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New Framework Connectivity Patterns in Templated Networks: The Creatinine Zinc Phosphites $C_4N_3OH_7\cdot ZnHPO_3$, $C_4N_3OH_7\cdot Zn(H_2O)HPO_3$, and $(C_4N_3OH_7)_2\cdot ZnHPO_3\cdot H_2O$

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The syntheses, crystal structures, and properties of $C_4N_3OH_7\cdot ZnHPO_3$, $C_4N_3OH_7\cdot Zn(H_2O)HPO_3$, and $(C_4N_3OH_7)_2\cdot ZnHPO_3\cdot H_2O$ are reported. These new creatinine zinc phosphites are built up from networks of vertex-sharing HPO_3 pseudopyramids and various types of ZnO_2N_2, ZnO_3N, and $ZnO_2N(H_2O)$ tetrahedra, resulting in extended structures of different dimensionalities (as sheets, clusters, and chains, respectively). They demonstrate the structural effect of incorporating "terminal" (nonnetworking) Zn–N and Zn–OH_2 moieties into zinc centers. Crystal data: $C_4N_3OH_7\cdot ZnHPO_3$, triclinic, $P\bar{1}$ (No. 2), $a = 8.9351(4)$ Å, $b = 9.5011(4)$ Å, $c = 9.9806(4)$ Å, $\alpha = 87.451(1)°$, $\beta = 85.686(1)°$, $\gamma = 89.551(1)°$, $Z = 4$; $C_4N_3OH_7\cdot Zn(H_2O)HPO_3$, monoclinic, $P2_1/c$ (No. 14), $a = 10.1198(7)$ Å, $b = 7.2996(5)$ Å, $c = 13.7421(9)$ Å, $\beta = 107.522(1)°$, $Z = 4$; $(C_4N_3OH_7)_2\cdot ZnHPO_3\cdot H_2O$, triclinic, $P\bar{1}$ (No. 2), $a = 10.7289(6)$ Å, $b = 10.9051(6)$Å, $c = 13.9881(8)$ Å, $\alpha = 89.508(1)°$, $\beta = 74.995(1)°$, $\gamma = 74.932(1)°$, $Z = 4$.

Introduction

Extended inorganic networks templated by organic cations now cover a remarkable range of compositions and structures.[1] With inspiration from the example of aluminosilicate zeolites, the applications of some of these materials as catalysts,[2] absorption agents,[3] and ion exchangers[4] have been investigated. Two areas of particular concern to synthetic and structural chemists are to devise rational and reliable syntheses for these materials[5] and to understand the resulting, often-complicated, crystal structures. A starting point for the latter task is to classify the *dimensionality* of the inorganic network as zero- (clusterlike), one- (chainlike), two- (layered), or three-dimensional (continuous).[6] Organically templated zinc phosphates (ZnPOs) demonstrate the existence of all four types of network. Examples from our own work (also showing that the use of the same template can lead to two or more completely different structures) include the anionic cluster compound[7] $N(CH_3)_4\cdot Zn(H_2PO_4)_3$, which contains isolated 4 rings (4 tetrahedral units) with two pendant H_2PO_4 moieties attached to the zinc node. Slightly different preparation conditions led to the one-dimensional $H_3N(CH_2)_3NH_3\cdot Zn(HPO_4)_2$ containing 4-ring ladders and $H_3N(CH_2)_3NH_3\cdot Zn_2(HPO_4)_2(H_2PO_4)_2$ which incorporates 12-ring pores into its layered (two-dimensional) structure.[8] Finally, $N(CH_3)_4\cdot Zn(HPO_4)(H_2PO_4)$ possesses a novel three-dimensional framework built up from an all-12-ring topology.[7] Numerous other ZnPOs showing great structural diversity have been prepared by many workers,[9-11] but all of them can be assigned to a particular framework dimensionality.

We are now studying organically templated zinc (hydrogen) phosphites containing (HPO_3^{2-}) units.[12-15] The pyra-

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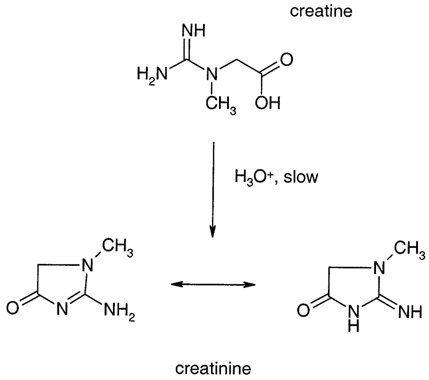
Chart 1



midal phosphite grouping can only make three P−O−Zn bonds; thus, its network structures are expected to be significantly different from those formed by tetrahedral phosphate groups. In fact, some of the resulting phases, such as $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_3)_2$,[13] are quite similar to corresponding zinc phosphates, whereas others, such as $[H_2N(CH_2)_2NH_2]_{0.5} \cdot ZnHPO_3$,[15] containing two separate, interpenetrating networks, akin to a coordination polymer, are novel. In this paper we describe our investigations into the creatinine (2-amino-3-methyl-1-imidazolin-5-one (**I**); Chart 1) zinc phosphite system and demonstrate how different degrees of ligation (Zn−N and Zn−OH_2 bonds) at the zinc center can lead to different dimensionalities for the inorganic component of the structure, resulting in novel structure types.

