

# Synthesis and Crystal Structures of Copper(II) Diphosphonatoalkanes: C<sub>4</sub> and C<sub>5</sub>

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Received July 5, 2001

Two copper alkylidenediphosphonates, Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>4</sub>H<sub>8</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**1**) and Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>5</sub>H<sub>10</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2.8H<sub>2</sub>O (**2**), have been synthesized and their crystal structures solved from X-ray powder data. Compound **1** is monoclinic, *C*2/*m*, with *a* = 20.035(6), *b* = 6.6713(2), and *c* = 4.3966(1) Å,  $\beta$  = 91.379(1) $^\circ$ , and *Z* = 2. Compound **2** is orthorhombic, *Pmmn*, with *a* = 22.3773(2), *b* = 6.7633(1), and *c* = 4.3529(1) Å, and *Z* = 2. Both structures consist of layers of CuO<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub> octahedra in which the layers are cross-linked by the alkyl chains into three-dimensional lattices. This pillared arrangement creates tunnels running parallel to the *c*-axis direction containing water molecules. Dehydration of the compounds is irreversible, but in the hydrated state, ammonia readily replaces the water.

## I. Introduction

A number of years ago, we reported on copper and zinc derivatives prepared from  $\alpha,\omega$ -alkylidenediphosphonic acids, (H<sub>2</sub>O<sub>3</sub>P)<sub>2</sub>R, where R = ethylene and propylene groups.<sup>1</sup> In the copper compounds, the Cu atoms are five-coordinate, forming layers of Cu–O<sub>3</sub>P groups cross-linked by the alkylene units. Four of the Cu coordination sites are filled by phosphonate oxygens and the fifth site by a water molecule. The coordination polyhedra are distorted square pyramids.

Since then, there has been a considerable amount of work on the preparation and structure delineation of similar types of compounds. Ferey et al.<sup>2</sup> prepared a variety of vanadium complexes hydrothermally from ethylene- and propylenediphosphonic acids. [V<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>]<sub>2</sub>·H<sub>2</sub>O contains dimeric units formed by face sharing of VO<sub>5</sub>OH octahedra.<sup>2a</sup> The dimers are linked together by the phosphonate group such that each phosphonate bridges three dimers to form layers, and the layers are then linked together by the alkyl chains. NH<sub>4</sub>[(VO)<sub>2</sub>(OH){O<sub>3</sub>P(CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>}]<sub>2</sub>·2H<sub>2</sub>O was obtained using NH<sub>4</sub>VO<sub>3</sub> as the source of vanadium.<sup>2b</sup> In this structure, the dimers consist of VO<sub>5</sub> groups sharing a corner. The phosphonate groups bridge three such dimers to form layers, which are then cross-linked by the propylene groups. The ammonium ion and water reside in the channels between the layers. Lowering the temperature of preparation from 200 °C to 170 °C produced a mixed-valence V<sup>IV</sup>–V<sup>V</sup> compound of composition (NH<sub>4</sub>)<sub>2</sub>[V<sub>2</sub>O<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>O<sub>3</sub>P(CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O.<sup>2b</sup>

Another dimeric vanadyl(IV) compound, (VO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>O<sub>3</sub>P(CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O, was most recently prepared.<sup>2c</sup>

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The dimers are formed from face-shared VO<sub>5</sub>(H<sub>2</sub>O) octahedra bonded into cross-linked layers by the propylenediphosphonate groups. The inorganic layers resemble those in VO(HPO<sub>4</sub>)·0.5H<sub>2</sub>O,<sup>3</sup> with the organic chains replacing the terminal phosphate hydroxyl groups.

An interesting series of pillared compounds has been prepared with the general formula LnH[O<sub>3</sub>P(CH<sub>2</sub>)<sub>n</sub>PO<sub>3</sub>]<sub>2</sub>, with *n* = 1–3 for several lanthanide ions.<sup>4</sup> The metal atoms are dodecahedrally coordinated in which the phosphonate groups chelate the metal atoms. Half of the oxygens then donate to an adjacent metal atom, while the third oxygen bridges across chains to form a layer. The layers are then cross-linked by the alkyl chains. The unpillared lanthanides of composition LnH(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> form similar layers of dodecahedrally coordinated metal atoms.<sup>5</sup>

Other related structures include diphosphonates of Sb(III),<sup>6a</sup> additional vanadium compounds,<sup>6b,c</sup> NaCo<sub>2</sub>[O<sub>3</sub>P(CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>]OH,<sup>6d</sup> and a variety of compounds with methylenediphosphonic acid.<sup>6d,7a–d</sup> Many of the one-carbon compounds have unusual structures that may contain open channels or exhibit interesting magnetic properties. Bellito et al. synthesized Cr<sub>2</sub>[O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>]<sub>2</sub>·3H<sub>2</sub>O<sup>8b</sup> and Fe<sub>2</sub>[O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O.<sup>8a</sup> The former compound is isostructural to Cu<sub>2</sub>[O<sub>3</sub>P(CH<sub>2</sub>)<sub>2</sub>PO<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O<sup>1a,c</sup>

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and exhibits Curie–Weiss behavior, with a negative Weiss constant indicative of strong antiferromagnetic interactions. The iron compound<sup>8a</sup> has almost the identical unit cell parameters as  $Zn_2[O_3P(CH_2)_2PO_3] \cdot 2H_2O$ .<sup>1a</sup> The iron(II) ions are in a  $d^6$  high spin configuration and exhibit antiferromagnetic behavior but also weak ferromagnetism below the critical temperature.

In this paper, we describe the synthesis and structures of two copper diphosphonates with  $C_4$  and  $C_5$  alkyl chains. Our objective was to determine how the length of the chains mediates the interlayer space and whether open channels can be prepared that would be relatively hydrophobic.

## II. Experimental Section

**Chemicals and Procedures.** Copper acetate monohydrate (Fisher, certified) was used as received. The dibromoalkanes 1,4- $C_4H_8Br_2$  (99%) and 1,5- $C_5H_{10}Br_2$  (97%) were from Aldrich and used as received. Triethyl phosphite was obtained from a commercial source and distilled prior to use.

