhedral links, and the P−H and Zn−N bonds are “terminal”. Each 8-ring is templated above and below by hydrogen bonds from organic entities belonging to adjacent sheets. The P−H bonds project into the 8-rings. The ZnO_3N and HPO_3 moieties strictly alternate, and the infinite sheets propagate normal to [100]. The minimum and maximum atom-to-atom dimensions (both involving O3···O3 separations) of the squashed 8-ring are 4.45 and 8.35 Å, respectively.

Crystal Structure of β-$ZnHPO_3{\cdot}N_4C_2H_4$. Final atomic positional and thermal parameters and selected geometrical data are presented in Tables 4 and 5, respectively. The building unit of β-$ZnHPO_3{\cdot}N_4C_2H_4$ is shown in Figure 4 and the complete structure in Figure 5.

β-$ZnHPO_3{\cdot}N_4C_2H_4$ contains the same building blocks as the α-polymorph. The tetrahedral zinc atom is surrounded by three O atoms (also bonded to P) and one nitrile N atom. The P atom makes three O atom bridges to Zn near neighbors and bonds to one H atom. The three O atoms form Zn−O−P bridges, with $\theta_{av} = 128.65°$. There are no unusual features associated with the geometry of the organic component of the structure.

In β-$ZnHPO_3{\cdot}N_4C_2H_4$, the polyhedral building blocks combine to yield an extended network with strong one-dimensional character (Figure 6) built up from twisted ladders of 4-ring loops sharing edges. The ZnO_3N and HPO_3 moieties strictly alternate,

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Table 4. Atomic Parameters for β-$ZnHPO_3{\cdot}N_4C_2H_4$

atom	*x*	*y*	*z*	U_{eq}
Zn1	0.41873(2)	0.86283(2)	0.04420(3)	0.0257
P1	0.64006(5)	0.96946(5)	0.22141(6)	0.0242
O1	0.56706(15)	0.87209(16)	0.1225(2)	0.0324
O2	0.36863(18)	0.90092(17)	−0.15449(18)	0.0386
O3	0.36674(16)	0.98221(17)	0.13694(18)	0.0340
N1	0.3835(2)	0.6872(2)	0.0709(3)	0.0413
N2	0.37363(19)	0.4705(2)	0.1459(2)	0.0340
N3	0.3792(2)	0.2566(2)	0.1168(3)	0.0460
N4	0.3894(2)	0.3834(2)	−0.0543(3)	0.0416
C1	0.37929(19)	0.5836(2)	0.1014(3)	0.0288
C2	0.38086(19)	0.3719(2)	0.0675(3)	0.0295
H1	0.726(2)	0.931(3)	0.246(3)	0.033(8)
H31	0.370(3)	0.249(3)	0.192(4)	0.038(8)
H32	0.385(4)	0.195(5)	0.066(5)	0.071(13)
H41	0.395(3)	0.320(4)	−0.097(4)	0.05(1)
H42	0.386(3)	0.456(5)	−0.087(5)	0.065(13)

Table 5. Selected Bond Distances[a] (Å) and Angles (deg) for β-$ZnHPO_3{\cdot}N_4C_2H_4$

Zn1−O1	1.965(2)	Zn1−O2	1.9178(17)
Zn1−O3	1.9152(17)	Zn1−N1	1.971(2)
P1−O1	1.5269(18)	P1−O2	1.5136(19)
P1−O3	1.5131(17)	P1−H1	1.23(3)
C1−N1	1.146(3)	C1−N2	1.293(3)
C2−N2	1.349(3)	C2−N3	1.322(3)
C2−N4	1.321(4)		
O1−Zn1−O2	107.39(9)	O1−Zn1−O3	110.58(8)
O2−Zn1−O3	110.13(8)	O1−Zn1−N1	107.0(1)
O2−Zn1−N1	109.94(9)	O3−Zn1−N1	111.68(9)
O1−P1−O2	113.39(11)	O1−P1−O3	113.85(11)
O2−P1−O3	109.6(1)	O1−P1−H1	106.1(15)
O2−P1−H1	106.4(15)	O3−P1−H1	107.0(15)
Zn1−O1−P1	130.51(11)	Zn1−O2−P1	127.02(11)
Zn1−O3−P1	128.43(11)	N1−C1−N2	174.8(3)
N2−C2−N3	117.3(2)	N2−C2−N4	124.2(2)
N3−C2−N4	118.4(2)	Zn1−N1−C1	168.8(3)
C1−N2−C2	117.8(2)		

