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Structural Diversity in 4,4′-Trimethylenedipyridine–zinc phosphite Hybrids: Incorporation of Neutral Guest Molecules in Hybrid Materials

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Six new zinc phosphite hybrids are prepared under a variety of reaction conditions from the primary building blocks, trimethylenedipyridine, zinc acetate, and phosphorous acid. Neutral guest molecules are incorporated into several of the structures. Under hydrothermal conditions at 130 °C, an anionic framework structure, **1**, templated on trimethylenedipyridinium, is obtained while a neutral ladder structure, **2**, is formed at room temperature. These reactions are done at an initial pH of 4.7–5.0. When the reaction is done at an initial pH of 7.8–8.0, a neutral layered motif is obtained with 1,3-dipyridylpropane pillars and neutral guests in the interstitial space. Structures with water, phenol, and catechol as the guests, compounds **3**, **4**, and **5**, respectively, are reported. The use of catechol as a template results in the breakup of the ZnPO sheet structure common to both **3** and **4**. When amino acids, including alanine, were added to the reaction medium, a neutral three-dimensional framework, **6**, is obtained with no incorporation of the potential template. The syntheses and structures of these new materials are reported.

Introduction

Templated zinc phosphites exhibit a variety of three-dimensional architectures that reflect the versatility of the ZnPO system.[1−12] Typically, the pseudotetrahedral $(HPO_3)^{2-}$ anion is three-connected and the Zn^{2+} cation is four-connected in these framework structures. Fully connected (3,4) nets built from HPO_3^{2-} and Zn^{2+} have the stoichiometry $3Zn^{2+}$:$4(HPO_3)^{2-}$ and a net anionic charge that requires extra framework cations as templates.[13] Hybrid frameworks form when one or more coordination site at zinc is occupied by a ligand other than $(HPO_3)^{2-}$, and the resulting structures are typically neutral with a composition of $1L$:$1Zn^{2+}$:$1(HPO_3)^{2-}$.[14] The role of L, either as a template or a ligand, is likely to be dictated by temperature, pH, and ligand basicity. At low pH, a nitrogen base may be more likely to adopt the role of a template in determining a three-dimensional structure, while at higher pH, the nitrogen base may act as a ligand to form a hybrid structure. The simple equilibrium represented in eq 1 is clearly important in determining the role of the ligand in the synthesis of hybrid structures.

$$Zn^{2+} + LH^{+} = ZnL^{2+} + H^{+} \tag{1}$$

In a recent example from the literature, the piperidinium ion, $(C_5H_{12}N)^+$, templates zinc phosphite to give a framework structure of composition, $(C_5H_{12}N)_2Zn_3(HPO_3)_4$.[9] The frame-

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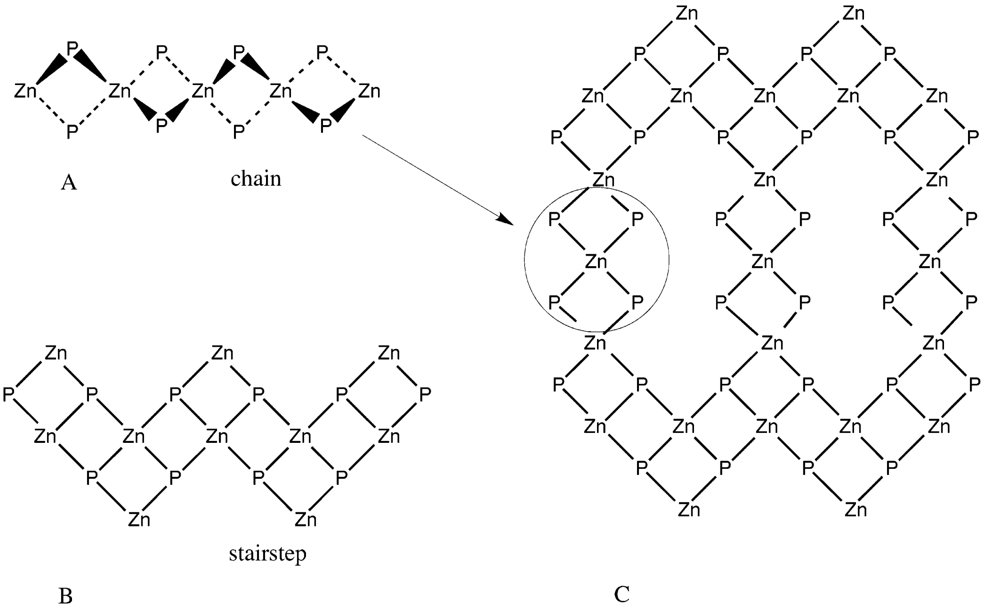
Scheme 1. (A and B) Schematic Representation of the Perpendicular Chain Motifs in $(NC_5H_{12})_2Zn_3(HPO_3)_4$[9] and (C) Combination of Chains to Give 16-Rings



work, which contains 16 rings, can be envisioned as being formed from $Zn(HPO_3)_2^{2-}$ chains and perpendicular $Zn(HPO_3)$ stair steps (Scheme 1). Both the anionic chain[15] and the stairstep[16] are common motifs in ZnPO structural chemistry. The resulting 16-ring channels are filled with piperidinium ions.