Thermogravimetric analyses (TGA) were performed under an atmosphere of dried oxygen using a DuPont Instruments TA 400 unit. The IR spectra were obtained on a Bio-Rad FTS-60 FT-IR spectrometer using KBr disk samples. The  $^{31}P$  MAS NMR spectrum was measured using a Bruker MSL-300 solid-state spectrometer in which the phosphorus nuclei resonate at 121.5 MHz and was externally referenced to aqueous 85%  $H_3PO_4$ . The  $^{31}P$  and  $^{13}C$  solution NMR spectra were recorded on a Varian 200XL broad-band spectrometer in which the phosphorus nuclei resonate at 81 MHz and the carbon nuclei resonate at 50 MHz; the measurements were conducted using aqueous samples, and the chemical shifts were externally referenced to aqueous 85%  $H_3PO_4$  for the  $^{31}P$  NMR spectra and to  $C_6D_6$  for the  $^{13}C$  NMR spectra. The X-ray energy-dispersive spectrometry studies were performed at the microscopy center at Texas A&M University. Galbraith Laboratories conducted carbon and hydrogen analyses.

Thermodiffraction data were collected on a Siemens D-5000 automated diffractometer equipped with an HTK10 heating chamber. The samples were packed onto platinum foil that served as both the sample holder and the heating system. The step size was  $0.04^\circ$  in  $2\theta$ , and the heating rate was  $0.5^\circ C/s$ . The delay time between reaching a set temperature and recording the diffraction pattern was 10 min.

**Preparation of 1,4-Butylenediphosphonic Acid ( $H_2O_3 \cdot PC_4H_8PO_3H_2$ ).** A three-necked, round-bottomed flask was charged with 8.3 mL (0.069 mol) of 1,4-dibromobutane and 35.5 mL (0.2 mol) of distilled  $P(OEt)_3$  and fitted with a water-cooled condenser, Claisen adapter, magnetic stir bar, and thermometer. The flask was purged with  $N_2$  and heated to  $165^\circ C$ . As the reaction proceeded, it was accompanied by distillation of ethyl bromide. The crude diethyl ester was then vacuum distilled and treated with 50 mL of concentrated HCl. This mixture was refluxed for 3 days and rotovaped to obtain a crude light cream colored solid. The yield was 14.8 g (98%). This solid was recrystallized from water and a total of 7.84 g (52% yield) recovered.  $^{31}P$  NMR: singlet 31 ppm.  $^{13}C$  NMR:  $-CH_2CH_2P$  doublet centered at 25.99 ppm,  $J_{C-P}$  133.62 Hz;  $-CH_2CH_2P$  doublet of doublets centered at 23.20 ppm,  $J_{C-C-P}$  18.00 Hz and  $J_{C-C-P}$  4.50 Hz.

**Preparation of 1,5-Pentylidendiphosphonic Acid.** This compound was prepared similarly to the 1,4 compound from 1,5-pentylidendibromide (0.044 mol). The yield was 3.57 g (34.1%).  $^{31}P$  NMR: singlet 31–32 ppm.  $^{13}C$  NMR:  $-CH_2CH_2CH_2P$  doublet centered at 26.36 ppm,  $J_{C-C-P}$  133.0 Hz;  $-CH_2CH_2CH_2P$  doublet centered at 21.90 ppm,  $J_{C-C-P}$  3.97 Hz;  $CH_2CH_2CH_2P$  triplet centered at 30.87 ppm,  $J_{C-C-C-P}$  16.56–16.66 Hz. A second crop of crystals was obtained by further concentration of the filtrate (2.36 g, overall yield 56.6%).

**Synthesis of  $Cu_2[(O_3PC_4H_8PO_3)(H_2O)_2] \cdot 2H_2O$ .** A 200 mL beaker was charged with 1.025 g (5.16 mmol) of  $Cu(OAc)_2$ ·

$2H_2O$  and 0.518 g (2.48 mmol) of  $C_4H_8(PO_3H_2)_2$ . A total of 50 mL of distilled deionized (ddi) water was added to the beaker, and the mixture was stirred for 4.5 h. The product was collected by filtration through a 0.45  $\mu m$  membrane. The pH of the green-blue filtrate was 2.55. The blue solid was washed with ddi water and dried in air. The yield was 0.935 g (87.7%). Elem anal. Calcd for  $Cu_2[((O_3P)_2C_4H_8 \cdot (H_2O)_2) \cdot 2H_2O$ : C, 11.62; H, 3.90. Found: C, 11.95; H, 4.39.

**Synthesis of  $Cu_2[(O_3PC_5H_{10}PO_3)(H_2O)_2] \cdot 2.8H_2O$ .** A 0.6450 g (3.23 mmol) portion of  $Cu(OAc)_2 \cdot H_2O$  was dissolved in 15 mL of ddi  $H_2O$  and added to a 250 mL round-bottomed flask; the pH of this solution was 5.19. Glacial acetic acid was added to the solution to reduce its pH to 1.92. A total of 0.2900 g of  $C_5H_{10}(PO_3H_2)_2$  (0.966 mmol) was dissolved in 10 mmol of ddi  $H_2O$ ; this solution was added to the acidified copper solution. The flask was covered, and the reaction mixture was stirred; within a day, a blue solid had precipitated. The mixture was stirred for an additional day and then filtered through a 45  $\mu m$  membrane; the pH of the filtrate was 1.88. The blue solid was washed with ddi  $H_2O$  and acetone. The solid was left to dry in air overnight and collected. The weight of the product was 0.363 g. A yield of 85% based upon the amount of phosphonic acid was used. TGA (2.5  $^\circ C/min$ ): 26.51–331.87  $^\circ C$ , 19.63% weight loss; 331.87–650.62  $^\circ C$ , 11.85% weight loss; 650.62–1030.41  $^\circ C$ , 0.36% weight gain. IR ( $cm^{-1}$ ): 3364 st br, 2962 m br, 2874 m br, 2254 w br,  $\sim$ 1630 w br, 1462 w sh, 1413 w sh, 1305 w sh, 1222 m sh, 1195 m sh, 1091 st br, 1048 st br, 989 st br, 789 w br, 595 m br, 557 m br, 523 m sh. Elem anal. Calcd for  $Cu_2[((O_3P)_2C_5H_{10})(H_2O)_2] \cdot 2.8H_2O$ : C, 13.60; H, 4.48. Found: C, 14.23; H, 4.84.

