Inorg. Chem. **2006**, *45*, 977–986

Inorganic Chemistry

Article

Rational Design and Synthesis of Porous Organic–Inorganic Hybrid Frameworks Constructed by 1,3,5-Benzenetriphosphonic Acid and Pyridine Synthons

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Received June 9, 2005

1,3,5-Benzenetriphosphonic acid, H_6BTP, 1,3,5-$[(HO)_2OP]_3C_6H_3$, was reacted hydrothermally with copper salts in the absence and presence of 4,4′-bipyridine (bpy) and 4,4′-trimethlyenedipyridine (tbpy) in a 1:1 molar ratio leading to three new organic–inorganic hybrid frameworks. Compound **1**, $\{Cu_6[C_6H_3(PO_3)_3]_2(H_2O)_8\}\cdot 5.5H_2O$, has three different copper ions that are interconnected by the highly charged $[1,3,5\text{-}(PO_3)_3C_6H_3]^{6-}$ anionic moieties. These moieties self-assemble through tetra-copper units to give a cagelike motif with two benzene rings parallel to each other at a distance of 3.531 Å which extend along the *a* axis and link with a grouping of four-coordinated copper units in the *b* axis direction to give the cross-linked layered structure. In compound **2**, $Cu\{C_6H_3[PO(OH)O]_2[PO(OH)_2]\}(C_{10}H_8N_2)$, the copper ions are in square pyramidal geometries and are interconnected via chelating and bridging BTP ligands into layers which are further cross-linked by bpy ligands into a pillared layered architecture. Compound **3**, $\{Cu_2C_6H_3[PO(OH)O]_2[PO_3](C_{13}H_{14}N_2)\}\cdot 3H_2O\cdot 0.5HCON(CH_3)_2$, contains tetra-copper units that are linked by BTP ligands and further linked by tbpy linkers in the *c* axis direction to produce a large channel-sized 3D framework.

Introduction

In the hybrid material synthesis field, the predictable topologies and properties of synthesized frameworks are of considerable interest to researchers. Studies toward building predictable structures by optimizing synthetic conditions vary from acid−base organic salt to hybrid metal−organic frameworks (MOFs).[1−3] Researches have been focused on reasonable design and controlled synthetic conditions, as well as structural characterization of those hybrid materials.[4] Conceptually, the architecture of the hybrid frameworks are often composed of multidentate ligands which could serve as bridges toward multimetal centers. In this aspect, the use of 1,3,5-benzenetricarboxylic acid has been fully developed through use of the three binding sites (variable bidentate or monodentate properties of the carboxylic acid group). Other linear carboxylic acids also have been applied toward this principle with the aid of other small ligands, such as bipyridine molecules. Those hybrid materials are suitable for different applications.[5,6] The reactions of $C_6H_3(COOH)_3$ (also known as the trimesic acid, Scheme 1), a rigid planar molecule, with different organic bases have been extensively

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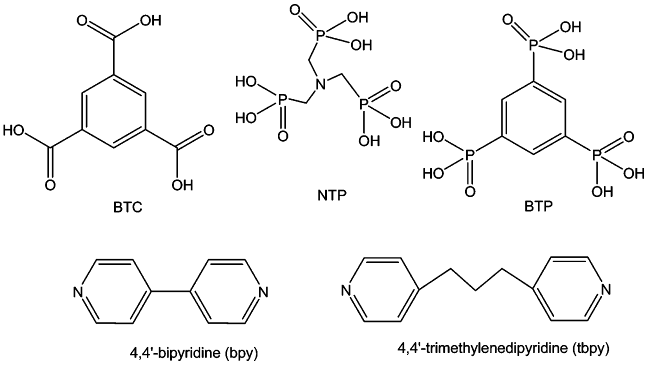
10.1021/ic0509377 CCC: $33.50 © 2006 American Chemical Society
Published on Web 01/10/2006

Scheme 1. Ligand Information



reported.[6−8] Because of its trigonal symmetry and complementary in-plane directional forces, trimesic acid tends to form multidimensional MOFs containing a large variety of metal centers especially with zinc. In particular, Prof. Yaghi's group reported on the hydrogen and methane storage properties of MOFs, which triggered the popularity of synthesis of discrete metal-carboxylate clusters with systematic variations in pore size and functionality. Surprisingly, its phosphorus-containing counterpart, the triphosphonic acid, 1,3,5-benzenetriphosphonic acid, has not been the subject of crystal engineering studies. There are only two reports on 1,3,5-$[(HO)_2OP]_3C_6H_3$, starting as late as 2002,[9] because of the synthetic difficulties of preparing this special ligand. This triphosphonic acid might function as a robust synthon for the construction of two/three-dimensional networks through the formation of strong hydrogen bonds. Most metal phosphonates based on nonfunctionalized monophosphonic acids, RPO_3H_2, and diphosphonic acids, $H_2O_3P{-}R{-}PO_3H_2$, adopt layered and pillared−layered structures.[10] We reported using nitrilotri(methylphosphonic acid) (Scheme 1) with various amines to produce aggregates showing three-dimensional hexagonal hydrogen bonding systems.[11] For its metal phosphonates, two different types of 1:1 (M/L) complexes have been isolated using various metal−ligand ratios in the synthesis, namely, $M[NH(CH_2PO_3H)_3(H_2O)_3]$ (M=Mn, Co, Ni, Cu, Zn, Cd) whose structures feature hydrogen-bonded 2D layers and dehydrated $Mn[NH(CH_2PO_3H)_3]$ whose structure is a 3D network. To explore the general idea for construction of a three-dimensional architecture with triphosphonic acid, BTP {1,3,5-benzene-triphosphonic acid, 1,3,5-$[(HO)_2OP]_3C_6H_3$} has been chosen as the building block. It certainly provides more binding sites for metal centers than the carboxylate group. Also the variable deprotonation of the ligand will provide more versatile building blocks. 4,4′-Bipyridine (bpy) and 4,4′-trimethylenedipyridine (tbpy) are good secondary linkers to develop interesting framework properties which have been widely used.[12] In this paper, we wish to report exploratory studies that produced three novel 3-dimensional copper−organic frameworks simultaneously incorporating H_nBTP^{n-6} residues and bipyridine ligands.

Experimental Section

Thermogravimetric (TG) analyses were carried out with a TGA Q500 from TA instruments, at a heating rate of 10 °C/min under an oxygen atmosphere. Infrared (IR) spectra were measured as KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer with spectral resolution of 2.00 cm^{-1}. ^1H, ^{31}P, and ^{13}C NMR spectra in solution were recorded on a Bruker Avance DRX 300 Hz instrument. Chemical shifts are given in parts per million. The infrared absorption spectrum of the ligand was measured on a Perkin-Elmer FT-IR 1600 spectrometer. SEM images were acquired at the Texas A&M University Microscopy and Imaging Center with a JEOL JSM-6400. Samples are prepared at the aluminum sample holder and coated with carbon. Starting materials with a purity of ca. 98% were obtained from Aldrich and used without any further purification.