Experimental Section

Synthesis. $C_4N_3OH_7 \cdot ZnHPO_3$. A 7.45 g (50 mmol) amount of creatine hydrate (Osmo Chemicals), 0.81 g (10 mmol) of ZnO (St Joseph's), 2.54 g (30 mmol) of H_3PO_3 (Alfa), and 18 g (1 mol) of H_2O were shaken in a HDPE bottle and placed in a 70 °C oven for 24 h. Product recovery by vacuum filtration resulted in a crusty mass of 1.32 g (yield based on Zn = 51%) of transparent needles and prisms (to 0.5 mm). The pH of the mother liquors was 5. $C_4N_3OH_7 \cdot ZnHPO_3$ has also been prepared from creatinine in place of creatine hydrate, but the crystal quality is worse.

$C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$. A 5.96 g (40 mmol) amount of creatine hydrate, 0.81 g (10 mmol) of ZnO, 3.38 g (40 mmol) of H_3PO_3, and 18 g of H_2O were reacted as above. Product recovery resulted in 1.69 g (yield = 61%) of small, transparent, prismatic blocks (pH of the mother liquors = 4).

$(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$. A 8.94 g (60 mmol) amount of creatine hydrate, 0.81 g (10 mmol) of ZnO, 1.69 g (20 mmol) of H_3PO_3, and 18 g of H_2O were reacted as above. Product recovery resulted in 2.84 g (yield = 76%) of transparent platy crystals (pH of the mother liquors = 6).

Characterization. X-ray powder patterns (Bruker D8 diffractometer, Cu Kα radiation, $\lambda = 1.541\ 78$ Å, $T = 25$ °C) for a ground portion of each sample were in good agreement with simulations on the basis of the appropriate single-crystal structure (see below) indicating phase purity and high crystallinity in each case. ^{31}P and ^{13}C MAS NMR data were collected on a Varian UNITY Inova spectrometer equipped with a Doty Scientific MAS probe and referenced to standards of 85% H_3PO_4 and $(CH_3)_4Si$, respectively.

Crystal Structure Determinations. Suitable crystals (for $C_4N_3OH_7 \cdot ZnHPO_3$, block, ∼0.38 × 0.17 × 0.11 mm; for $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$, triangular plate, ∼0.31 × 0.23 × 0.05 mm; for $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$, faceted chunk, ∼0.15 × 0.14 × 0.08 mm) of each compound were mounted on thin glass fibers with cyanoacrylate adhesive. Intensity data for each phase were collected on a Bruker SMART 1000 CCD diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å, $T = 20 \pm 2$ °C) with the aid of the SMART and SAINT software packages.[16] Absorption corrections were applied using SADABS[17] with resulting correction factor ranges of 0.669−0.928 for $C_4N_3OH_7 \cdot ZnHPO_3$ [7546 reflections scanned, 5731 unique ($R_{Int} = 0.015$), 4775 with $I > 2\sigma(I)$], 0.858−0.928 for $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$ [6722 reflections scanned, 2771 unique ($R_{Int} = 0.035$), 2023 with $I > 2\sigma(I)$], and 0.798−0.948 for $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$ [11524 reflections scanned, 6924 unique ($R_{Int} = 0.035$), 4342 with $I > 2\sigma(I)$].

The starting positional parameters for the non-hydrogen atoms were located by direct methods[18] in space groups $P\bar{1}$ (No. 2) for $C_4N_3OH_7 \cdot ZnHPO_3$ and $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$ and $P2_1/c$ (No. 14) for $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$, which were assumed for the remainder of the crystallographic studies. After isotropic refinement, most of the hydrogen atom positions for each phase could be discerned in difference Fourier maps. The phosphite P−H ($d = 1.32$ Å) and creatinine C−H and N−H atoms were relocated at idealized positions and refined by riding on their parent atoms. For $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$, the water-molecule H atoms were refined by riding in their as-found positions. For $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$, the water-molecule H atoms were not located. The final difference maps were satisfactory ($C_4N_3OH_7 \cdot ZnHPO_3$: min/max $\Delta\rho = -0.62/+0.48$ e Å^{-3}; $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$: min/max $\Delta\rho = -0.43/+0.58$ e Å^{-3}; $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$: min/max $\Delta\rho = -0.34/+0.63$ e Å^{-3}). All calculations were performed with SHELXL-97;[19] details are summarized in Table 1.