**X-ray Data Collection and Structure Solutions,  $Cu_2(O_3PC_4H_8PO_3) \cdot 4H_2O$  (1).** The sample was prepared by packing the finely ground solid into a flat plastic sample holder. Data were collected over a 2  $\text{\AA}$  range of 5–80° on a Rigaku DMAX/B diffractometer fitted with a rotating Cu anode and graphite monochromator; the counting time per 0.01° step was 20 s at 50 kV and 180 mA. The powder pattern was indexed using 20 reflections in the program VISIND,<sup>9</sup> the best solution indexed all of the reflections and had a figure of merit  $M(20)$ <sup>10</sup> of 33.9 in the monoclinic system. The space group  $C2/m$  was chosen based upon an examination of the systematic absences in the data; the absence of reflections having  $h+k=2n+1$  was indicative of  $C$  centering with no other systematic absence observed. Initial unit cell dimensions were  $a=20.059 \text{\AA}$ ,  $b=6.800 \text{\AA}$ ,  $c=4.400 \text{\AA}$ , and  $\beta=91.37^\circ$ . The powder pattern was decomposed using the LeBail method<sup>11</sup> in the GSAS<sup>12</sup> software (profile function no. 2) to obtain integrated intensities; the pattern was truncated to eliminate the first peak, the shape of which was very difficult to match. The background was fit by using refined coefficients in a cosine Fourier background function (background function no. 2 in GSAS), as well as fixed points. After successive refinement of the background, the zero-point error, the profile parameters, and the lattice parameters, the final  $R_{wp}$  and  $R_p$  values with a hydrogen atom in an arbitrary position were 1.45% and 1.11%, respectively. The quantitative intensity data obtained from the profile fitting were used in Sir92,<sup>13</sup> a direct methods program in the TEXSAN<sup>14</sup> software package, to obtain the positions of the Cu and P atoms. These positions were used to initiate the Rietveld refinement<sup>15</sup> in GSAS; the remaining atomic positions were determined except for the water molecules using difference Fourier maps during the Rietveld refinement. Two disordered

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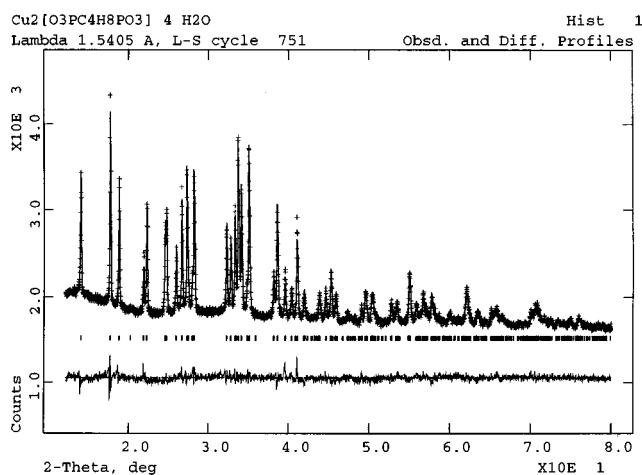
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**Table 1. Crystallographic Data for the Copper Diphosphonates**

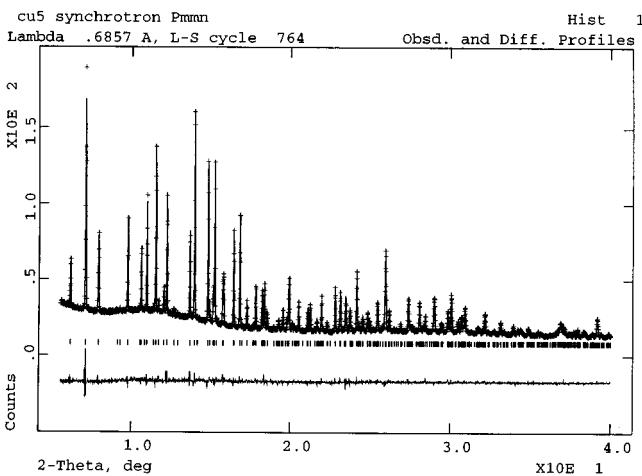
	compound 1	compound 2
formula	$\text{Cu}_2\text{P}_2\text{O}_{10}\text{C}_4\text{H}_{16}$	$\text{Cu}_2\text{P}_2\text{O}_{10.8}\text{C}_5\text{H}_{19.6}$
FW	413.20	441.63
space group	$\text{C}2/m$	$\text{Pmmn}$
$a, \text{\AA}$	20.0305(6)	22.3773(2)
$b, \text{\AA}$	6.6713(2)	6.7633(1)
$c, \text{\AA}$	4.3966(1)	4.3529(1)
$\alpha, \beta, \gamma$ (deg)	$\beta = 91.379(1)$	$\alpha = \beta = \gamma = 90$
$Z$	2	2
$V, \text{\AA}^3$	587.34(2)	658.80(2)
$d_{\text{calc}}, \text{g/cm}^3$	2.336	2.226
$\mu, \text{mm}^{-1}$	7.519	
radiation	Cu rotating anode	synchrotron
source ( $\lambda, \text{\AA}$ )	1.5406, 1.5444	0.6857
pattern range (2 $\theta$ , deg)	12–80	5.5–40
no. of reflections	409	416
no. of soft constraints	17	21
$R_{\text{wp}}$	1.75%	3.20%
$R_{\text{p}}$	1.31%	2.53%
$R_{\text{F}}$	6.3%	4.9%
$\chi$	0.64	3.8

water positions within the cavity (vide infra) were located from the Fourier difference map after initial Rietveld refinement of the full pattern. The occupancies of these disordered water molecules were each constrained to be unity. Atomic positions were refined with soft constraints consisting of Cu–O<sub>eq</sub> bonds [2.00(5) Å], Cu–O<sub>ax</sub> bonds [2.20(5) Å], and P–O bond lengths of 1.52(5) Å and the P–C bond [1.75(5) Å] for the tetrahedral P and C–C bonds [1.54(5) Å] for the carbon backbone. Angle constraints were applied to phosphorus and carbon atoms for tetrahedral geometry [109.5(1.0)°]. Rietveld refinement of the full pattern total profile refinement of 40 parameters against 6799 data points leads to  $R_{\text{p}} = 1.3$  and  $R_{\text{wp}} = 1.8$  with  $\chi = 0.64$  and  $R_{\text{F}} = 6.3\%$  (for 409 observations). The preferred orientation was corrected along the [100] axis using the March–Dollase model.<sup>16,17</sup> Summaries of the crystallographic parameters are listed in Table 1.

**Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>5</sub>H<sub>10</sub>PO<sub>3</sub>)·(H<sub>2</sub>O)]·2.8H<sub>2</sub>O (2).** The powder pattern for compound 2 was collected on a STOE diffractometer fitted with a position-sensitive detector in the angular range 2–130° in 20 h by the Debye–Scherrer method. The pattern was indexed in the orthorhombic system with refined cell dimensions  $a = 22.3775(2)$  Å,  $b = 6.7754(2)$  Å, and  $c = 4.3534(1)$  Å. Although the space group  $\text{Pmmn}$  was chosen, there was some ambiguity in the choice because of the very small  $c$  axis. There were only three  $hkl$  reflections with  $h + k = 2n + 1$ . The powder pattern was decomposed by the LeBail method using profile function no. 4 in GSAS to better treat low-angle peak asymmetry and anisotropy peak broadening. The structure was solved in EXPO<sup>18</sup> and refined in GSAS. The carbon chain and water molecules were found to be disordered about the mirror plane requiring a disorder model in the structure refinement. Atomic positions were refined with soft constraints as indicated for compound 1. Water molecules in the cavity were found to be disordered about the mirror position. One water molecule is disordered over two positions, and their occupancies were summed to 1. The second water molecule was also disordered near the intersection of two perpendicular mirror planes of the space group; however, only two of the four disorder positions are occupied with a total water content of greater than 1. Rietveld refinement of the full pattern total profile refinement of 48 parameters against 11 149 data points leads to  $R_{\text{p}} = 4.3\%$  and  $R_{\text{wp}} = 3.3\%$  with  $\chi = 1.78$  and  $R_{\text{F}} = 12\%$  (1115 observations).



**Figure 1.** Observed (+) and calculated (–) profiles for the Rietveld refined structure for compound 1. The bottom curve is the difference plot on the same intensity scale.



**Figure 2.** Rietveld difference plot for compound 2.

To better fit the positions of the water molecules and the disordered carbon chain, a synchrotron data set of compound 2 was collected in a 0.2 mm quartz capillary tube from 5.5 to 40° with 0.005° increments in 2 $\theta$  ( $\lambda = 0.6857$  Å). GSAS was used in full pattern Rietveld refinement of the profile parameter. Profile function no. 2 with a cosine Fourier background function was used to fit the profile parameters in the LeBail mode with a dummy hydrogen atom in an arbitrary position which gave  $R_{\text{p}} = 2.4\%$  and  $R_{\text{wp}} = 3.1$ . The structural model from the STOE data was then used in full pattern Rietveld refinement. From the difference Fourier map, the second disordered water position was located. However, the carbon atoms in the alkyl backbone were not disordered in these data refinement. Rietveld refinement of the full pattern of parameters against 6899 data points gave  $R_{\text{p}} = 2.53\%$  and  $R_{\text{wp}} = 3.2\%$  with  $\chi = 3.80$  and  $R_{\text{F}} = 4.9\%$  (41 parameters and 388 observations). A summary of crystallographic parameters of the synchrotron data is listed in Table 1.

### III. Results

Crystallographic data for both copper compounds are given in Table 1. The final X-ray observed and Rietveld refined patterns are shown in Figures 1 and 2 and the positional and thermal parameters in Tables 2 and 4 for the C<sub>4</sub> and C<sub>5</sub> compounds, respectively. The structures of the two compounds are similar. The Cu atoms in compound 1 reside at centers of symmetry at (1/4, 1/4, 0) and are octahedrally coordinated by four phosphonate oxygens and two water molecules. The phosphonate

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**Table 2. Positional and Thermal Parameters for Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>4</sub>H<sub>8</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (1)**

	x	y	z	Occ	$U_{\text{iso}} \times 100$
Cu	0.25	0.25	0	1	3.6(1)
P	0.1750(2)	0.5	0.4788(8)	1	3.3(1)
O1	0.1815(2)	0.3040(6)	0.3008(7)	1	4.1(2)
O2	0.2723(3)	0	0.253(1)	1	3.3(3)
C1	0.0961(3)	0.5	0.667(2)	1	1.3(2)
C2	0.0369(2)	0.5	0.438(2)	1	1.4(2)
O1W <sup>a</sup>	0.0643(2)	0	0.050(3)	0.60(1)	8.2(3)
O2W	0.1766(3)	0.038(2)	0.754(2)	0.5	8.6(3)
O1WA <sup>a</sup>	0.0871(7)	0	0.290(4)	0.38(1)	9.5(3)

<sup>a</sup> O1W and O1WA are the disordered water molecules within the tunnel, and their occupancies sum up to 1.

**Table 3. Select Interatomic Distances (Å) and Angles (deg) for Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>4</sub>H<sub>8</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (1·2H<sub>2</sub>O)<sup>a</sup>**