Synthesis of the Ligand. Scheme 2 gives the synthetic route for 1,3,5-benzenetriphosphonic acid. Synthesis is according to the literature with modified conditions.[9]

Hexaethyl 1,3,5-benzenetriphosphonate (IIa). 1,3,5-Tribromobenzene (**I**, 6.30 g, 20 mmol) and 1,3-diisopropylbenzene (50 mL) were heated to 180 °C for 15 min under nitrogen. After the reaction mixture was cooled to room temperature, under nitrogen, nickel(II) bromide (1.00 g, 4.6 mmol) was added, and the reaction

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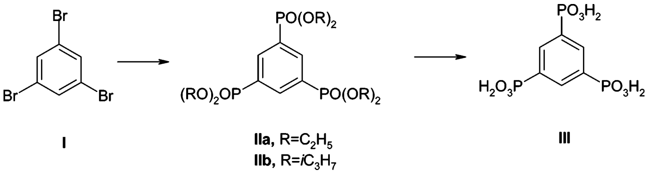
Scheme 2. Synthetic Route for H_6BTP



mixture was heated to 180 °C while stirring. Triethyl phosphite (15 mL, 87.5 mmol) was added dropwise at 175−180 °C during 5 h. The mixture was heated at the same temperature and stirred under nitrogen for the next 5 h. Then volatile components, including 1,3-diisopropylbenzene, were distilled off under reduced pressure to obtain a dark viscous residue. Chromatography of the residue was performed on a column of silica gel eluted with $CHCl_3$ (commercial chloroform containing 1% ethanol was used). Yield: 3.69 g (38%). Colorless liquid. R_f: 0.37 (silica gel plate with fluorescent indicator 254 nm; $CHCl_3/CH_3OH$ eluent, 10:1 v/v; visualization with UV lamp). Found: P, 18.83%. $C_{18}H_{33}O_9P_3$ (486.37) requires P, 19.10%. ^1H NMR (300 MHz, $CDCl_3$): δ 8.42−8.28 (m, 3H, C_6H_3), 4.24−4.00 (m, 12H, $POCH_2C$), 1.31 (t, $^4J_{PH} = 7$ Hz, 18H, $POCCH_3$). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ 17.01 (s).

Hexaisopropyl 1,3,5-benzenetriphosphonate (IIb). 1,3,5-Tribromobenzene (**I**, 3.30 g, 10 mmol) and 1,3-diisopropylbenzene (25 mL) were heated to 155 °C for 15 min under nitrogen. After the reaction mixture was cooled to room temperature, under nitrogen, nickel(II) bromide (0.38 g, 1.7 mmol) was added, and the reaction mixture was heated to 150°C while stirring. Triisopropyl phosphite (10.5 mL, 45.8 mmol) was added dropwise at 150 °C during 3 h. The mixture was heated at the same temperature and stirred under nitrogen for next 1 h. Then volatile components, including 1,3-diisopropylbenzene, were distilled off under reduced pressure to obtain a dark viscous residue. Chromatography of the residue was performed on a column of silica gel eluted with ethyl acetate. Yield: 1.68 g (28%) of a liquid which solidified at room temperature. mp: 50−52 °C. R_f: 0.09 (silica gel plate with fluorescent indicator 254 nm; $CH_3COOC_2H_5$; visualization with UV lamp). ^1H NMR (300 MHz, $CDCl_3$): δ 8.44−8.33 (m, 3H, C_6H_3), 4.82−4.67 (m, 6H, POCHC), 1.39 (d, $^3J_{HH} = 6.2$ Hz, 18H, $POCCH_3$), 1.25 (d, $^3J_{HH} = 6.2$ Hz, 18H, $POCCH_3$). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ 15.08 (s).

1,3,5-Benzenetriphosphonic Acid (III). Hexaethyl 1,3,5-Benzenetriphosphonate. IIa (3.14 g, 6.45 mmol), concentrated hydrochloric acid (20 mL), and distilled water (20 mL) were refluxed for 14 h. The hydrolyzed solution was evaporated to dryness. Then the residue was dissolved in distilled water (20 mL); the solution was decolorized with charcoal, and the filtrate was evaporated under reduced pressure to yield **III** as a white solid. Yield: 1.85 g (90%). IR (KBr, cm^{-1}): ν_{max} 3354, 3090, 2891, 2327, 1135, 1006, 942, 692, 537, 514, 472. ^1H NMR (300 MHz, D_2O): δ 8.11 (t, $^3J_{PH} = 13.7$ Hz). ^{31}P {^1H} NMR (121 MHz, D_2O): δ 14.72 (s). ^{13}C NMR (75 MHz,D_2O): δ 135.2 (t, $^2J_{PC} = 9.7$ Hz), 133.2 (dt, $^1J_{PC} = 181.0$ Hz, $^3J_{PC} = 12.6$ Hz).

Hexaisopropyl 1,3,5-Benzenetriphosphonate. IIb (2.25 g, 3.95 mmol), concentrated hydrochloric acid (30 mL), and distilled water (30 mL) were refluxed for 24 h. The hydrolyzed solution was evaporated to dryness. Then the residue was dissolved in distilled water (30 mL); the solution was treated with charcoal, and the filtrate was evaporated under reduced pressure to yield **III** as a white solid. Yield: 1.11 g (88%). IR (KBr, cm^{-1}): ν_{max} 3091, 2795, 2271, 1137, 1011, 943, 692, 537, 515, 473. ^1H NMR (300 MHz, D_2O): δ 8.23−8.12 (m). ^{31}P {^1H} NMR (121 MHz, D_2O): δ 14.71 (s). ^{13}C NMR (75 MHz, D_2O): δ 135.46−134.99 (m), 133.02 (dt, $^1J_{PC} = 181.6$ Hz, $^3J_{PC} = 12.7$ Hz).

Synthesis of the Copper Compounds. The general procedure for the synthesis of the copper compounds was as follows. Fifty milligrams (0.15 mmol) of 1,3,5-benzenetriphosphonic acid (abbreviated as BTP) was dissolved in 2 mL of water. $CuCl_2{\cdot}6H_2O$ or $Cu(ClO_4)_2{\cdot}6H_2O$ (0.15 mmol) and 0.15 mmol of organic bases [4,4′-bipyridine, $(C_5H_4N)_2$ and 4,4′-trimethylenedipyridine, $(C_5H_4N-CH_2CH_2CH_2-C_5H_4N)$] were dissolved in 2 mL DMF; then the two solutions were mixed. The solution was sealed into a Teflon-lined pressure vessel and heated at 150 °C for 24 h. After the mixture was cooled to room temperature, blue and deep-blue crystals were recovered. Crystals were recovered for all three compounds in ca. 70% yield based on the original copper amount.

Anal. for $\{Cu_6[C_6H_3(PO_3)_3]_2(H_2O)_8\}{\cdot}5.5H_2O$, **1**: C, 9.9; H, 1.72. Calcd: C, 11.54; H, 2.65.

Anal. for $Cu\{C_6H_3[PO_2(OH)]_2[PO(OH)_2]\}(C_{10}H_8N_2)$, **2**: C, 35.81; H, 2.40; N, 5.11. Calcd: C, 35.84; H, 2.42; N, 5.23.

Anal. for $\{Cu_2C_6H_3[PO_2(OH)]_2[PO_3](C_{13}H_{14}N_2)\}{\cdot}3H_2O{\cdot}0.5CH_3HCON(CH_3)_2$, **3**: C, 32.62; H, 3.79; N, 4.30. Calcd: C, 33.73; H, 3.94; N, 4.30.

X-ray Crystallography. Data collection (2.53° < θ < 24.27°) was performed at 110 K on a Bruker Smart CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation using a cold nitrogen stream (Oxford). Data reduction and cell refinement were performed with the SAINT program, and multiscan absorption corrections were applied.[13] Crystal structures were solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms.[14] The crystallographic data are summarized in Table 1. Table 2 lists the important bond distances in the three compounds. All bond distances and angles for the three compounds are deposited as Supporting Information. SHELXTL, Mercury, and Diamond software were used to visualize the structures.