Results

Crystal Structure of $C_4N_3OH_7 \cdot ZnHPO_3$. This phase contains 26 non-hydrogen atoms, all on general positions. Selected geometrical data are presented in Table 2, and the structure is shown in Figures 1 and 2.

Both of the tetrahedrally coordinated zinc atoms are surrounded by three O atoms (also bonded to P) and one N atom, the latter being the imidazole-like nitrogen atom[20] of a creatinine molecule (see Chart 1). Because this molecule is directly bonded to Zn by formal donation of its electron lone pair (i.e., a Lewis base), it could be described as a ligand rather than a template.[12] The average Zn−O bond length of 1.929(2) Å is distinctly shorter than the average Zn−N bond

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Table 1. Crystallographic Parameters

	$C_4N_3OH_7$·$ZnHPO_3$	$C_4N_3OH_7$·$Zn(H_2O)HPO_3$	$(C_4N_3OH_7)_2$·$ZnHPO_3$·H_2O
empirical formula	$ZnPO_4N_3C_4H_8$	$ZnPO_5N_3C_4H_{10}$	$ZnPO_6N_6C_8H_{17}$
fw	258.48	276.49	389.61
a (Å)	8.9351 (4)	10.1198 (7)	10.7289 (6)
b (Å)	9.5011 (4)	7.2996 (5)	10.9051 (6)
c (Å)	9.9806 (4)	13.7421 (9)	13.9881 (8)
α (deg)	87.451 (1)	90	89.508 (1)
β (deg)	85.685 (1)	107.522 (1)	74.995 (1)
γ (deg)	89.551 (1)	90	74.932 (1)
V (Å^3)	844.04 (6)	968.03 (11)	1523.42 (15)
Z	4	4	4
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
T (°C)	20 ± 2	20 ± 2	20 ± 2
λ(Mo $K\alpha$) (Å)	0.710 73	0.710 73	0.710 73
ρ_{calc} (g/cm^3)	2.034	1.897	1.690
μ (mm^{-1})	3.09	2.70	1.76
R(F)[a]	0.030	0.032	0.042
wR(F^2)[b]	0.084	0.076	0.096

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

Table 2. Selected Bond Distances (Å)[a] and Angles (deg) for $C_4N_3OH_7$·$ZnHPO_3$

Zn1−O6	1.9049(16)	Zn1−O4	1.9065(15)
Zn1−O2	1.9601(14)	Zn1−N1	2.0299(16)
Zn2−O5	1.9126(16)	Zn2−O1	1.9266(14)
Zn2−O3	1.9625(14)	Zn2−N4	2.0445(15)
P1−O2	1.5113(14)	P1−O3	1.5163(15)
P1−O1	1.5239(14)	P2−O6	1.5022(17)
P2−O5	1.5036(16)	P2−O4	1.5158(15)
N1−C1	1.359(2)	N1−C4	1.374(2)
C1−O7	1.224(2)	C1−C2	1.513(3)
C2−N2	1.447(3)	N2−C4	1.326(2)
N2−C3	1.454(3)	C4−N3	1.312(2)
N4−C5	1.366(3)	N4−C8	1.374(2)
C5−O8	1.218(2)	C5−C6	1.510(3)
C6−N5	1.447(3)	N5−C8	1.325(2)
N5−C7	1.462(2)	C8−N6	1.317(3)

P1−O1−Zn2	136.27(10)	P1−O2−Zn1	157.36(11)
P1−O3−Zn2	132.28(9)	P2−O4−Zn1	132.72(11)
P2−O5−Zn2	153.61(11)	P2−O6−Zn1	156.98(13)

N3−H3···O8	0.95	1.82	2.724(2)	157.8
N3−H4···O2	0.95	2.03	2.905(2)	152.0
N3−H4···O1	0.95	2.33	3.110(2)	138.7
N6−H5···O7	0.95	1.93	2.864(2)	166.2
N6−H6···O3	0.95	2.01	2.861(2)	147.6

[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.

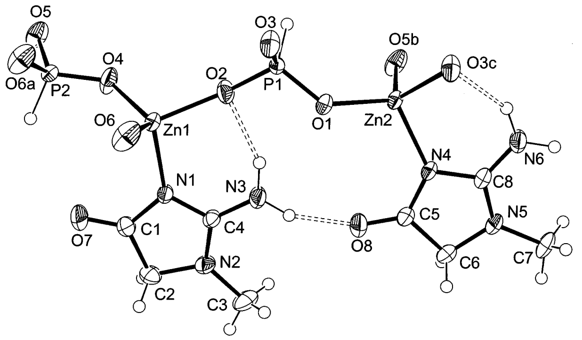

Figure 1. Fragment of $C_4N_3OH_7$·$ZnHPO_3$ (50% thermal ellipsoids) showing the atom labeling scheme, with H bonds indicated by dashed lines. Symmetry codes: (a) $-x, -y, -z$; (b) $-x, 1 - y, -z$; (c) $-x, 1 - y, 1 - z$.