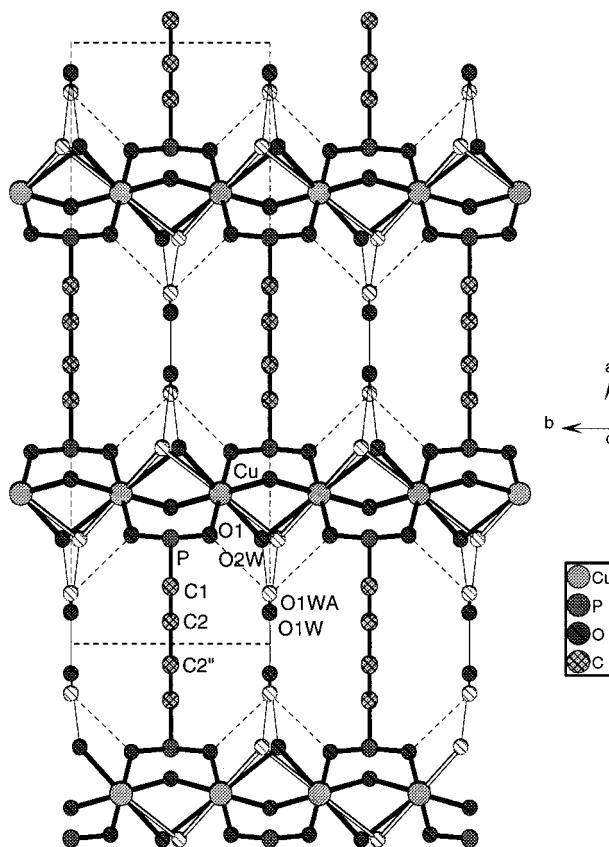
Cu—O1	1.962(3)	2 ×	Cu—O2	2.048(3)	2 ×
Cu—O2W	2.293(10)		Cu'—O2W	2.635(8)	
P—O1	1.531(3)	2 ×	P—O2'	1.564(4)	
P—C1	1.800(6)		C1—C2	1.535(7)	
C2—C2''	1.585(7)		O1W···O2W	2.637(8)	
O1W···O1W''	2.602(9)		O1WA···O2W	2.70(2)	
O2W···O1WA	3.01(1)		O1···O1WA	2.77(1)	
O1—Cu—O2	86.1(2)		O1—Cu—O2''	92.5(2)	
O1—Cu—O2W	88.8(4)		O1—O2''—Cu'	109.1(2)	
O1—P—O2	108.8(2)		O2—P—C1	103.8(4)	
O1—P—C1	108.7(2)		O1—P—O1'	117.3(4)	
P—C1—C2	111.9(5)		C1—C2—C2''	119.2(8)	

<sup>a</sup> Prime and unprimed atoms are related by a mirror plane at  $1/2b$ ; double primed and unprimed atoms are related by an inversion center; the starred atom is related to unstarred atoms by  $y + 1$ .

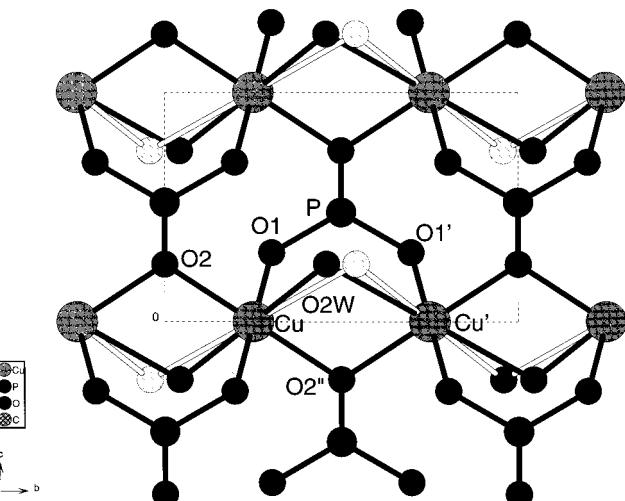
**Table 4. Positional and Thermal Parameters for Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>5</sub>H<sub>10</sub>PO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]·2.8H<sub>2</sub>O**

name	x	y	z	$U_{\text{iso}} \times 100$	Occ
Cu1	0	0.5	0	1.15(3)	1
P1	0.0666(1)	0.75	0.4999(8)	0.99(5)	1
O1	0.0186(2)	0.75	0.2368(9)	1.01(9)	1
O2	0.0596(1)	0.9363(4)	0.6905(6)	0.81(9)	1
C1	0.1388(4)	0.75	0.308(1)	1.0(2)	1
C2	0.1932(3)	0.75	0.544(2)	1.0(2)	1
C3	0.25	0.75	0.366(2)	1.0(2)	1
O1W	0.0687(2)	0.25	0.245(1)	7.7(2)	1
O2W	0.1855(5)	0.25	0.934(4)	7.5(2)	0.55
O2WA	0.2018(7)	0.294(4)	0.241(4)	8.4(2)	0.21
O3WA	0.1354(11)	0.295(5)	0.654(5)	8.0(2)	0.16
O4WA	0.25	0.25	0.824(9)	6.8(2)	0.22

groups O1—P—O1' bridge across Cu atoms and are situated alternately above and below the mean plane of the metal atoms. This connectivity results in chains of the type Cu—OPO—Cu running along the *b*-axis direction (Figure 3). The third phosphonate oxygen, O2, is situated in a direction nearly perpendicular to the chains and bonds to two Cu atoms of an adjacent chain (Figure 4). The chains are thereby linked into layers, which are in turn linked into a three-dimensional structure by the alkyl chains. The O1 and O2 atoms form the equatorial plane of a CuO<sub>6</sub> octahedron, where each of these oxygen atoms originates from a different phosphonate group. The coordination of the Cu atoms is completed by bonding to a water oxygen, O2W, and its centrosymmetric equivalent. However, this water molecule is disordered over two sites at 50% occupancy, as shown in Figure 3, by light and dark oxygen atoms. This water molecule is located slightly off the mirror plane at  $1/2b$ . Therefore, it makes long and short bonds to two contiguous copper atoms in the *b*-axis direction, but there can only be half-occupancy of the two sites.

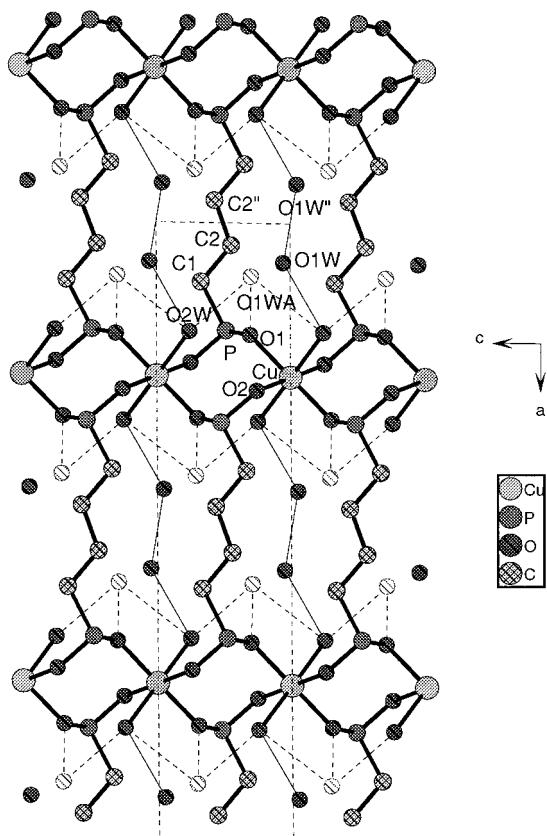


**Figure 3.** Schematic representation in ball-and-stick form of Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>4</sub>H<sub>8</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (1). The drawing is a projection as viewed down the *c* axis.