Hydrogen atoms bonded to carbon and hydrogen atoms attached to O(3w) and O(8w) in compound **1** were located in difference Fourier maps and refined isotropically. The disordered O(1wb), O(2wa), and Cu(3A) atoms were refined isotropically. Cu(3) is disordered in two positions Cu(3) and Cu(3A) with a ratio of 3:1. The O(1w), O(2w), O(4w), and O(7w) water molecules were not assigned hydrogen atoms. The O(1w), O(2w), and O(7w) waters were disordered in two positions with the refinement of occupancies for each. Only the O(6w) and O(8w) atoms are fully occupied. The occupancy of the nondisordered O(3w), O(4w), and O(5w) atoms are in the range of 58−67%. When the crystal structure was treated by SQUEEZE for highly disordered lattice water molecules, 36 electrons per symmetrically independent part were found, which is close to the required value (40) for four lattice water molecules. The disordered parts are omitted from the diagrams of compound **1** except in Figure 1.

In compound **2**, all atoms are well positioned and fully occupied. There was no disorder. All hydrogen atoms were found from the final Fourier map.

In compound **3**, the pyridine rings of the tbpy are disordered in two positions with equal occupancy. The dihedral angle between those two planes is 28.5°. The trimethylene groups are also disordered in two positions with the final refinement of the occupancies of the C(9) and C(10) atoms. C(14), C(15), and O(7) of the disordered DMF solvent molecule and the disordered O(2w)

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Table 1. Crystal Data and Structure Refinement for Complexes **1**, **2**, and **3**

	1	**2**	**3**
mol formula	$\{Cu_6[C_6H_3(PO_3)_3]_2(H_2O)_8\}$ $\cdot 5.5H_2O$	$Cu\{C_6H_3[PO_2(OH)]_2[PO(OH)_2]\}$ $(C_{10}H_8N_2)$	$\{Cu_2C_6H_3[PO_2(OH)]_2[PO_3](C_{13}H_{14}N_2)\}$ $\cdot 3H_2O\cdot 0.5HCON(CH_3)_2$
fw	1248.13	535.75	729.97
cryst color, habit	blue, blocks	deep blue, needles	deep blue, platelets
dimensions (mm)	0.07 × 0.05 × 0.02	0.14 × 0.04 × 0.03	0.20 × 0.12 × 0.03
cryst syst	triclinic	triclinic	orthorhombic
a (Å)	10.022(2)	8.1224(11)	20.3854(16)
b (Å)	10.182(3)	8.4351(12)	7.9172(6)
c (Å)	10.619(3)	16.413(2)	17.7768(14)
α (deg)	72.983(4)	102.345(2)	90
β (deg)	62.182(4)	94.634(2)	90
γ (deg)	63.997(4)	113.694(2)	90
V (Å^3)	856.0(4)	988.3(2)	2869.1(4)
space group	$P\bar{1}$	$P\bar{1}$	$Pbam$
Z	1	2	4
ρ_{calcd} (g cm^{-3})	2.422	1.800	1.693
F(000)	609	542	1492
θ range (deg)	2.67−24.71	1.29−27.60	2.76−24.71
completeness to θ	97.9%	98.6%	99.5%
μ (mm^{-1})	4.055	1.403	1.716
T (K)	110(2)	110(2)	110(2)
λ (Å)	0.71073	0.71073	0.71073
reflns measured	7811	11840	13562
data/params	5805/296 $R_{int} = 0.0461$	4516/340 $R_{int} = 0.0392$	2524/263 $R_{int} = 0.0332$
Final R indices ($I > 2.0\sigma(I)$)	$R = 0.0446$, R_w=0.098	$R = 0.0356$, $R_w = 0.0764$	$R = 0.0539$, $R_w = 0.1490$
R indices (all data)	$R = 0.0644$, $R_w = 0.1049$	$R = 0.0475$, $R_w = 0.0808$	$R = 0.0633$, $R_w = 0.1593$
GOF on F^2	1.073	1.020	1.087
peak, hole (e Å^{-3})	1.016, −0.673	0.390, −0.501	1.652, −0.549

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, and **3**

			complex **1**[a]				
Cu(1)−O(2)	1.877(6)	Cu(1)−O(3)	1.921(7)	Cu(1)−O(4)	1.937(6)	Cu(1)−O(1)	1.937(6)
Cu(2)−O(9)	1.926(6)	Cu(2)−O(10)	1.932(5)	Cu(2)−O(5)	2.024(5)	Cu(2)−O(8w)	1.995(5)
Cu(2)−O(6w)	2.203(8)	Cu(3)−O(8)	1.889(7)	Cu(3)−O(6)	1.946(6)	Cu(3)−O(5w)	1.983(9)
Cu(3)−O(5)	2.039(4)	Cu(3)−O(7wa)	2.090(2)	Cu(3)−O(7wb)	2.243(1)	Cu(1)−O(3w)	2.648(6)
P(1)−O(8)#1	1.522(6)	P(2)−O(5)	1.550(5)	P(3)−O(4)#4	1.530(5)	P(2)−O(6)#3	1.524(7)
P(1)−O(3)#2	1.530(6)	P(2)−C(3)	1.792(9)	P(2)−O(10)#3	1.523(5)	P(3)−O(9)	1.532(5)
P(1)−O(2)	1.497(6)	P(1)−C(1)	1.797(8)	P(3)−O(1)	1.530(6)		
			complex **2**[b]				
Cu(1)−O(2)	1.960(2)	P(1)−O(2)	1. 505(2)	P(2)−O(4)	1.506(2)	P(3)−O(7)	1.4823(19)
Cu(1)−O(4)	1.967(2)	P(1)−O(1)	1.552(2)	P(2)−O(6)	1.517(2)	P(3)−O(8) 1	.558(2)
Cu(1)−N(2)	2.023(2)	P(1)−O(3)	1.520(2)	P(2)−O(5)	1.557(2)	P(3)−O(9)	1.5598(19)
Cu(1)−N(1)	2.042(2)	P(1)−C(11)	1.801(3)	P(2)−C(13)	1.799(3)	P(3)−C(15)	1.789(3)
Cu(1)−O(7)#1	2.192(2)						
O(2)−Cu(1)−O(4)	161.49(7)	O(2)−Cu(1)−O(7)#1	106.6(7)	O(4)−Cu(1)−N(1)	90.71(8)	O(4)−Cu(1)−O(7)#1	91.65(7)
O(2)−Cu(1)−N(2)	87.66(8)	N(2)−Cu(1)−O(7)#1	91.53(8)	N(2)−Cu(1)−N(1)	172.85(9)	N(1)−Cu(1)−O(7)#1	95.62(8)
O(4)−Cu(1)−N(2)	89.11(8)	O(2)−Cu(1)−N(1)	90.26(8)				
			complex **3**[c]				
N(1)−Cu(1)	2.022(4)	Cu(1)−O(1)	1.922(3)	Cu(1)−O(4)	1.932(3)	P(1)−O(1)	1.514(3)
Cu(1)−O(5)	2.076(2)	Cu(1)−O(1W)	2.248(3)	P(1)−O(2)	1.507(3)	P(1)−O(1)	1.571(3)
O(5)−Cu(1)#1	2.076(2)	P(2)−O(4)	1.512(3)	P(2)−O(4)#1	1.512(3)	P(2)−O(5)#2	1.547(4)
P(2)−C(4)#1	1.817(7)	P(2)−C(4)	1.817(7)	O(5)−P(2)#2	1.547(4)	P(1)−C(1)	1.805(4)
O(1)−Cu(1)−O(4)	173.90(1)	O(1)−Cu(1)−O(1W)	92.38(1)	O(1)−Cu(1)−O(5)	91.19(1)	O(4)−Cu(1)−O(1W)	93.37(1)
O(4)−Cu(1)−N(1)	88.89(2)	N(1)−Cu(1)−O(1W)	97.72(2)	N(1)−Cu(1)−O(5)	166.92(2)	O(5)−Cu(1)−O(1W)	94.71(1)
O(4)−Cu(1)−O(5)	86.33(2)	O(1)−Cu(1)−N(1)	92.34(1)				