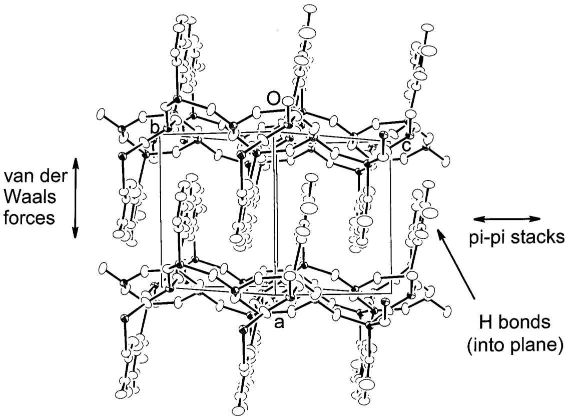

Figure 2. Unit-cell packing for $C_4N_3OH_7$·$ZnHPO_3$ viewed approximately down [011] showing the different, roughly orthogonal, weak bonding interactions that define the extended structure.

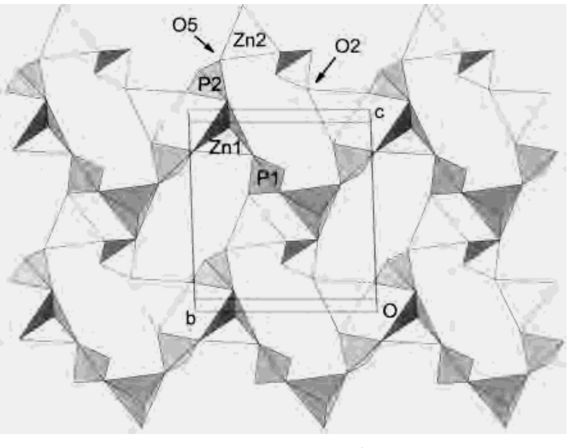

Figure 3. Polyhedral view of part of a 4.8^2 tetrahedral sheet in $C_4N_3OH_7$·$ZnHPO_3$ showing the connectivity of the ZnO_3N and HPO_3 units. The minimum and maximum dimensions of the squashed 8-ring are noted in the text.

length of 2.037(2) Å. Each P atom makes three O atom bridges [d_{av}(P−O) = 1.512 (2) Å] to Zn near neighbors and bonds to one H atom, thus showing normal behavior for phosphorus(III).[12] The six framework O atoms form Zn−O−P bridges, with $\theta_{av} = 144.9°$. The geometrical parameters for creatinine show no unexpected features and both asymmetric molecules are essentially planar [non-hydrogen atom root-mean-square (rms) deviation from the best least-squares plane = 0.019 for the N1 molecule and 0.020 for the N4 molecule]. The refinement makes clear that the terminal nitrogen atoms (N3 and N6) are doubly protonated; thus, overall, these ligands are neutral, in accordance with the charge-balancing requirement.

The ZnO_3N and HPO_3 building blocks in $C_4N_3OH_7$·$ZnHPO_3$ combine to generate a structure with strong two-dimensional character containing infinite tetrahedral sheets (Figure 3) built up from 4-ring and 8-ring loops (i.e., four or eight polyhedral centers, respectively). The minimum and maximum atom-to-atom dimensions of the squashed 8-ring are 5.36 Å (O2···O2) and 9.18 Å (O5···O5), respectively. The ZnO_3N and HPO_3 moieties strictly alternate and the layers propagate in the (100) plane. The pendant creatinine groups project away from the sheets, and intersheet bonding (Figure 2) involves an interleaving motif of these groupings. The P−H bonds also project away from the layers.

Table 3. Selected Bond Distances(Å)[a] and Angles (deg) for $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$

Zn1−O1	1.8981(19)	Zn1−O2	1.9358(19)
Zn1−O4	1.943(2)	Zn1−N1	2.0034(19)
P1−O3	1.5000(19)	P1−O1	1.5106(19)
P1−O2	1.5184(19)	N1−C4	1.363(3)
N1−C1	1.369(3)	C1−O5	1.222(3)
C1−C2	1.506(4)	C2−N2	1.448(4)
N2−C4	1.337(3)	N2−C3	1.450(3)
C4−N3	1.312(3)		
P1−O1−Zn1	141.16(12)	P1−O2−Zn1	137.50(13)

O4−H41···O3	0.95	1.67	2.617(3)	178.2
O4−H42···O3	0.77	1.85	2.612(3)	175.6
N3−H3D···O5	0.86	2.09	2.913(3)	159.3
N3−H3E···O2	0.86	2.05	2.832(3)	151.4

[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.