N3−H31···O2	0.84(4)	2.25(4)	2.944(3)	140(3)
N3−H32···O3	0.86(5)	2.41(5)	2.912(3)	118(4)
N3−H32···O1	0.86(5)	2.43(5)	3.186(3)	147(5)
N4−H41···O1	0.82(4)	2.14(4)	2.919(3)	157(4)

[a] For the hydrogen bonds, the four values correspond to the N−H, H···O, and N···O separations and and the N−H···O bond angle, respectively (N3−H32 is bifurcated).

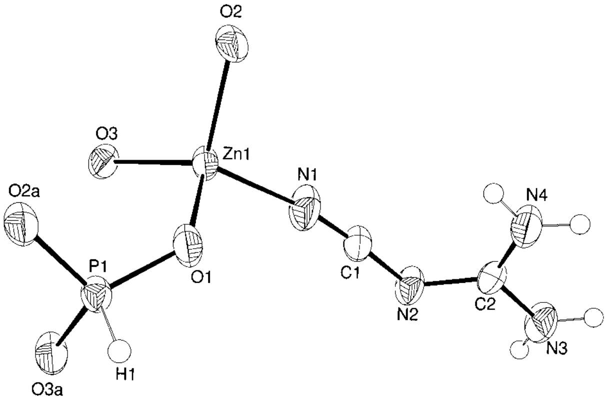

Figure 4. Fragment of the β-$ZnHPO_3{\cdot}N_4C_2H_4$ structure (50% thermal ellipsoids) showing the atom labeling scheme. Symmetry-related atoms are indicated by O2a, etc.

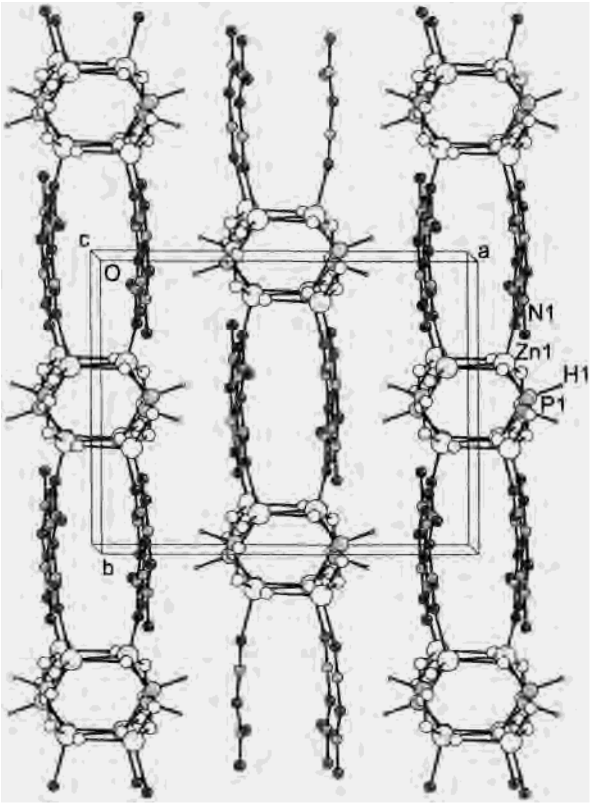

Figure 5. Structure of β-$ZnHPO_3{\cdot}N_4C_2H_4$ viewed down [001]. The four-ring ladders propagate toward the viewer. The 2-cyanoguanidine groups interleave in the [010] direction, and interaction between the sheets of chains in the [100] direction is through van der Waals' forces.