[a] Symmetry transformations used to generate equivalent atoms: #1 1-x, 1-y, 2-z; #2 2-x, 1-y, 1-z; #3 1-x, -y, 2-z; #4 1-x, 1-y, 1-z; #5 2-x, 2-y, -z. [b] Symmetry transformations used to generate equivalent atoms: #1 x+1,y+1,z [c] Symmetry transformations used to generate equivalent atoms: #1 x,y,-z #2 -x,-y+1,-z

were refined with isotropic thermal parameters. All hydrogen atoms were placed at the calculated positions. Hydrogen atoms of water molecules were located from suitable hydrogen bonding distances with the neighboring oxygen atoms. The final difference map has the highest peak of 1.65 e Å^{-3}, 0.04 Å close to Cu(1).

Results and Discussion

Hexaethyl 1,3,5-benzenetriphosphonate (**IIa**) and hexaisopropyl benzene-1,3,5-triphosphonate (**IIb**) were obtained by a catalytic Arbuzov reaction from 1,3,5-tribromobenzene and triethyl phosphite or triisopropyl phosphite in the presence of nickel(II) bromide (Scheme 2). After purification by column chromatography of the phosphonates (**II**), a simple hydrolysis reaction yielded 1,3,5-benzenetriphosphonic acid (**III**) as a white solid, very soluble in water and methanol. Hexaisopropyl 1,3,5-benzenetriphosphonate (**IIb**) at 180 °C undergoes decomposition probably to a mixture of partially dealkylated hexaisopropyl 1,3,5-benzenetriphosphonates. Two

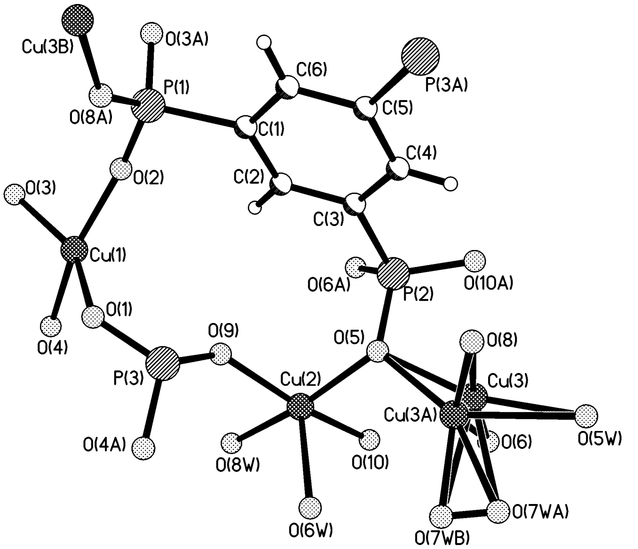

Figure 1. Molecular structure of compound **1** showing a view of the asymmetric unit of **1** with the labeling scheme. All lattice water molecules are omitted for clarity.

synthetic approaches have been achieved using different precursors in ester form to optimize the synthetic conditions. High temperature favors the Arbuzov reaction which produced 10% more hexaethyl 1,3,5-benzenetriphosphonate(180 °C) than hexaisopropyl benzene-1,3,5-triphosphonate (150 °C). The hydrolysis reaction achieved the same level of conversion for the two esters.

Crystal Structure of $\{Cu_6[C_6H_3(PO_3)_3]_2(H_2O)_8\}\cdot 5.5H_2O$, 1. 1,3,5-Benzenetriphosphonic acid, BTP, was reacted with $CuCl_2\cdot 6H_2O$ hydrothermally in the presence of DMF at 150 °C in a 1:1 molar ratio, and the reaction yielded irregular block-shaped crystals which are depicted in a SEM (Scanning Electron Microscopy) image reported as Supporting Information Figure S1. The ORTEP diagram of the unit cell is shown in Figure 1 with all of the solvent molecules omitted for clarity. The symmetry of the space group requires that six water molecules be present, but the refinement of the water occupancy factors led to the presence of 5.5 water molecules. Part of the difficulty has to do with the disorder present in the crystals. The crystals are triclinic, space group $P\bar{1}$, $Z = 1$ (Table 1). A unit cell consists of six copper atoms, two BTP ligands, eight coordinated water molecules, and ideally, six lattice water molecules. The molecule is sited on a center of symmetry with one-half of the molecule as the asymmetric portion. Six protons of BTP have been replaced by Cu atoms using DMF as the co-solvent, and all of the phosphonate oxygen atoms are bonded to the copper atoms. Cu(1) is coordinated to four oxygen atoms of the PO_3 groups from four different ligands with bond lengths in the range of 1.877(6)−1.943(7)Å. The bond angles of the copper center are 163.7(2), 152.9(2), 94.3(2), 94.8(2), 86.5(2), and 91.7(2)° for O(2)−Cu(1)−O(4), O(3)−Cu(1)−O(1), O(2)−Cu(1)−O(3), O(1)−Cu(1)−O(2), O(3)−Cu(1)−O(4), and O(4)−Cu(1)−O(1), respectively, which confirms the square pyramid arrangement of the Cu(1) atom. The Cu(1) sits 0.0886 Å above the plane and is 2.648 Å from O(3w) making the coordination environment of Cu(1) an elongated pseudo-square pyramid. Cu(2) is five coordinated, where Cu(2), O(5), O(9), O(10), and O(8w) compose the basal plane and O(6w) occupies the apex position of the square pyramid. The Cu(3) atom is disordered in two positions with a ratio of 3:1. Both disordered copper atoms are five coordinated with O(5), O(6), O(8), and two additional water molecules, O(5w) and O(7w). The O(7w) atom is also disordered in two positions with almost equal occupancy. The copper atoms form two distinct groupings of two Cu square planar arrangements. One of them consists of two Cu(1) square planar groupings connected by O(3)−P(1)−O(2) bridges and the other consists of a group of four Cu2/Cu3 square pyramids (Figure 2a). The groups of two are connected to the cluster of four in alternate layers along the *b* axis. This is seen more clearly in Figure 2b, where the yellow polyhedra are the square planar coppers and the green square pyramids are in alternating rows along the *b* and *c* axes. In the space represented by A there are six tetrahedra terminating in carbon atoms pointing into the space: three up and three down. These carbon atoms represent the connections of the phosphonate groups to the hexagonal rings. There are thus two such rings at a distance of 3.53 Å roughly parallel to each other. The square planar Cu(1) groups also connect to each other in the *a* axis direction to form a three-dimensional framework (Figure 2c). The B type pores are filled with water molecules that hydrogen bond to the coordinated water molecules.