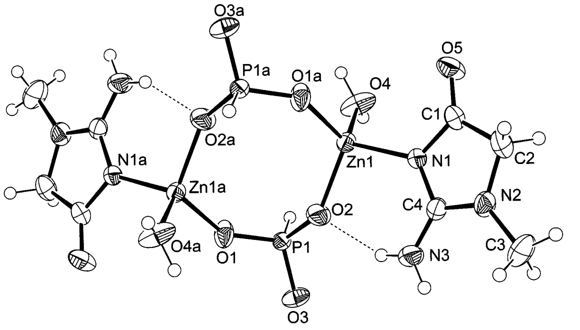

Figure 4. Cluster unit in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ (50% thermal ellipsoids) with intracluster H bonds indicated by dashed lines. Symmetry code: (a) $-x, -y, -z$.

Hydrogen bonding is significant in stabilizing this structure. Both the NH_2 moieties make two N−H···O bonds (Figure 1, Table 2): one to an acceptor phosphite O atom in the same sheet; one to an acceptor O═C group in an adjacent creatinine molecule but also part of the same sheet. There are no hydrogen bonding interactions involving the P−H bond, which is expected, as this H atom does not show acidic behavior.[21] There are no *inter*sheet hydrogen bonds in this phase.

Crystal Structure of $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$. This phase contains 14 non-hydrogen atoms, all on general positions. Selected geometrical data are presented in Table 3, and the structure is shown in Figures 4 and 5.

The tetrahedral zinc atom is surrounded by three O atoms (one water molecule + two also bonded to P) and one N atom belonging to an essentially planar (rms deviation from the best least-squares plane = 0.032 Å) creatinine molecule. The P atom makes two O atom bridges to Zn near neighbors, one terminal P−O vertex and one P−H bond. The average Zn−O and P−O bond lengths are 1.926(3) and 1.510(3) Å, respectively, and the average bond angle of the two O atoms forming Zn−O−P bridges is 139.3°. Once again, the terminal nitrogen atom N3 of the creatinine species is doubly protonated.

The building blocks in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ combine to yield a simple but novel cluster, consisting of a single 4-ring loop of alternating ZnO_3N and HPO_3 moieties. Inversion symmetry generates the complete cluster, which is neutral. The clusters stack in the [010] direction and are arranged to form pseudosheets in the (001) plane (Figure 5). There are both *intra*cluster and *inter*cluster hydrogen bonds in this phase. The $N3H_2$ moiety makes one intracluster N−H···O bond (Figure 4) and one N−H···O link to a similar adjacent unit. The bound water molecule (O4) makes two intercluster Zn−O−H···O bonds. As before, the P−H bond does not participate in H bonding.

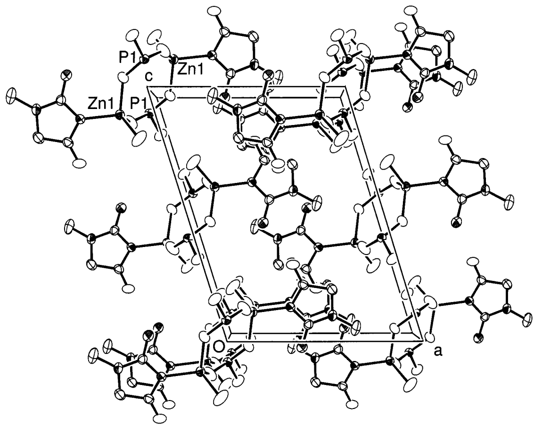

Figure 5. Unit cell packing in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ (50% thermal ellipsoids).

Crystal Structure of $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$. This complex phase contains 46 non-hydrogen atoms, all on general positions. Selected geometrical data are presented in Table 4, and the structure is shown in Figures 6 and 7.

Both the tetrahedrally coordinated zinc atoms are surrounded by two O atoms (also bonded to P) and two creatinine N atoms [$d_{av}(Zn{-}O) = 1.954$ (2) Å; $d_{av}(Zn{-}N) = 1.989$ (2) Å]. The P atoms both make two O atom bridges to Zn near neighbors and also possess $P{-}O_t$ (t = terminal) and P−H vertexes [$d_{av}(P{-}O_t) = 1.502$ (2) Å; $d_{av}(P{-}O_{Zn}) = 1.525$ (2) Å]. Of the six framework O atoms, four form Zn−O−P bridges ($\theta_{av} = 130.2°$) and two are terminal to P. The geometrical parameters for the essentially planar (rms deviation from the best least-squares plane = 0.036, 0.017, 0.052, and 0.023 Å, for the N1-, N4-, N7-, and N11-containing molecules, respectively) creatinine species are normal, and once again, the terminal nitrogen atoms (N3, N6, N9, and N12) are doubly protonated. The dihedral angle between the planes described by the N1- and N4-containing molecules (both attached to Zn1) is 83.96(7)°; thus, to a first approximation they are perpendicular A similar value of 84.44(7)° arises for the N7 and N11 moieties attached to Zn2. All the NH_2 moieties make two N−H···O bonds (Figure 6), and it is notable that each of the four Zn−O−P chain oxygen atoms (O1, O2, O4, and O5) acts as an intrachain acceptor for such a bond.