Piperazinium also templates zinc phosphite to give a framework of composition $(C_4H_{12}N_2)_{0.5}Zn_3(HPO_3)_4 \cdot H_3O$.[8] This structure is built from similar $Zn(HPO_3)_2^{2-}$ chains that pillar neutral $Zn(HPO_3)$ sheets that have the 4.8^2 topology,[17] another common structural motif in these materials. The pillars are anchored to nearest-neighbor zinc atoms to give 12-ring channels. Alternatively, piperazine templates a related composition, $(C_4H_{12}N_2)Zn_3(HPO_3)_4$,[2] in which $Zn(HPO_3)_2^{2-}$ chains occur in the structure. When zinc phosphite is templated in the presence of propylamine, neutral sheets of the 4.8^2 topology again form. These are also pillared by $Zn(HPO_3)_2^{2-}$ chains to give 12-ring channels,[1] which are filled with propylammonium cations.

Imidazole ligands typically bind zinc to form hybrid structures[16,18] although examples are known in which the imidazole group acts as both ligand and template.[19] Chelating ligands, such as 2,2′-bipyridine, commonly coordinate to give molecular structures or hybrids.[20−22] Bridging dipyridine ligands, such as 4,4′-bipyridine, have recently been used to construct a variety of hybrid solids including pillared layered structures.[11] The use of dipyridines that have structural flexibility, such as 4,4′-trimethylenedipyridine, leads to a variety of metal−organic framework structures.[23,24]

Here we report that 4,4′-trimethylenedipyridine, TMDP, reacts with zinc phosphite to form a pillared framework structure with a new 16-ring topology at high temperature and diprotonated ligand as the template. In contrast, at low temperature or at higher pH, hybrid structures are formed in which the ligand binds directly to zinc. Significantly, the neutral guest molecules, water, phenol, and catechol, may be incorporated into the framework under some reaction conditions.

Experimental Section

Materials and Measurements. All commercially available chemicals are of reagent grade and used as received without further purification. Elemental analyses of C, H, and N were performed by Galbraith laboratories, Inc. Thermogravimetric measurements were performed on a TGA Q500 thermal analyzer under flowing N_2 with the heating rate of 10 °C min^{-1}. TGA traces for all samples are included as Supporting Information.

$(4,4'-(C_5H_4N)_2(CH_2)_3)Zn_3(HPO_3)_4$, 1. Zinc acetate dihydrate (220 mg, 1.0 mmol), phosphorous acid (164 mg, 2.0 mmol), $4,4'-(C_5H_4N)_2(CH_2)_3$ (300 mg, 1.5 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was placed in an oven for 10 days at 130 °C. The sample contained crystals of **1** and a microcrystalline solid which were collected by filtration. The bulk sample did not give satisfactory results from elemental analysis. A comparison of the calculated powder diffraction pattern and the experimental powder pattern (Supporting Information) show that the most of the material is an unidentified phase. The TGA of a manually separated crystalline sample of **1** shows a 2.2% weight loss by 200 °C, up to 400 °C an additional

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Table 1. Crystal Data and Structure Refinement Parameters for **1**−**5**

	1	**2**	**3**
empirical formula	$C_{6.5}H_9NO_6P_2Zn_{1.5}$	$C_{26}H_{42}N_4O_{17}P_4Zn_4$	$C_{13}H_{22}N_2O_9P_2Zn_2$
fw	358.15	1068.0	543.01
T/K	100	100	100
space group	*Pccn*	*C2/c*	*Pccn*
a/Å	10.1034(7)	23.860(4)	9.6220(14)
b/Å	25.1550(16)	5.1324	24.389(4)
c/Å	9.1040(6)	32.021(5)	8.4590(11)
α/deg			
β/deg		97.364(12)	
γ/deg			
V/Å^3	2313.8(3)	3888.9(10)	1985.1(5)
Z	8	4	4
μ/mm^{-1}	3.425	2.678	2.627
R1^a [$I > 2s(I)$]	0.0322	0.0513	0.0310
wR2^b [$I > 2s(I)$]	0.1150	0.0905	0.0708

	4	**5**	**6**
empirical formula	$C_{19}H_{22}N_2O_7P_2Zn_2$	$C_{38}H_{42}N_4O_{10}P_2Zn_2$	$C_{13}H_{18}N_2O_7P_2Zn_2$
fw	583.07	907.4	506.97
T/K	100	100	100
space group	*Pnma*	*Pna*2$_1$	*C2/c*
a/Å	9.9947(3)	18.0264(5)	16.6901(10)
b/Å	23.8866(9)	12.4289(3)	14.9412(9)
c/Å	9.5533(11)	17.6357(11)	16.0256(10)
α/deg			
β/deg			117.730(6)
γ/deg			
V/Å^3	2280.7(3)	3951.3(2)	3537.3(4)
Z	4	4	8
μ/mm^{-1}	2.287	1.357	2.933
R1^a [$I > 2s(I)$]	0.0329	0.0345	0.0225
wR2^b [$I > 2s(I)$]	0.0667	0.0690	0.0584

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

6.2% weight loss is observed, and from 430 to 500 °C the sample loses 25% for a total weight loss of 35%. The material is a glassy black solid after being heated to 500 °C. The templating ligand corresponds to 27% of the mass of the sample. Selected IR bands: 3443(b), 3041(w), 3015(w), 2945(w), 2865 cm^{-1}(w).

(4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2\cdot 2.5H_2O$, 2. Zinc acetate dihydrate (220 mg, 1.0 mmol), phosphorous acid (164 mg, 2.0 mmol), 4,4′-$(C_5H_4N)_2(CH_2)_3$ 300 mg, 1.5 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was left at room temperature for 2 weeks during which time crystals of **2** formed. The crystals were collected by filtration. Yield 240 mg, 90% based on zinc acetate. Selected IR bands: 3094(w), 3061(w), 2966(w), 2608 cm^{-1}(b). Anal. Calcd for (4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2$: C, 31.90%; H 3.30%; N 5.53%; found (for a dried sample): C 31.14%; H 3.55%; N 5.52%. The TGA of a fresh sample of **2** shows a weight loss of 8.2% from 25 to 150 °C; the calculated value for loss of water is 8.4%. Further heating results in an additional loss of 19.1% by 350 °C.