**Figure 4.** Ball-and-stick representation of compound 1 as viewed down the *a* axis but of only one Cu—O<sub>3</sub>P layer, with the alkyl chains omitted.

Thus, one CuO<sub>6</sub> octahedron would have two centrosymmetrically related water molecules at a bond distance of Cu—OW = 2.29(1) Å, and the adjacent copper would have two longer Cu—OW bonds of 2.64(1) Å (Table 3). A second water molecule, O1W (and O1WA), is contained within the channels created by the alkyl pillars. It, too, is disordered over two nonsymmetry related sites because it occurs on the mirror plane parallel to the *a* axis at  $1/2b$ , which requires 50% occupancy per site. The bond distances and angles are all very regular, as shown

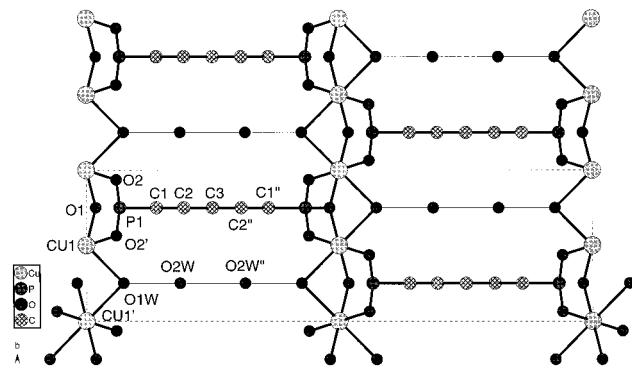


**Figure 5.** Ball-and-stick representation of compound **1** in projection as viewed down the *b* axis. The thin solid line indicates hydrogen bonding between the water bonded to Cu and water within the tunnel, O1W, and the dotted line indicates H bonds involving O1WA (also in Figure 3).

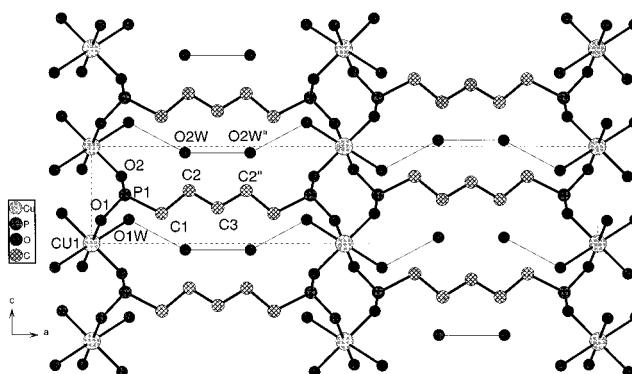
by the values in Table 3. A strong Jahn–Teller effect is observed, in that the Cu–OH<sub>2</sub> axial bonds are significantly longer than the Cu–O(P) bonds.

The characteristic feature of the structure is the channels that run parallel to the *c* axis (Figure 3). The distance between alkyl pillars in the *b*-axis direction is 6.6 Å, and the interlayer distance is  $1/2a \sin \beta$  or 10.03 Å. Because the layer thickness is approximately 4.4 Å, the free space between layers is 5.6 Å and that between the pillars about 4.0 Å. In the *c*-axis direction, the pillars are one unit cell apart or  $\sim$ 4.4 Å apart. These pillars are close enough together so as to form a hydrophobic wall of the tunnel (Figure 5). In the *a*-axis direction, the alkyl chains are staggered alternately at 0 and  $1/2b$ , accounting for the long *a* axis. Hydrogen bonds exist between the water molecule bonded to Cu and the water within the tunnels O2W–O1W, 2.637(8) Å, and O2W–O1WA, 2.70(2) Å. There is also a strong hydrogen bond between O1W and its centrosymmetrically related counterpart O1W" of 2.602(9) Å and a weak bond of 3.01 Å between O2W and O1WA (Figure 5).

**Cu<sub>2</sub>[(O<sub>3</sub>PC<sub>5</sub>H<sub>10</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·2.8H<sub>2</sub>O (2).** This compound has essentially the same structure as the C<sub>4</sub> compound, as can be seen by reference to Figures 6 and 7. In the C<sub>5</sub> compound, the carbon atoms of the chain are cis to each other, whereas they are trans in the C<sub>4</sub> compound. This difference in the chain conformation requires the P–C bonds to tilt in the same direction in adjacent layers in compound **2** but in opposite directions in the C<sub>4</sub> compound (Figure 5). This difference results



**Figure 6.** Schematic representation of compound 2 as viewed down the *c* axis. Only the O2W water molecule is shown.



**Figure 7.** Schematic representation of compound **2** as viewed down the *b* axis. Only the O<sub>2</sub>W water molecule in the tunnel is shown.

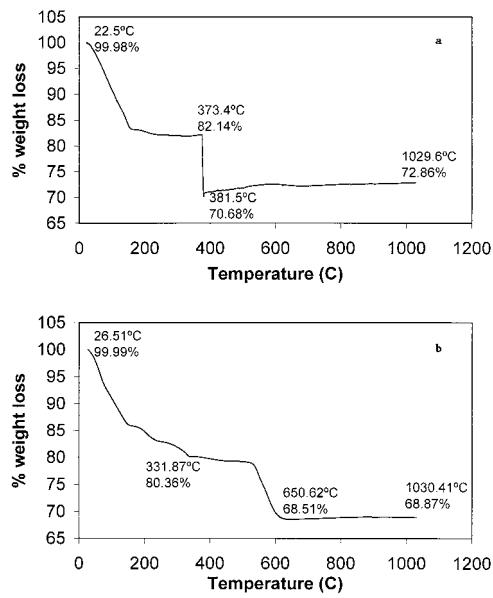
**Table 5. Select Interatomic Distances (Å) and Angles (deg) for Cu<sup>2+</sup>[O<sub>3</sub>PC<sub>5</sub>H<sub>10</sub>PO<sub>3</sub>](H<sub>2</sub>O)<sub>2</sub>]·2.8H<sub>2</sub>O (2·2.8H<sub>2</sub>O)<sup>a</sup>**