The ZnO_2N_2 and HPO_3 building blocks in $C_4N_3OH_7{\cdot}ZnHPO_3$ combine to generate a novel structure with strong one-dimensional character containing single, corrugated, chains (Figure 8) of alternating zinc- and phosphorus-centered tetrahedra, propagating in the [010] direction. Overall, the structure also has pseudolayered character, with

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(21) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinmann: New York, 1997.

Table 4. Selected Bond Distances(Å)[a] and Angles (deg) for $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$

Zn1−O5	1.953(2)	Zn1−O1	1.956(2)
Zn1−N4	1.986(3)	Zn1−N1	1.997(3)
Zn2−O2	1.947(3)	Zn2−O4	1.958(2)
Zn2−N7	1.980(3)	Zn2−N10	1.992(3)
P1−O6	1.499(3)	P1−O5	1.523(2)
P1−O4	1.524(2)	P2−O3	1.504(3)
P2−O2	1.524(2)	P2−O1	1.528(2)
N1−C1	1.365(5)	N1−C4	1.365(4)
C1−O7	1.227(4)	C1−C2	1.507(5)
C2−N2	1.444(5)	N2−C4	1.324(5)
N2−C3	1.450(4)	C4−N3	1.313(5)
N4−C5	1.366(4)	N4−C8	1.369(4)
C5−O8	1.223(4)	C5−C6	1.511(5)
C6−N5	1.431(5)	N5−C8	1.333(4)
N5−C7	1.447(4)	C8−N6	1.302(5)
N7−C12	1.365(5)	N7−C9	1.374(5)
C9−O9	1.212(5)	C9−C10	1.525(5)
C10−N8	1.437(5)	N8−C12	1.339(4)
N8−C11	1.458(5)	C12−N9	1.300(5)
N10−C13	1.355(5)	N10−C16	1.372(4)
C13−O10	1.223(4)	C13−C14	1.518(5)
C14−N11	1.458(5)	N11−C16	1.320(5)
N11−C15	1.444(5)	C16−N12	1.316(5)

P2−O1−Zn1	128.23(15)	P2−O2−Zn2	132.20(15)
P1−O4−Zn2	126.20(15)	P1−O5−Zn1	134.20(15)

N3−H3D···O6	0.86	2.10	2.910(4)	157.7
N3−H3E···O1	0.86	2.06	2.845(4)	151.6
N6−H6C···O3	0.86	2.05	2.863(4)	158.4
N6−H6D···O5	0.86	2.00	2.792(4)	153.1
N9−H9A···O6	0.86	2.04	2.844(4)	156.2
N9−H9B···O2	0.86	2.04	2.836(4)	153.2
N12−H12A···O3	0.86	2.06	2.866(4)	156.1
N12−H12B···O4	0.86	2.09	2.879(4)	152.1

[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.

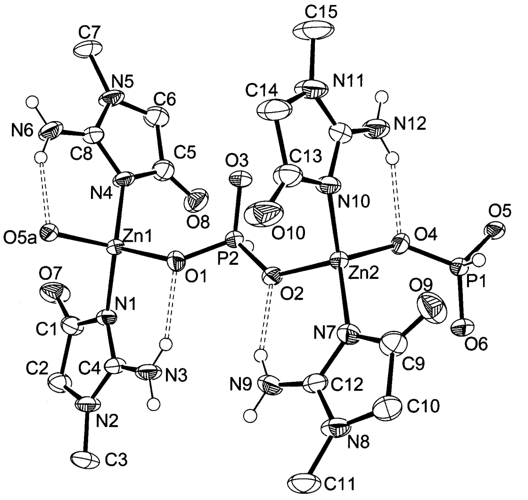

Figure 6. Fragment of $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$ (50% thermal ellipsoids) with water molecule O atoms and C−H hydrogen atoms omitted for clarity. Symmetry code: (a) *x*, 1 − *y*, *z*.

sheets of chains propagating in the (011) plane (Figure 7) and intersheet connectivity established by H bonds and van der Waals forces.