(4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2\cdot 3H_2O$, 3. Zinc acetate dihydrate (220 mg, 1.0 mmol), phosphorous acid (164 mg, 2.0 mmol), 4,4′-$(C_5H_4N)_2(CH_2)_3$ (300 mg, 1.5 mmol), NaOH (60 mg, 1.5 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was left at room temperature for 1 week during which time crystals of **3** formed. Yield 230 mg, yield 85% based on zinc acetate. Selected IR bands: 3333(b), 2972(w), 2865 cm^{-1}(w). Anal. Calcd for (4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2$: C, 31.90%; H 3.30%; N 5.53%; found (for a dried sample): C 31.52%; H 3.42%; N 5.56%. A freshly prepared sample of **3** loses 10.3% of its mass in the TGA from 25 to 100 °C (calcd for three water molecules 9.9%). The material is stable until 420 °C. At 500 °C, it loses a total of 38% of its mass to yield a glassy black solid.

(4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2\cdot$phenol, 4. Zinc acetate dihydrate (220 mg, 1.0 mmol), phosphorous acid (164 mg, 2.0 mmol), 4,4′-$(C_5H_4N)_2(CH_2)_3$ (300 mg, 1.5 mmol), NaOH (80 mg, 1.5 mmol), phenol (188 mg, 2 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was left at room temperature for 1 week during which time crystals of **4** formed. Selected IR bands for the crystals: 3295(b), 3060(w), 3045(w), 3018(w), 2990(w), 2929(w), 2861(w), 2706(w), 2608 cm^{-1}(w). The bulk sample did not give satisfactory results for elemental analysis; however, a comparison of the calculated powder diffraction pattern and the experimental powder pattern for the material (Supporting Information) shows that the bulk of the isolated solid is compound **4**. A crystalline sample continuously loses mass in the TGA from 25 to 500 °C until 50% of the mass remains.

(4,4′-$(C_5H_4N)_2(CH_2)_3$)$_2Zn_2(HPO_3)_2\cdot$(catechol)$_2$, 5. Zinc acetate dihydrate (220 mg, 1.0 mmol), phosphorous acid (164 mg, 2.0 mmol), 4,4′-$(C_5H_4N)_2(CH_2)_3$ (297 mg, 1.5 mmol), catechol (220, 2 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was left at room temperature for 1 week during which time crystals of **5** formed. Selected IR bands from a crystalline sample: 3490(m), 3205(b), 3095(w), 3062(m), 2950(m), 2932(m), 2862(m), 2695 cm^{-1}(m). The bulk sample did not give satisfactory results for elemental analysis. A comparison of the calculated powder diffraction pattern and the experimental powder pattern (Supporting Information) show that the bulk of the material is an unidentified phase. A crystalline sample continuously loses mass in the TGA from 25 to 500 °C until 45% of the mass remains.

(4,4′-$(C_5H_4N)_2(CH_2)_3$)$Zn_2(HPO_3)_2(H_2O)$ 6, Zinc acetate dihydrate (219.5 mg, 1.0 mmol), phosphorous acid (164.0 mg, 2.0 mmol), 4,4′-$(C_5H_4N)_2(CH_2)_3$ (297 mg, 1.5 mmol), NaOH (80 mg, 2.0 mmol), alanine (180 mg, 2.0 mmol), and 6 mL of water were added to a heavy-walled glass tube and sealed under vacuum. The tube was left at room temperature for 1 week during which time crystals of **6** formed. Yield 235 mg, 96% based on zinc acetate. Selected IR bands: 3660(b), 3443(b), 3042(w), 2988(w), 2946(w), 2901 cm^{-1}(w). Anal. Calcd for $(4,4'\text{-}(C_5H_4N)_2(CH_2)_3)Zn_2(HPO_3)_2(H_2O)$: C, 30.80%; H 3.55%; N 5.52%; found: C 31.33%; H 3.47%; N 5.63%. In the TGA 2.6% weight loss is observed up to 200 °C. This roughly corresponds to loss of coordinated water, 3.6%. From 250 to 350 °C, an additional 9.0% weight loss is observed, and from 430 to 500 °C, the sample loses additional mass until 63% of the mass remains.

Crystallographic Analyses. Low-temperature (100 K) single-crystal X-ray diffraction measurements for complexes **1**−**6** were collected on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector. Crystals were mounted on a nylon CryoLoop (Hampton Research) with Krytox Oil (DuPont). The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.[25] The structures were solved by SHELXTL-NT[26] and refined by full-matrix least-squares. The final refinements involved an anisotropic model for all non-hydrogen atoms. A summary of all crystallographic data is given in Table 1. Thermal ellipsoid plots with numbering schemes are included in the Supporting Information. Details for the crystallographic determination of each compound are given in the Supporting Information.

Results and Discussion

Synthesis. Our typical synthetic protocol for the preparation of hybrid materials is to charge a heavy-walled glass tube with reactants and water, freeze the system, evacuate, and seal with a flame. The sealed tube is then placed in an oven at 130 °C for up to 10 days. Upon cooling, the tubes are examined and crystalline product, if any, is collected by filtration. This procedure, with TMDP as the ligand component, leads to an anionic framework structure, **1**, similar to other templated zinc phosphite systems.[8,9] (The structures are described in the subsequent section.) In several instances, imperfections in the sealed glass tube precluded subjecting the sample to elevated temperatures, and after 1−2 weeks, these tubes also yielded a crystalline product. Compound **2** has a two-dimensional neutral motif of zinc phosphite ladders bridged by the bifunctional ligand (see below). The quality of these crystals varied from tube to tube, and we speculated that the synthesis of **2** could be improved at higher pH to give zinc a chance to compete more effectively for the ligand. However, in reactions in which the initial pH is adjusted to 7.8−8.0 by the addition of NaOH, yet another structure, **3**, is obtained. This material is best described as a pillared layer structure with the TMDP acting as the pillar. Hydrogen-bonded chains of water fill the channels.