The O(3w) atom is involved in hydrogen bonds to O(5w) and O(9) acting as a double hydrogen bond donor: O(3w)−H···O(5w) = 2.602 Å (symmetry operation is x, $y + 1$, $z - 1$) and O(3w)−H···O(9) = 2.769 Å (symmetry operation is $1 - x$, $1 - y$, $1 - z$). O(3w) also acts as a hydrogen bond acceptor with O(5w)-H···O(3w) = 2.602 Å and 172.98° with a symmetry code of x, $y - 1$, $z + 1$. The remaining oxygen atoms of the coordinated water molecules (O5w, O6w, and O8w) form strong to weak hydrogen bonds in the range of 2.598−3.247 Å resulting in a stabilization of the nonfully occupied lattice water molecules.

Crystal Structure of $Cu\{C_6H_3[PO_2(OH)]_2[PO(OH)_2]\}(C_{10}H_8N_2)$, 2. Compound **2** crystallized in the triclinic space group $P\bar{1}$ with one BTP, one bpy, and one central copper atom per asymmetric unit as shown in Figure 3. Two protons of BTP have been displaced leaving two negative charges on every three phosphonate groups. The overall charge of BTP is therefore −2 and defined as $\{1,3\text{-}[(HO)O_2P]_2\text{-}5\text{-}[(HO)_2OP]C_6H_3\}^{2-}$. The crystal morphology of the compound is different from that of compound **1** as shown in Figure S2. The crystals aggregate into a nestlike topology with very small needle-shaped crystals (S2). The single crystal which was chosen for the X-ray diffraction was separated from the aggregates under an optical microscope. The surface of the crystal is very smooth indicating its good quality. No disorder exists in this compound. The copper atom is coordinated with three oxygen atoms from three different neighboring BTP ligands and two nitrogen atoms from two bpy synthons forming a distorted square pyramid. The bpy groups connect the copper square pyramids along the *b* axis as shown in Figure 4a), and oxygen atoms from

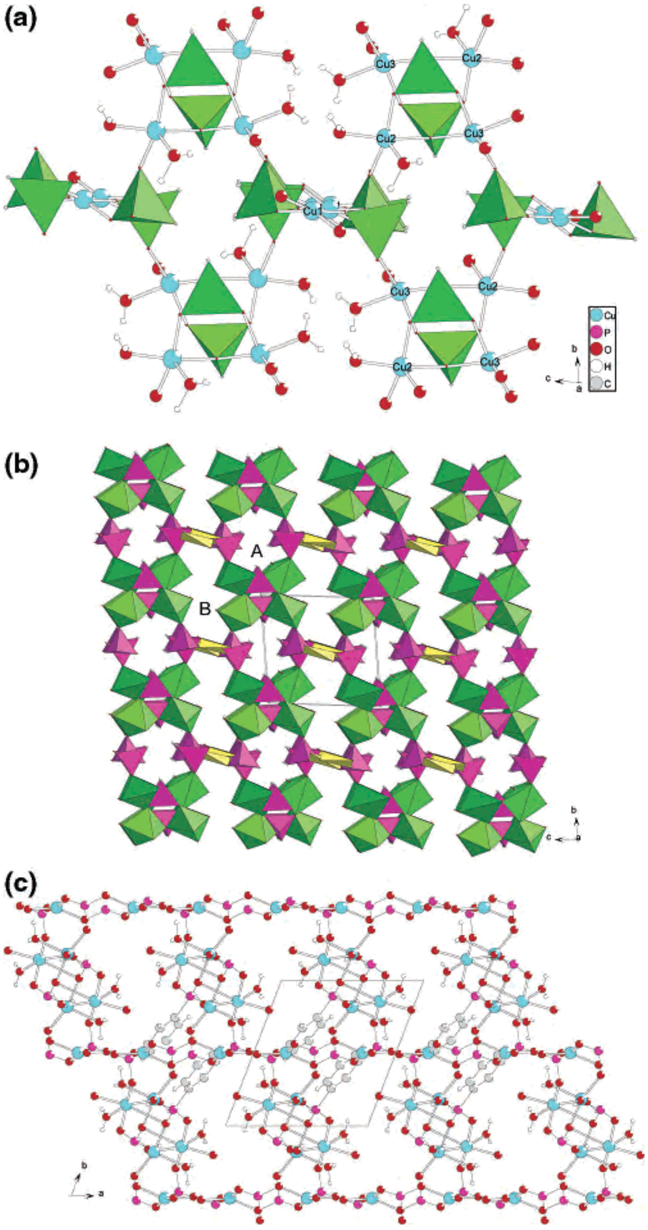

Figure 2. (a) Connection of the different units in compound **1** viewed down the *a* axis (green tetrahedron, CPO_3; red circle, O; cyan circle, Cu; small open circle, hydrogen). (b) Polyhedral diagram of compound **1** viewed down the *a* axis (purple tetrahedron, CPO_3; yellow square planar, Cu(1)-O_4; green polyhedron, Cu(2)O_5 and Cu(3)O_5). A shows the pseudohexagonal channel packed with benzene rings, and B shows the channel packed with the lattice water molecules. (c) The connection of the different units in compound **1** viewed down the *c* axis (red circle, O; cyan circle, Cu; gray circle, C; purple circle, P; small open circle, H). The distance between the two parallel benzene rings is 3.5Å.

two of the phosphonate tetrahedra form part of the square pyramid and connect them along the *a* axis. This connectivity forms layers as shown in Figure 4b. In the *c* axis direction, the phosphonate oxygens (O(7) atoms) next to the P(1) atom in Figure 3 connect the layers through the benzene ring that does not overlap with the pyridine rings. The P−O bonds that are in the range of 1.482(2)−1.505(2) Å have been assigned as the P═O bonds. Four longer P−O bonds (1.552(2), 1.557(2), 1.557(2), and 1.560(2) Å) have been defined as P−OH bonds. The deprotonated $P-O^-$ bond lengths are shorter than the former four in the range of 1.517−1.520 Å.

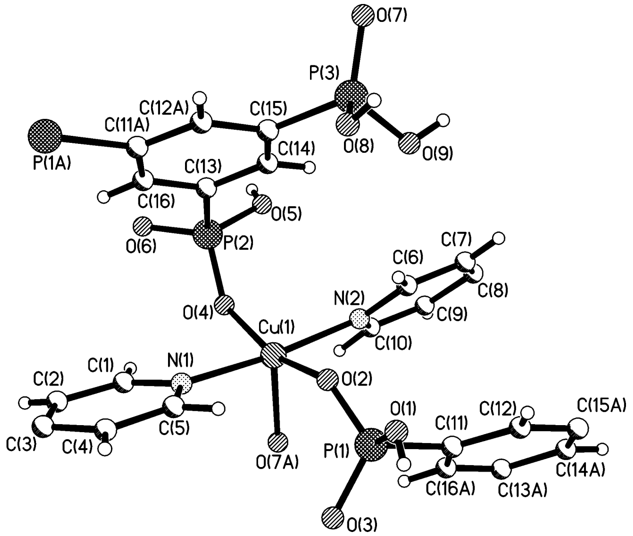

Figure 3. Molecular structure of compound **2** showing a view of the asymmetric unit of **2** and the labeling scheme.