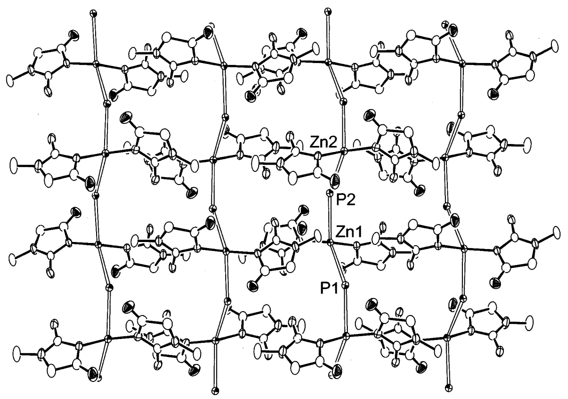

Figure 7. Extended packing in $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$ showing Zn−O−P bonds as open lines. The approximate view direction is down [100].

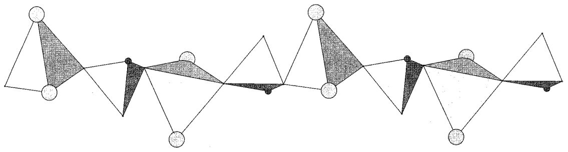

Figure 8. Polyhedral representation of a single tetrahedral chain of alternating ZnO_2N_2 and HPO_3 units in $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$. N atoms are represented by large circles, and phosphite H atoms, by small circles.

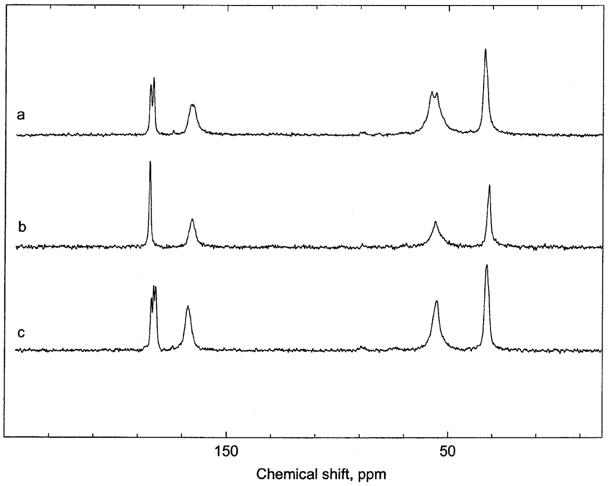

Figure 9. ^{13}C CP-MAS NMR spectra for (a) $C_4N_3OH_7 \cdot ZnHPO_3$, (b) $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$, and (c) $(C_4N_3OH_7)_2 \cdot ZnHPO_3 \cdot H_2O$.

NMR Data. The ^{13}C and ^{31}P spectra for the title compounds are shown in Figures 9 and 10, respectively. The ^{13}C spectra each show four well-separated resonances, of roughly equal intensity, some of which are broadened or split, at $\delta \approx 183$, 165, 55, and 31 ppm (relative to a standard of Me_4Si). These must correspond to the four chemically distinct carbon atoms in the creatinine moieties. On the basis of simple chemical shift calculations,[22] we attribute these four signals to the carbonyl (e.g. C1 or C5 in Figure 1), guanidinium-like (C4 or C8), methylene (C2 or C6), and terminal methyl (C3 or C7) carbon atoms, respectively. The calculated chemical shifts are 190, 120−160 (uncertain), 56.2, and 30.4 ppm, respectively. The corresponding solution-phase (solvent D_2O) ^{13}C chemical shifts of creatinine are 191.5, 171.8, 58.9, and 32.7 ppm, respectively.

The doublets and broad peaks seen in Figure 9 may represent partial resolution of these signals due to multiple crystallographic environments, although the broadening may also arise from $^{13}C-^{15}N$ coupling. We note that the terminal

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(22) Brown, D. W.; Floyd, A. J.; Sainsbury, M. *Organic Spectroscopy*; Wiley: Chichester, U.K., 1998.

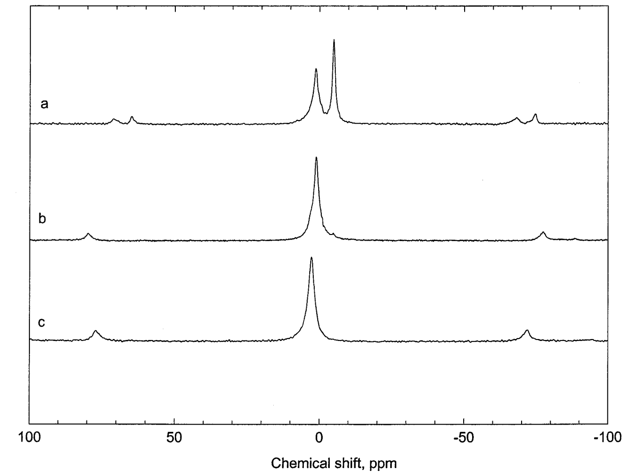

Figure 10. ^{31}P DP-MAS NMR spectra for (a) $C_4N_3OH_7{\cdot}ZnHPO_3$, (b) $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$, and (c) $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$.

methyl and carbonyl signals for $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ are very sharp, as expected for a material containing crystallographically unique species.