Interestingly, when phenol is added to the reaction medium, we find that it completely replaces water as the pore-filling guest. This structure, **4**, again has TMDP pillars, although in a different configuration than observed in **3**. The phenol guest is disordered in the structure in such a way to suggest that catechol could occupy the same space in the lattice. When catechol is added as a potential guest, however, we find that it disrupts the formation of the characteristic 4.8^2 sheets by forming strong hydrogen bonds with the P═O group of phosphite.

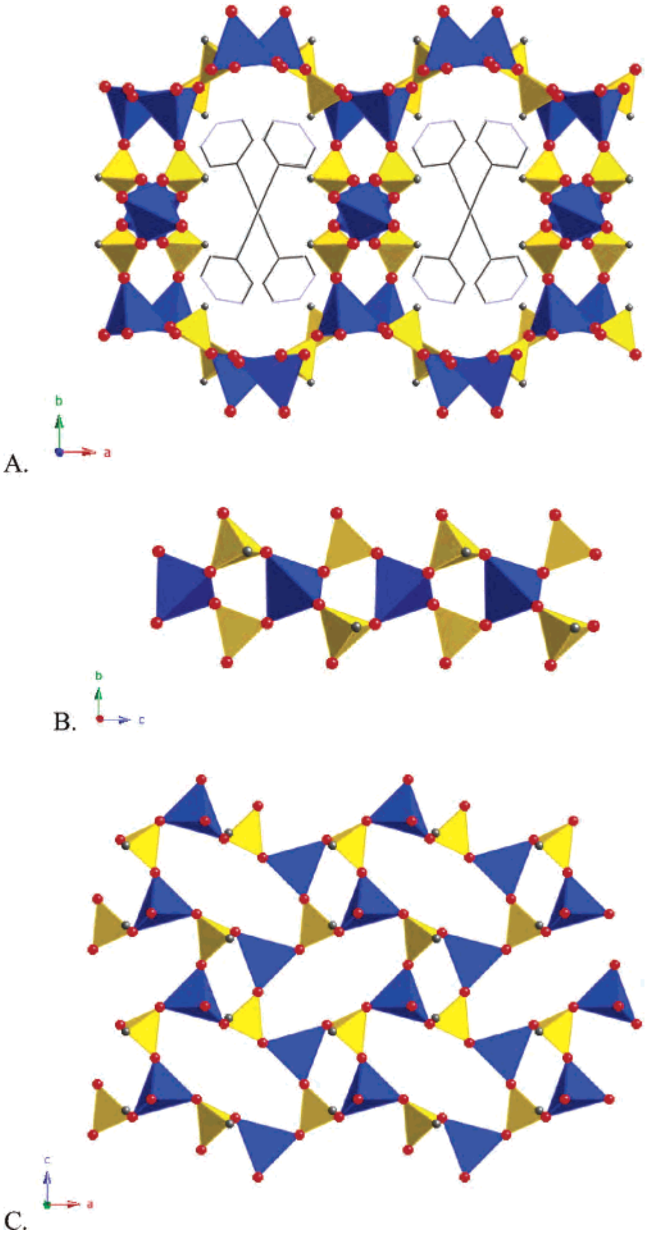

Figure 1. Schematic representations of the structure of **1**. Zinc, blue tetrahedra; phosphorus, yellow tetrahedra. Oxygen atoms are represented as red circles, and the protonated TMDP ligand is drawn in stick form. (A) Packing diagram view down the 16-ring channels filled with protonated TMDP. (B) View of the $[Zn(HPO_3)_2]^{2-}$ chain that serves as the pillar in **1**. (C) Projection of the 4.8^2 sheet onto the *xz* plane.

Attempts to incorporate other guests such as the amino acids, alanine, phenylglycine, and serine, resulted in yet another new structure, **6**, that does incorporate any guests and has a neutral inorganic framework interwoven by polymeric chains of Zn(TMDP). One factor in generating structure **6** may be an initial reaction pH of 5.8, although we observe that the catechol structure is obtained at room temperature over a pH range of 4.8−8.

Description of the Crystal Structures. Thermal ellipsoid plots for each compound, **1**−**6**, are deposited as Supporting

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Table 2. Hydrogen-Bonding Contacts in **1**−**5**

1		2		3		4		5	
N1−O5	2.721(3)	O7−O9	2.815(6)	O4−O5	2.809(3)	O4−O2	2.875(5)	O6−O8	2.736(5)
N1−H1B−O5	169[a]	O7−O9	2.799(7)	O5−O4	2.821(3)	O4−H4−O2	150[a]	O6−O10	2.638(4)
		O7−O9	2.890(6)	O5−O3	2.805(3)			O3−O9	2.772(5)
		O9−O2	2.779(6)	O4−H4B−O5	152(7)			O3−O7	2.648(4)
		O8−O4	2.837(5)	O5−H5B−O4	166(4)			O7−O8	2.673(5)
		O7−H7E−O9	169(6)	O5−H5B−O3	172(3)			O6−H8C−O8	150[a]
		O7−H7F−O9	176(8)					O6−H10A−O10	163[a]
		O9−H9B−O7	155(8)					O3−H9C−O9	147[a]
		O9−H9A−O2	158(8)					O3−H7−O7	164[a]
		O8−H8E−O4	156(5)					O7−H8−O8	114[a]

[a] No esd is given because the hydrogen-bond positions in these compounds were calculated and not refined.