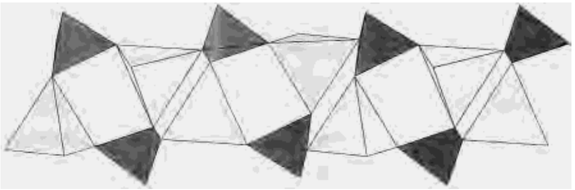

Figure 6. Detail of the β-$ZnHPO_3{\cdot}N_4C_2H_4$ structure in polyhedral form showing the infinite chains of ZnO_3N (light shading) and HPO_3 (dark shading) groups built up from twisted, edge-sharing 4-ring ladders.

and the chains propagate along [001]. The P−H vertexes protrude away from the chains, roughly in the *a* direction, and the 2-cyanoguanidine groups interleave with similar neighbors from an adjacent chain in the [010] direction (Figure 5). Hydrogen bonding is significant in stabilizing the [010] interchain interactions. Two of the guanidine hydrogen atoms form simple N−H···O links, and H32 partakes in a bifurcated N−H···(O,O) bond. The fourth H atom (H42) is not involved in hydrogen bonding. Thus, the interaction between sheets of chains in the [100] direction is by means of van der Waals' forces only.

Discussion

α- and β-$ZnHPO_3{\cdot}N_4C_2H_4$, the first mixed organic/inorganic hydrogen phosphites, have been successfully prepared and characterized. The mild-condition preparation of two polymorphs of 2-cyanoguanidine zinc hydrogen phosphite as single crystals is typical of the fecundity of solution-mediated, hydrothermal synthesis.[1] Unfortunately, little insight into *how* these phases form by "self-assembly" from (presumably) the same constituent building blocks is afforded by these reactions. The 2-cyanoguanidine species has carried out what is usually termed a templating function[1] in terms of its hydrogen-bonding capability,[14] but the resulting structures bear little resemblance to each other, although, interestingly, their densities are almost identical. The presence of direct Zn−N(ligand) bonds is uncommon, but not unprecedented, in organically templated zincophosphate structures.[18] The serendipitous use of strontium nitrate as a "magic ingredient" to redirect the reaction from β-$ZnHPO_3 \cdot N_4C_2H_4$ to α-$ZnHPO_3 \cdot N_4C_2H_4$ has parallels with the use of magnesium nitrate to prepare $(CN_3H_6)_2 \cdot (VO_2)_3(PO_4)(HPO_4)$ in good yield[19] and zinc oxide to prepare $Ba_2(VO)(PO_4) \cdot 2H_2O$.[20] The Sr^{2+} ions may act to regulate pH or control the quantity of hydrogen phosphite anions in solution.[21]

The relationship between these phases and organically templated zinc phosphates built up from an all-tetrahedral network of ZnO_4 and PO_4 units is of some interest. The layer *motif* of α-$ZnHPO_3 \cdot N_4C_2H_4$ can be described in terms of the 4.8^2 sheet topology[22] as found in various aluminosilicate zeolite structures. The 4.8^2 nomenclature indicates that each nodal atom (Zn or P) participates in one 4-ring and two 8-rings. In zeolite-like phases, the Zn−N and P−H bonds are replaced by T−O−T′ (T = tetrahedral atom) links, and an infinite three-dimensional framework results. However, similar interrupted (by $Zn-OH_2$ and P−OH links) networks based on a 4.8^2 sheet have been seen in zincophosphates such as $N_2C_6H_{14} \cdot Zn_2(HPO_4)_3$,[23] although the overall structure is three-dimensional in this case.

The 4-ring ladder *motif* of β-$ZnHPO_3 \cdot N_4C_2H_4$ corresponds closely to similar one-dimensional network structures constructed from ZnO_4 and HPO_4 building blocks observed in phases such as $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_4)_2$[24] and the isostructural cobaltophosphate[25] $H_3N(CH_2)_3NH_3 \cdot Co(HPO_4)_2$, although in these cases the cationic template does not bond directly to zinc or cobalt. Some aluminophosphates such as $C_{10}N_2H_9 \cdot Al(PO_4)(H_2PO_4)$[26] adopt similar chain structures based on 4-ring ladders of AlO_4 and PO_4 groups. In all these phases, hydrogen bonding is assumed to be a key feature in stabilizing the resulting crystal structure, but the precise details vary and are as yet poorly understood.

Organically templated (or ligated) zinc hydrogen phosphites have proven to be a rich field, and we will report further examples of these phases shortly.

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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