Cu–O1	2.024(2)	2×	Cu–O2	1.944(3)
Cu–O1W	2.596(5)	2×	P–O1	1.568(5)
P–O2	1.517(3)	2×	P–C1	1.821(7)
C1–C2	1.591(10)		C2–C3	1.488(6)
O1W…O2W	2.84(1)		O2W…O2W''	2.89(2)
O1W…O2WA	2.87(2)			
O1–Cu–O2	91.5(2)		O1–Cu–O1W	78.3
O2–Cu–O1W	89.55		O1–P–O2	109.2(2)
O2–P–O2'	112.4(3)		O1–P–C1	105.8(3)
O2–P–C1	110.0(2)		P–C1–C2	112.6(4)
C1–C2–C3	108.5(4)		C2–C3–C2''	117.3(7)
Cu–O1–Cu'	113.3(2)			

<sup>a</sup> Primed atoms are related to their unprimed counterpart by a mirror at  $1/4$ b; double primed and unprimed atoms are related by a twofold axis along  $(\frac{1}{4}, \frac{1}{4}, z)$  or  $(\frac{1}{4}, \frac{3}{4}, z)$ .

in a monoclinic unit cell for the even-numbered carbon chain compounds and an orthorhombic one for the odd-numbered carbon chain.

In compound **2**, the copper atom is at the origin of the unit cell, but the CuO<sub>6</sub> octahedra are coordinated in the same way as that for the C<sub>4</sub> compound. However, the coordinated water molecule is not disordered. The Cu–O bond distances are regular; the Cu–O1W distances [2.596(5) Å] are on average longer than the copper to bonded water distance in compound **1** but not unusually long.<sup>19</sup> Although the C1–C2 bond distances are long and the C2–C3 bonds are short, the average is 1.54 Å. All of the bond angles are reasonable, and the water molecules form a loose hydrogen-bonded array within the tunnels.

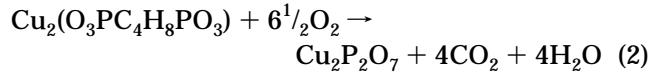
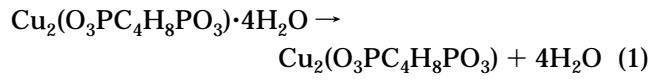


**Figure 8.** TGA weight loss curves for (a)  $\text{Cu}_2[(\text{OPC}_4\text{H}_8\text{PO}_3)(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  and (b)  $\text{Cu}_2[(\text{O}_3\text{PC}_5\text{H}_{10}\text{PO}_3)(\text{H}_2\text{O})_2]\cdot 2.8\text{H}_2\text{O}$ .

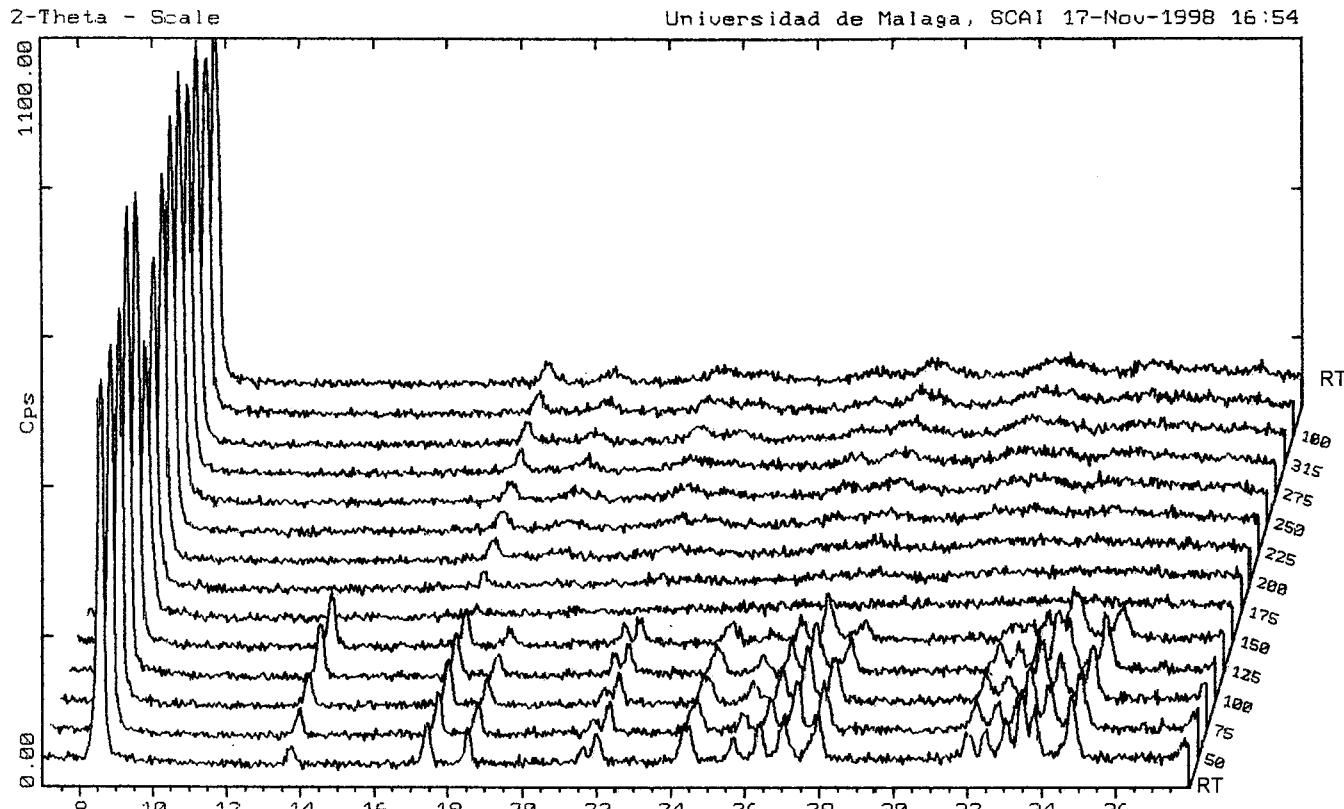
O1W, the water molecule bonded to copper, forms one long (2.84 Å) and one short (2.69 Å) hydrogen bond to O2W (Figure 6). O2W also forms a hydrogen bond to O2W" (2.89 Å, its symmetry equivalent atom related by a twofold rotation). Additional water molecules of low occupancy are also present in the tunnel, forming a loose array of hydrogen bonds. There are a total of 2.8 water molecules within the tunnels.