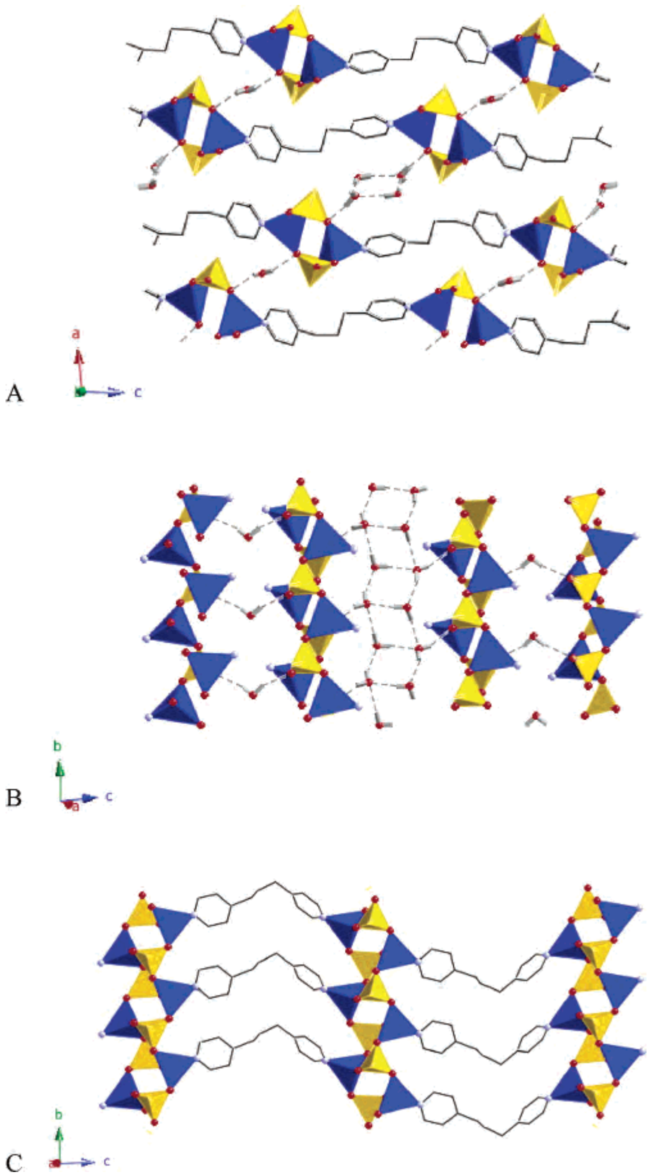

Figure 2. Three views of the structure of **2**. (A) A side-on view of the stacking of the two-dimensional hybrid sheets. The layers are separated, alternatively, by isolated water molecules and a chain of hydrogen-bonded waters. (B) A view of the layer formed by the Z$_2$P$_2$ ladders and the hydrogen-bonded water molecules. (C) A view of the two-dimensional hybrid sheets formed from Zn$_2$P$_2$ ladders and the bridging TMDP ligands.

Information. Crystallographic data for compounds **1**−**6** are given in Table 1.

The framework of **1** is shown in Figure 1. The structure consists of puckered 4.8^2 sheets of composition, Zn(HPO$_3$), and inorganic zinc phosphite chains that serve as pillars (parts C and B of Figure 1, respectively). Each zinc atom in the 4.8^2 layer serves as an anchor point for a pillar to the next layer. Within an eight ring, alternating zinc atoms support pillars to the same side of the 4.8^2 layer. The pillars consist of Zn(HPO$_3$)$_2^{2-}$ chains. The resulting structure has 16-atom channels and a net framework composition of Zn$_3$(HPO$_3$)$_4^{2-}$. The TMDP ligand is diprotonated and fills the 16-ring channels (Figure 1A); the dipyridinium ions are hydrogen bonded to oxygen atoms in the framework that are 13.8 Å apart. (Hydrogen-bonding parameters for all the structures are given in Table 2.) The phosphite hydrogen atoms are directed toward the inside of the channels and define a rectangle of dimension 6.8 Å × 10.1 Å. Thus, the templates