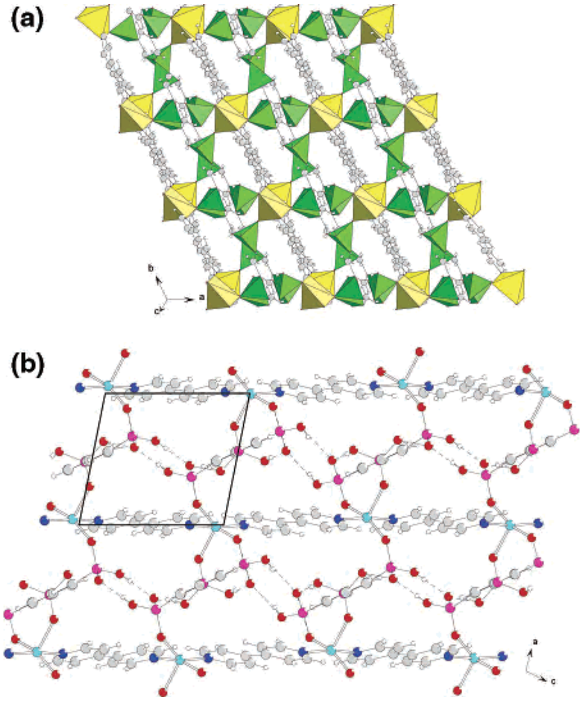

Figure 4. (a) Polyhedral diagram of compound **2** viewed down the ⟨111⟩ plane (green tetrahedron, CPO_3; yellow polyhedron, CuO_3N_2). (b) Hydrogen bonding scheme of compound **2** viewed down the *b* axis (cyan, Cu; gray, C; blue, N; red, O; purple, P; small open circle, H; dotted line represents the hydrogen bonds). The channels running down the *b* axis are shown by solid lines.

In compound **2**, there are four pairs of P−OH···O hydrogen bonds. They are in the range of 2.54−2.58 Å. O(6) and O(3) serve as double hydrogen bond acceptors. The dianionic moiety $\{1,3\text{-}[O(HO)OP]_2\text{-}5\text{-}[(HO)_2OP]C_6H_3\}^{2-}$ motifs assemble with intermoleuclar hydrogen bonds along the *ac* plane to form zigzag layers as a result of the planar stacking of the benzene rings. The pseudo-rectangular channel formed by the hydrogen bonding as viewed down the *b* axis is bounded by four copper atoms and is about 11.1 × 8.1 Å with the hydrogen bonds packed inside as shown in Figure 4b. The whole structure of compound **2** can be described as

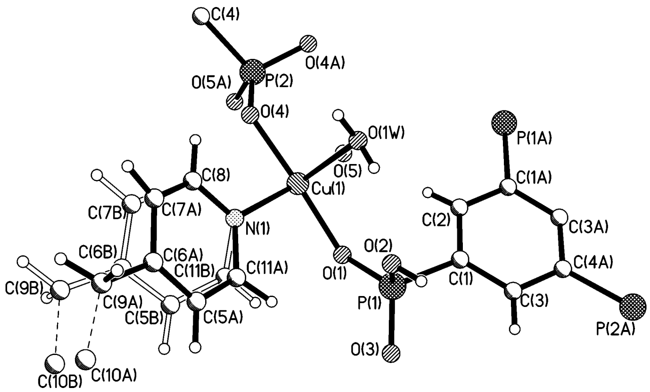

Figure 5. View of the asymmetric unit of **3** showing the labeling scheme; all solvents have been omitted for clarity.

3D with layered interwoven material as shown in Figure 4a. The 4,4′-bipyridine and copper polyhedra form linear chains running along the *b* axis which are interconnected with three different tetrahedra of the PO_3 groups of the BTP ligands by sharing corners in an up−down or zigzag manner extended in the *ab* plane as viewed from the ⟨111⟩ plane.

In the solid-state, typical P−OH···O−P distances in the range of 2.45−2.60 Å were reported for the organic ammonium salts of phosphonic acids.[7] To the best of our knowledge, the lower limit is determined by a distance of 2.413 Å reported for an aggregate of nitrilotri(methylphosphonic acid) with phenanthroline[11] and 2.415(2) Å in a linear chain crown ether phosphonate.[15] Recently, a short OH···O distance in BTP with 4-(dimethylamino)pyridine was reported that has a value of 2.431(2) Å.[9] In the dimer structure of the 1,3,5-benzenetrimethylphosphonic acid, two similar OH···O bonds of 2.442 and 2.484 Å were found with the negative charge assisted hydrogen bonding.[15]

Crystal Structure of $\{Cu_2C_6H_3[PO_2(OH)]_2[PO_3](C_{13}H_{14}N_2)\}\cdot 3H_2O\cdot 0.5HCON(CH_3)_2$, 3. The chemical formula of compound **3** in the crystal form, as obtained from the X-ray diffraction structural analysis, is shown in the title above. The asymmetric unit of the crystal depicting the nature of the disorder is shown in Figure 5. The asymmetric unit contains one copper atom, half of a BTP ligand, half of tbpy, half of an acetone, and one disordered water molecule. Figure S3 shows the SEM image of the crystallized material's morphology. Four protons have been displaced from the BTP ligand. The anionic ligand has been defined as $\{1,3\text{-}[(HO)O_2P]_2\text{-}5\text{-}[O_3P]C_6H_3\}^{4-}$ requiring two Cu^{2+} for charge balance. Copper is five-coordinated with one nitrogen atom from tbpy, three oxygen atoms from three neighboring BTP ligands, and one additional water molecule which occupies the axial position with a slightly longer bond distance (Cu(1)−O(1w) 2.248(3) Å). The N(1), O(1), O(4), and O(5) atoms are coplanar with a deviation 0.0618 Å, and the copper atom fits perfectly inside the equatorial plane. The bond distance of P(1)−O(2) (1.571(2) Å) is significantly longer than the uncoordinated P(1)−O(3) bond (1.507(3) Å) and coordinated P(1)−O(1), P(2)−O(4), and P(2)−O(5) bonds (1.514(3), 1.512(3), and 1.547(4) Å, respectively). Therefore, the O(2) atom has been designated as a P−OH group. The O(5) atom bridges neighboring copper atoms which results in a longer P−O bond. Figure 6a delineates how the BTP group bonds to the copper atoms and connects them to each other. The BTP ring is divided in half by a mirror plane producing two P1 phosphonate groups and a third phosphonate group, P2. This latter group is designated P(2)O(4)O(4A)O(5). The O(5) atom of the P(2) phosphonate group bridges across two copper atoms, while the O(4) and O(4A) atoms of this group each bond two other copper atoms. Each P(2) phosphonate group thus bonds to four copper atoms. A second P(2) phosphonate group, related to the first one by a center of symmetry, bonds through O(4) to the two copper atoms bridged by O(5) of the first phosphonate group and in turn its O(5) bridges the copper atoms bonded to O(4) of the first