The ^{31}P spectra, all occurring close to $\delta = 0$ ppm (referenced to 85% H_3PO_4), show two lines of essentially equal intensity for $C_4N_3OH_7{\cdot}ZnHPO_3$, one line for $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ and one line for $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$. The two line spectrum for $C_4N_3OH_7{\cdot}ZnHPO_3$ presumably corresponds to the two P atom sites, although, because they are so chemically similar, it is hard to guess which resonance corresponds to which P atom. $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ has a single distinct P atom; thus, one line is expected. On the basis of its structure, we would expect two lines for the $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$ spectrum, but presumably, they overlap. Making this assumption, the ^{31}P NMR data are all consistent with the crystal structures reported above.

Discussion

Three new creatinine zinc phosphites, $C_4N_3OH_7{\cdot}ZnHPO_3$, $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$, and $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$, have been prepared by typical solution-phase reactions and structurally characterized. As is typical for hydrothermally prepared networks,[1] three completely different structures have arisen from the same starting materials. In all cases, the creatine starting material is transformed to creatinine before formation of the crystalline product. It is not yet clear whether the this transformation plays a key role in directing the synthesis of these products, or whether, as for $C_4N_3OH_7{\cdot}ZnHPO_3$, both creatine and creatinine can result in the same product.

A notable feature of these three materials is the different degree of ligation by the organic species and water at the zinc centers. If all four vertexes of the Zn-centered tetrahedron make Zn−O−P links, and the phosphite groups make three P−O−Zn bonds, then the resulting structures can be topologically regarded as (4,3)-connected nets.[23] Here, the occurrence of Zn−N and Zn−OH_2 bonds prevent the formation of a full complement of Zn−O−P links. Thus, $C_4N_3OH_7{\cdot}ZnHPO_3$ has one “blocked” Zn vertex (a Zn−N link) and $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ and $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$ have two blocked vertexes (as Zn−N + Zn−OH_2 and two Zn−N bonds, respectively). The presence of direct Zn−N(ligand) bonds is uncommon, but not unprecedented, in organically templated zincophosphate structures.[24] For example, the recently reported phase[25] $(C_3N_2H_4)_3{\cdot}Zn_4P_3O_{11}(OH)$ contains both ZnO_3N and ZnO_2N_2 tetrahedra in its layered structure. Zn−OH_2 links have also been seen in zincophosphates.[24] A neutral template/ligand, as found here, is very unusual for zincophosphates, with $(C_3N_2H_4)_3{\cdot}Zn_4P_3O_{11}(OH)$ the only known example, but has already been seen in other zincophosphites such as α-$ZnHPO_3{\cdot}C_2N_4H_4$[12] and $[H_2N(CH_2)_2NH_2]_{0.5}{\cdot}ZnHPO_3$.[15]

In terms of tetrahedral connectivity, the simple, zero-dimensional cluster in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_3$ and the simple chain in $(C_4N_3OH_7)_2{\cdot}ZnHPO_3{\cdot}H_2O$ are novel. A similar 4-ring-based cluster has been seen for zincophosphates[7,9] but with the addition of pendant dihydrogen phosphate moieties attached to Zn and an overall negative charge. Very recently,[26] we have also reported a neutral, molecular, creatinine zinc phosphate, $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$, although its crystal symmetry is different from that of the phosphite described here. The 4.8^2 sheets in $C_4N_3OH_7{\cdot}ZnHPO_3$ represent a recurring motif in zincophosphite chemistry: similar layers have been seen in α-$ZnHPO_3{\cdot}C_2N_4H_4$[12] and $[H_2N(CH_2)_2NH_2]_{0.5}{\cdot}ZnHPO_3$,[15] although the degree of sheet puckering and 8-ring window squashing varies widely for the inorganic sheet in these phases.

The combination of subtle effects that generate the overall structure in these types of phases are well exemplified by the case of $C_4N_3OH_7{\cdot}ZnHPO_3$. Figure 2 shows that three types of weak, secondary (compared to strong, well-defined covalent bonds) bonding interaction define the way that the 4.8^2 sheets stack: N−H$\cdots$O hydrogen bonding between adjacent, pendant organic groups occurs in the [011] direction, pseudo-π−π stacking between creatinine rings in the $[01\bar{1}]$ direction, and van der Waals’ forces in the [100] (sheet stacking) direction. Rationalizing the interplay of such subtle and relatively weak chemical forces represents a major challenge in terms of predicting and understanding these types of materials.

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

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