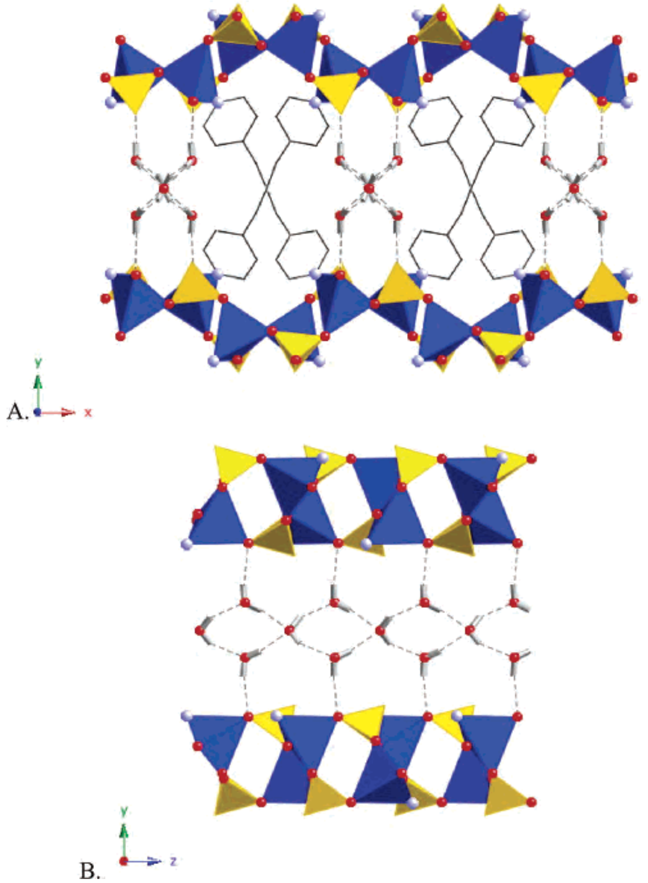

Figure 3. (A) View down the channels formed in **3** from the 4.8^2 layers and the TMDP pillars. Zinc atoms are represented in dark blue, phosphorus in yellow, oxygen in red, and nitrogen in light blue. Water fills the channels. (B) A view parallel to hydrogen-bonded chain of water molecules that fills the channels.

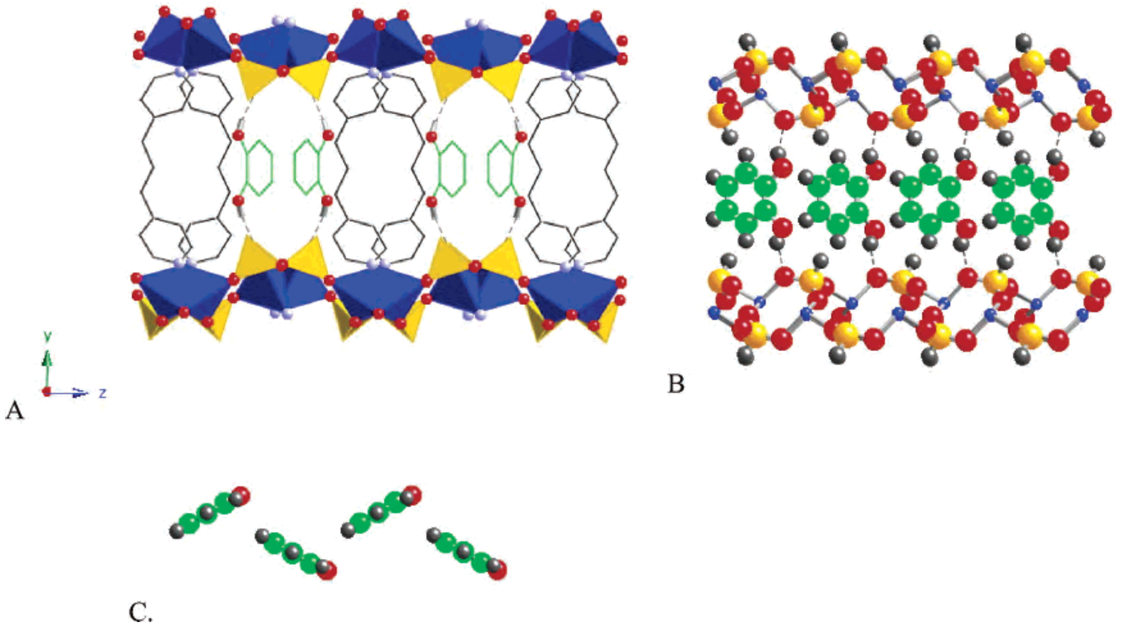

Figure 4. (A) View down the channels formed in **4** from the 4.8^2 layers and the TMDP pillars. Zinc atoms are represented in dark blue, phosphorus in yellow, oxygen in red, and nitrogen in light blue. Phenol fills the channels. (B) A view parallel to the molecular wire of phenols. The orientation of the phenol is disordered; each oxygen position is 50% occupied. The phenol oxygen is alternatively hydrogen bonded to the upper and lower zinc phosphite layers. (C) A view orthogonal to the view in B to show the C−H−π interaction in the phenol chain.

occupy cavities within the channels that are larger than the channel opening.

The structure of **2** is shown in Figure 2; the composition is $(4,4'\text{-}(C_5H_4N)_2(CH_2)_3)Zn_2(HPO_3)_2{\cdot}2.5H_2O$. One-dimensional ladders of $Zn(HPO_3)$ are connected by 1,3-dipyridylpropane ligands to form two-dimensional hybrid sheets, as shown in Figure 2C. The neutral sheets are separated by interlayer water molecules, as shown in Figure 2A as viewed down the $Zn_2(HPO_3)_2$ ladders. The stacking arrangement can be described as $1A{:}4H_2O{:}1B{:}1H_2O$ where A and B refer to different orientations of the two-dimensional sheets. The stoichiometry is five water molecules per two Zn_2P_2 four-rings and the layers are separated, alternatively, by isolated water molecules and a chain of hydrogen bonded water molecules. The water molecules and the $Zn_2(HPO_3)_2$ ladders form a hydrophilic sheet connected by hydrogen bonds, as shown in Figure 2B.