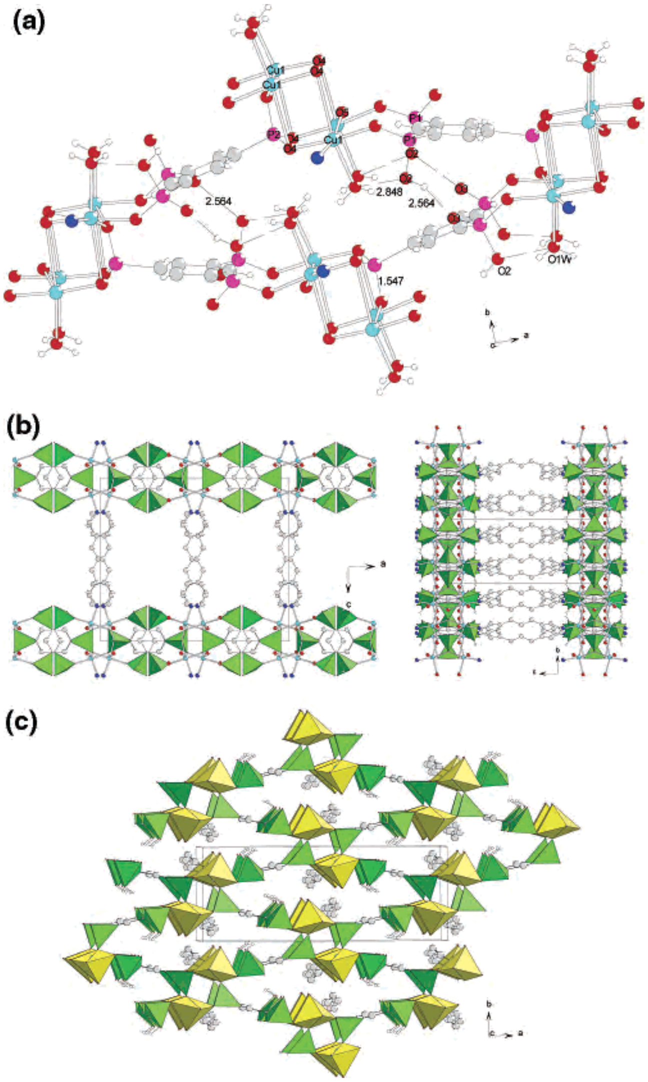

Figure 6. (a) Tetra-copper units repeated in compound **3** viewed down *c* axis (cyan, Cu; gray, C; blue, N; red, O; purple, P; small open circle, H; dashed lines are hydrogen bonds). All solvent molecules are omitted for clarity. (b) Cell packing information for compound **3** along the *ac* and *bc* plane (cyan, Cu; gray, C; blue, N; red, O; small open circle, H; green tetrahedron, CPO_3) All solvent molecules are omitted for clarity. (c) Cell packing information of compound **3** viewed down *c* axis (gray, C; small open circle, H; green tetrahedron, CPO_3; yellow polyhedron square pyramid, CuO_4N). All solvent molecules are omitted for clarity.

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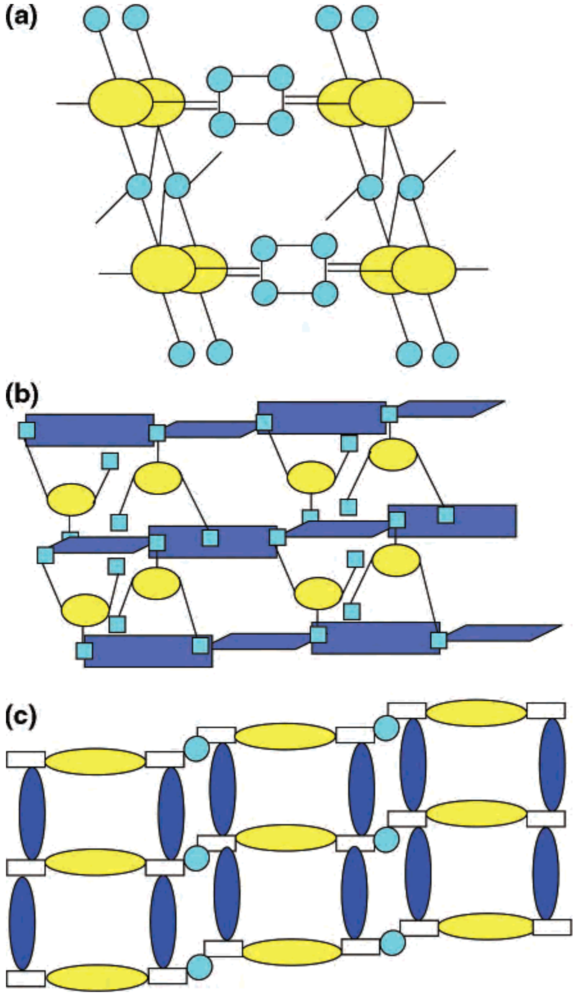
(15) Mehring, M.; Schürmann, M.; Ludwig, R. *Chem.*−*Eur. J.* **2003**, *9*, 837.

P(2) phosphonate group. The P(1) phosphonate groups of two additional BTP ligands each bond to copper through their O(1) oxygens and one oxygen to each of the coordination spheres of the four copper atom clusters. Each BTP thus bonds to four copper atoms in one cluster through P2 and connects along the *a* axis to two copper atoms in an adjacent cluster through the P1 phosphonate groups. The coordination sphere of each copper is completed by a pyridine nitrogen atom and one axial water molecule. The tbpy ligands then connect these groups in the direction perpendicular to the *a* axis in the *c* axis direction (Figure 6b). As a result, an eight-membered ring of 2Cu(1), 2(O5), 2P(2), and 2O(4) and a six-membered ring of P(2), 2O(4), 2Cu(1), and O(5) construct a consecutive robust synthon, tetra-copper unit, which is connected with four tbpy units and four BTP ligands as shown in Figure 6a. (Only the N atoms of the tbpy groups are shown in Figure 6a.) These tetra-copper units are similar to those present in compound **1**. If viewed from the framework construction, the tetra-copper units have the symbolic features of a so-called SBU (secondary building unit). The BTP ligand serves as a pentadentate ligand with three oxygen atoms of one phosphonic acid group (fully deprotonated PO_3) and the other two from P(1) groups (monodeprotonated) because of their symmetry. The P(2)−O_3 group has an η^4:μ^2 coordination sphere. The benzene ring tilts in a way that allows the other two PO(OH)O groups to coordinate with two copper atoms along the ⟨001⟩ plane. Only the protonated O(2) atom and O(3) do not bond to copper. The protonated P−OH groups act as hydrogen donors and are hydrogen bonded to the uncoordinated double bonded P−O(3) atoms (four pairs of hydrogen bonds; O(2)−H···O(3) = 2.564 Å). O(2) atoms also form hydrogen bonds with the coordinated O(1w) atoms with an O···O distance of 2.848 Å as illustrated in Figure 6a. Because of the symmetry, the coordinated water molecules are at a suitable distance to form long hydrogen bonds (3.016 Å). Those hydrogen bonds inside the four benzene rings help to stabilize the structure. The tetra-copper unit, as shown in Figure 6a, is viewed down the *c* axis which runs through the *ab* plane and forms infinite end-on packing columns such as the “sausage”. Scheme 3 shows the connections for compound **3** in cartoon form. The distance between the two nonbridged copper atoms is 3.34 Å. The bpy units extend along the *b* axis and link all the tetra-copper units together to form the 3D layered structure as shown in Figure 6b. The bpy linkers have two disordered positions, which have been refined to 50% of each. The dihedral angle of the two benzene rings is 28.5°. But the trimethylene groups between the two pyridine rings have upper and lower configurations as depicted in Figure 6c. The flexibility of the trimethylene groups in the bpy linkers provides a more versatile framework in compound **3**. Larger channels have been constructed with a size of 14 × 9.1 Å. The lattice water and acetone are packed inside the channel and are hydrogen bonded to the each other.