Efforts to generate **2** by performing the reaction at higher pH led to the formation of a new compound, **3**. The structure of **3** is similar in some respects to the structure of **1**. Specifically in **3**, neutral 4.8^2 sheets are pillared by TMDP groups that bridge zinc atoms in adjacent layers whereas in **1** the 4.8^2 sheets are pillared by inorganic $(Zn(HPO_3)_2)^{2-}$ chains (compare Figures 3A and 1A.) The resulting interstitial space between pillars is quite large and accommodates a chain of hydrogen-bonded water molecules. The distance between closest phosphite hydrogen atoms in adjacent layers is 8.130 Å, and the distance between closest oxygen atoms is 9.244 Å. A view of the hydrogen-bonded chain of water molecules is given in Figure 3B. One water molecule is connected by hydrogen bonds to four water molecules in a tetrahedral arrangement, and the other crystallographically unique water molecule is connected to two water molecules in the chain and is a hydrogen-bond donor to the zinc

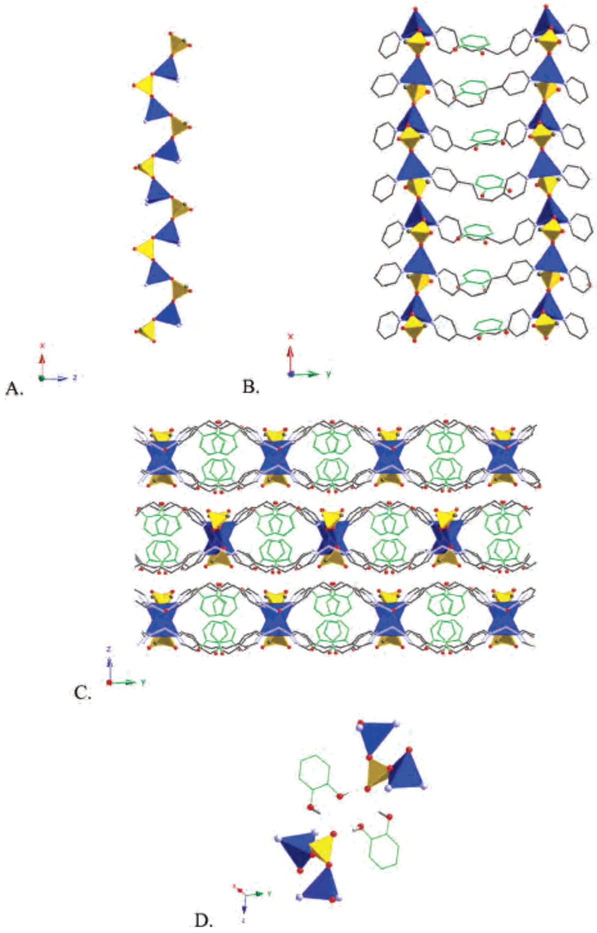

Figure 5. (A) View of the one-dimensional ZnPO chains. (B) A view of the hybrid sheet formed from the ZnPO chains linked by the TMDP ligands. (C) A view of the stacking of the hybrid sheets. The catechol ligand is shown in green. This projection gives the impression of a hydrophobic cavity. (D) A representation of the hydrogen-bonding contacts between two catechols and two phosphites.

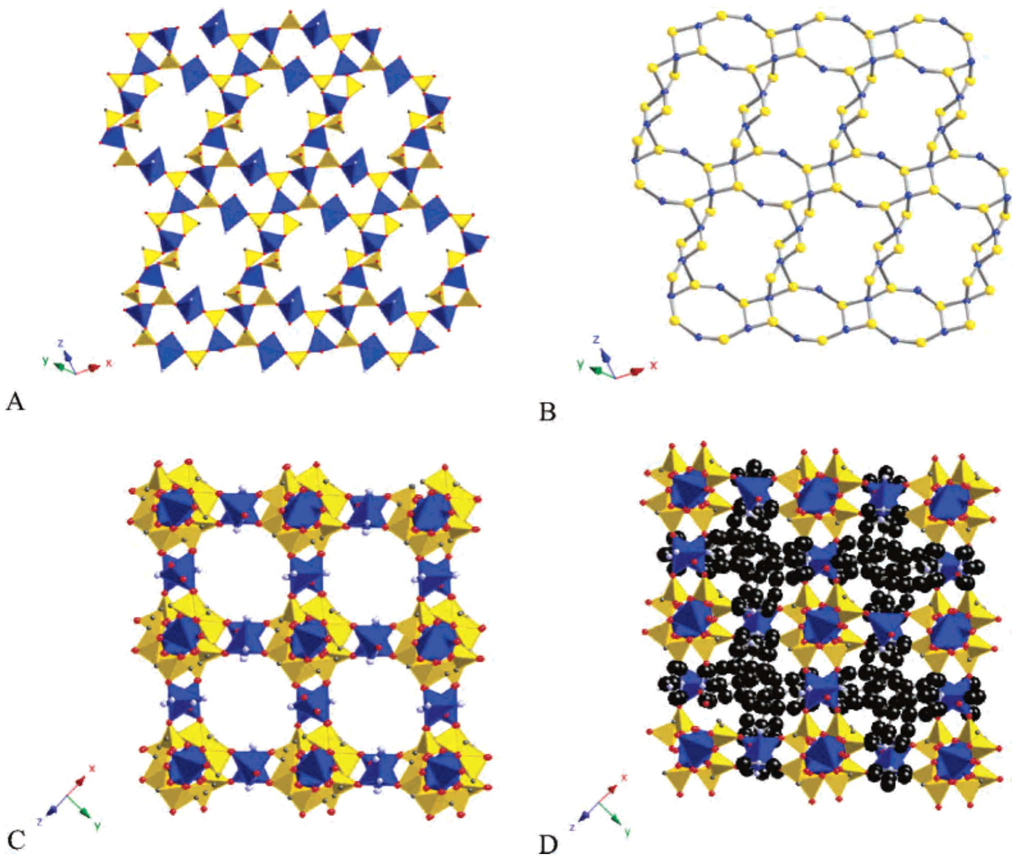

Figure 6. (A) View of one of two identical orthogonal sheets of zinc phosphite in **6**. Zinc atoms are represented in dark blue, phosphorus in yellow, and oxygen in red. (B) An alternative representation of the view in (A) in which only the zinc and phosphorus positions are shown. The sheet structure is formed from intersecting 4-ring chains and 4.8 ladders to give 16-rings. (C) A view that shows the intersection of the sheets represented in (A) to give new 16-rings. (D) An identical projection of the structure of **6** as given in (C) with the carbon atoms of the TMDP ligand added to show the hybrid composite formed by TMDP and zinc phosphite.