IR Analyses. IR spectra were recorded between 4000 and 400 cm^{-1} and are shown in the Supporting Information. The region between 4000 and 1400 cm^{-1} can be selected to study the lattice water and the P−O−H groups. Compounds **1** and **3** showed an intense and broad band in the O−H stretching vibration region at 3460−3230 cm^{-1}, which is consistent with the presence of lattice water molecules interacting via hydrogen bonding. The corresponding bending H−O−H (δHOH) vibration bands of the water molecules in **1** and **3** are located at ca. 1637 and 1604 cm^{-1}, respectively. The sharp intense peak of compound **3** at 1630 cm^{-1} is assigned to the C=O from the DMF molecule. All benzene ring multiple bond vibration bands are located at 1580 cm^{-1} for **1**, 1600 cm^{-1} for **2**, and 1512 cm^{-1} for **3**. The symmetrical and unsymmetrical vibration bands of PO_2 from $PO(OH)O^-$ groups in compounds **1** and **3** were observed at 1120 and 1005 cm^{-1}, respectively. The shoulders centered at 2320 and 1050 cm^{-1} are attributed to the hydrogen phosphonates (P−OH) because of the unprotonated POH groups in those two compounds which are clearly missing from compound **2**. Asymmetric vibrating stretching bands of the POH (ν(P−OH)) groups of the above two compounds are situated at 930 and 950 cm^{-1}, respectively. In compound **2**, the sharp peak that occurs at 980 cm^{-1} was assigned to $\nu_s(PO_3)$,

Scheme 3. Connections of (a) Compound **1**[a], (b) Compound **2**[b], and (c) Compound **3**[c] Depicted in Cartoon Style



[a] The yellow ovals represent the BTP ligand and the cyan circles are the copper centers. [b] The blue rectangles are the bpy motifs, the yellow ovals represent the BTP ligand, and the light blue squares are the copper centers. [c] The black rectangles are the copper atom clusters, the yellow ovals represent the BTP containing ligands, and the blue are the tbpy linkers.

and its unsymmetrical vibrations occur at 1050 and 1010 with two different coordination environments of PO_3 groups.[16] All compounds also showed typical C−H stretching vibrations and bending vibrations of low intensities of CH inside the benzene rings near 2850 and 1460 cm^{-1}, respectively.

TGA Analyses. The thermogravimetric studies of compound **1** demonstrated a number of weight losses indicating a complexity of the decomposition process (see Supporting Information Figure S8). Compound **1** continuously lost weight from the beginning. It showed that eleven water molecules were lost up to 230 °C from a total of 13.5 mol expected. No further weight loss was observed until 600 °C indicating that at least 2.5 mol of water was lost prior to the TGA. The total weight loss is 23.7% as opposed to the calculated weight loss of 27.6% for the final product to be copper pyrophosphate, $Cu_2P_2O_7$, confirming this earlier loss. The TGA curve of **2** shows that there is no weight loss until 300 °C confirming that there are no water molecules present. There are two steps of weight loss: first, the release of one water molecule formed by the condensation of hydrogen phosphonate groups, and second, the pyrolysis of the organic group. Those two processes overlap. The total weight loss of 56.7% corresponds to the final residue being $0.5Cu_2P_2O_7$ (57.2%).[17] The TGA curve of compound **3** has four weight loss regions. Compound **3** begins to lose the lattice water at 40 °C. The observed weight loss at 130 °C (8.2%) is in agreement with the calculated value of 7.8% for the loss of all three uncoordinated water molecules. There are two regions of weight loss (36.8%) in the temperature range of 150−600°C which could be assigned to a condensation of the two hydroxyl groups in the BTP ligand, loss of half an DMF molecule, and the burning of the 4,4′-tbpy molecule with a theoretical weight loss value of 35.6%. The final burning of the BTP ligand and transformation of phosphonic moieties occur at 600−900 °C. The process is complete with a total weight loss of 62.8% which is somewhat higher than that for the calculated final residue $Cu_2P_2O_7$ (58.8%). This discrepancy was shown to result from a small amount of a second-phase contamination (see Supporting Information for the second phase structure, Figure S9). The existence of the second phase also explained the discrepancy of the elemental analysis for compound **3**. The impurity which was formed together with compound **3** has been identified by X-ray single-crystal diffraction. The structure solution revealed a structure with 2D polymeric copper centers connected by formic acid moleucles, resulting from the decomposition of the DMF solvent used in the hydrothermal synthesis.

Conclusions

1,3,5-Benzenetriphosphonic acid is a relatively new synthon being the phosphonic acid analogue of trimesic acid. Its major difference is the tetrahedral nature of the phosphoric acid groups relative to the planar carboxyl groups. In this paper and the previous one,[18] we have reacted BTP with amines and copper in 1:1 ratios to explore the type of behavior that results to provide a basis for designed structures. In our present studies, we demonstrate that the 3-fold symmetrical phosphonic acid, BTP, reacted with $Cu(ClO_4)_2$ in the presence of DMF with 4,4′-bpy and 4,4′-tbpy leading to the formation of 3D supramolecular layered architectures. The phosphonic acid moieties form robust anionic motifs in **1** with −6 charges. BTP exhibited different deprotonation steps as shown in compounds **2** and **3**: −2 and −4 anions were formed, respectively, dependent on the synthetic conditions. Tetra-copper SBUs were obtained in compounds **1** and **3**, both being composed of five-coordinated copper centers with bridged BTP ligands. Particularly, in compound **2**, the ligand only released two protons, and the copper center is five coordinated, the low degree of deprotonation blocked further connection to other copper centers. All compounds exist as layers with two pyridyl fragment molecules acting as pillars interconnecting the layers which extend the structure to three-dimensional systems. With the use of 4,4′-bpy, as well as 4,4′-tbpy, three-dimensional supramolecular architectures were successfully achieved. In the case of an earlier report,[9] one and two protons have been deprotonated in the 4-(dimethylamino)pyridine case ($pK_a = 9.33$). In our preliminary potentiometric titration experiment, the log K_n^H values of the BTP are $\log K_1 = 8.56$, $\log K_2 = 7.43$, $\log K_3 = 6.71$, $\log K_4 = 2.61$, and $\log K_5 = 1.44$ (the last one is lower than 1, $\log K_n^H = [H_nL]/[H_{n-1}L][H]$).[19] The first three protons are easily deprotonated. There is a gap of 4.1 log units for the third and fourth protons. When the number of the protonation sites and their localization are considered, this decrease in the constant values can be rationalized in terms of minimization of the electrostatic repulsion between positive charges in the protonated species. The ligand itself has C_3 symmetry on which three positive charges could be easily delocalized with minimum electrostatic repulsion. Also, in those negatively charged moieties aggregated by hydrogen bonds, the removal of a proton from the hydrogen bond strength in the dimer is increased from ca. 43 kJ mol^{-1}, calculated for $[t\text{-}C_4H_9PO(OH)_2]$, to ca. 83 kJ mol^{-1}, for $\{[t\text{-}C_4H_9PO(OH)O]\}\{[t\text{-}C_4H_9PO(OH)_2]\}^{-1}$.[15] In the future, stronger amines will be used to achieve variable process deprotonation. In a larger sense, the use of phosphonic acids provides a vast array of synthons for more complementary designed highly stable hydrogen-bonded structures to be constructed.

Acknowledgment. The authors acknowledge with thanks the financial support from the Department of Energy, Basic

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Sciences Division through Grant DE-FG03-00ER 15806 and the R. A. Welch Foundation under Grant A623. Dr. Jerzy Zoñ wishes to thank Prof. Roman Gancarz (Wroclaw) for helpful discussion on the NMR spectra of BTP. This work was supported in part by US−Poland NSF Grant OISE−043490 and Wroclaw University of Technology (J.Z.). Thanks go to Dr. Andrey V. Prosvirin and Dr. Kim R. Dunbar for assistance with the magnetic measurements. Thanks to Dr. Lev Zakahov for his helpful discussion of the crystallographic work.

Supporting Information Available: Crystallographic data in CIF files, SEM pictures, IR, TGA, and magnetic measurements of the three compounds and the CIF file for the second phase of compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0509377