phosphite sheet. The oxygen−oxygen distances between hydrogen-bonded water molecules within the chain are in the range 2.799−2.889 Å, and the closest distance between oxygen atoms of water and phosphite oxygen is 2.837 Å. The TGA shows that water can be removed under relatively mild conditions. A nitrogen BET surface area measurement on a sample of **3** dried at 120 °C gives a nominal surface area of 5.2 m^2 g^{-1}. This value suggests that the pores vacated by water collapse upon dehydration. A similar structure, with 4,4′-bipyridine as the organic pillar, has recently been reported.[11]

As noted above, when the synthesis of **3** is conducted in the presence of phenol as a potential alternative guest, we find that phenol is preferentially incorporated into the structure to give **4** (Figure 4). The incorporation of a neutral molecule other than water or solvent is rare in the preparation metal−organic frameworks. [27] Although, the neutral 4.8^2 layer pattern is retained, these sheets are flatter than in either **1** or **3**. As in **3,** the TMDP ligand serves as a pillar between adjacent ZnPO layers. The propane portions of the pillars are more parallel, and the pyridine bonds into the concave rather than the convex portion of the ZnPO layer. The nearest-neighbor phosphite hydrogen atoms between layers are 6.755 Å apart, and the distance between closest oxygen atoms is 8.614 Å. Thus, the layers are closer together than in **3**. The pillars define channels in the structure that are filled with phenol. The phenol is disordered with half the OH groups directed toward one layer and the other half directed toward the adjacent layer. The projection of phenol shown in Figure 4 thus looks like catechol. (Catechol, however, leads to a different ZnPO structure, as shown below.) The phenol guests line up to form a molecular wire with nearest-neighbor C−C distances of 3.767 Å. The closest distance between phenol oxygen and ZnPO oxygen is 2.881 Å. Similar molecular wires have been proposed to form upon the impregnation of nitroaniline into the noncentrosymmetric zeolite, ALPO-5.[28,29]

As noted above, the disorder of phenol in **4** suggests that catechol could fit in the same space. Catechol is indeed incorporated as a guest into a hybrid structure of all the reaction components; however, the catechol group disrupts the formation of the 4.8^2 sheets by strongly hydrogen bonding to the P═O group. Thus, the phosphite is only two-connected in the structure; this limits the connectivity of ZnPO to two dimensions. Zinc is also two connected in the ZnPO portion of the structure with the remaining two coordination sites occupied by nitrogen from the TMDP ligand. The ZnPO

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chains are shown in Figure 5A; these chains can be visualized as being ‘cut’ from a 4.8^2 sheet. The connection of these chains into sheets linked by TMDP is shown in Figure 5B, and the stacking of sheets is shown in Figure 5C. The projection of the stacked sheets gives the impression of cavities that hold the catechol guests. The sheets, however, are simply wavy, and the catechol is tucked into the trough of the wave; the hydrophobic portion of the catechol is directed toward the propyl backbone on the TMDP ligand, and the hydroxy groups are directed toward the phosphite of an adjacent sheet. The nearest-neighbor oxygen contacts between catechol and phosphite are shown in Figure 5D. The hydrogen bonding is limited to islands of two catechols and two phosphites and does not extend through the entire structure. Catechol is reported to cocrystallize with 2-hydroxylphenyl phenylphosphonate; in these structures, catechol and the phosphonate, which has two hydrogen bond acceptors, form a chain that extends throughout the structure.[30]

Different views of the structure of **6** are shown in Figure 6. The structure is comprised of identical intersecting sheets, shown in Figure 6A and B to give a square motif, as shown in Figure 6C. The sheets are constructed from anionic $Zn(HPO_3)_2^{2-}$ chains connected by Zn^{2+} ions to give a layer that contains 4-rings, 8-rings, and 16-rings. The zinc atoms in the chains, Zn2, are tetrahedrally coordinated to four phosphite oxygen atoms; the zinc that connects the chains, Zn1, has a distorted trigonal bipyramidal geometry. Zinc(1) is bonded to two phosphite oxygen atoms, two nitrogen atoms from different TMDP ligands, and one water oxygen atom (this water position is fractionally occupied according to the disorder model used to refine the structure.) One nitrogen atom and the water molecule are in the axial position with an N−Zn−O angle of 166.12°. The equatorial atoms, N2, O6, and O2, are nearly coplanar with angles of 115.69°, 120.26°, and 115.10°. The TMDP ligands and Zn2 combine to make TMDP −Zn chains that extend through the entire structure. The TMDP ligands completely fill the pores of the neutral ZnPO framework. A view of the composite ZnPO framework interwoven with ZnTMDP polymers is shown in Figure 6C.

Conclusion

Zinc phosphite hybrids constructed with the flexible linker trimethylenedipyridine form a wide variety of framework structures. These hybrid structures are unique in their ability to incorporate neutral guest molecules that have hydrogen-bond donor capacity. With a different ligand, the systems may have the potential to incorporate small-molecule pharmaceuticals including chiral guests. If chiral groups could be incorporated, it may be possible to induce the formation of enantiopure helical ZnPO chains in a hybrid structure.

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Supporting Information Available: X-ray crystallographic files, in CIF format, ORTEPs for compounds **1**−**6**, and TGA plots for compounds **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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