**Thermal Analysis.** The TGA for compound **1** is given in Figure 8a and that for compound **2** in Figure 8b. For both compounds, the water loss begins immediately on

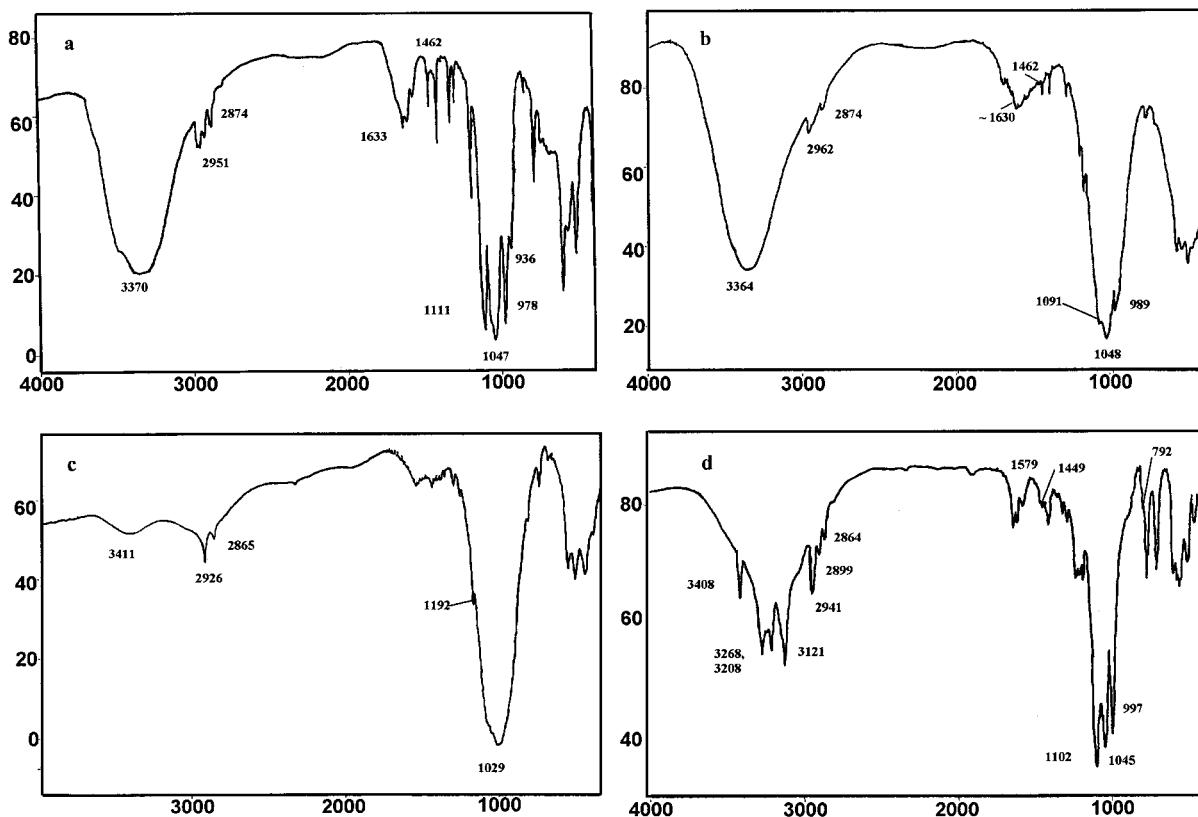
heating, indicative of how loosely the water molecules in the tunnels are held. The first weight loss in compound **1** amounts to 17.86% (to 150 °C), and the total weight loss is 27.14%. An X-ray pattern of the final product showed it to be  $\text{Cu}_2\text{P}_2\text{O}_7$ . On this basis, the formula weight should be 413.16. The calculated formula weight for  $\text{Cu}_2(\text{O}_3\text{PC}_4\text{H}_8\text{PO}_3)\cdot 4\text{H}_2\text{O}$  is 413.2, in excellent agreement with the thermally determined value. The first weight loss of 17.86% is then equivalent to the loss of 4 mol of water, which includes both the water in the tunnel and that bonded to Cu. The process is complete at 373 °C, but even the bulk of the bound water is lost at 150 °C. The organic portion burns up in a narrow range from 373 to 382 °C. The increase in weight above this temperature results from the uptake of oxygen to form the pyrophosphate. The reactions are



Compound **2** exhibits a more complex thermal weight loss curve. The initial weight loss (to 150 °C) amounts to 14.23%, followed by a second loss of 2.56% (230 °C) and a third of 2.85% (332 °C). The total weight loss is 31.13%. On this basis, the formula weight should be 437.1. This formula requires the presence of 4.5–4.6 mol of water compared to 4.8 mol obtained from the X-ray data refinement and a formula weight of 441.6. In fact, the loss of 4.8 mol of water on the basis of the higher formula weight amounts to 19.57%, which is very close to that observed at 331.9°. The total calcula-



**Figure 9.** Thermodiffractogram for compound **1**. A similar set of diffraction patterns is observed for compound **2**.



**Figure 10.** FT-IR spectrum of (a)  $\text{Cu}_2[(\text{O}_3\text{PC}_4\text{H}_8\text{PO}_3)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**), (b)  $\text{Cu}_2[(\text{O}_3\text{PC}_5\text{H}_{10}\text{PO}_3)(\text{H}_2\text{O})_2] \cdot 2.8\text{H}_2\text{O}$  (**2**), (compound **1** dehydrated at 150 °C, soaked in water for 24 h, gently dried to remove surface water, and rinsed with acetone) (c), and compound **1** exposed to ammonia vapor for 80 min (d).

lated weight loss on the basis of 4.8 water molecules is 31.84% as compared to 31.13% observed. Thus, the nonbonded water is close to the observed amount of 2.8 mol and the formula  $\text{Cu}_2[(\text{O}_3\text{PC}_5\text{H}_{10}\text{PO}_3)(\text{H}_2\text{O})_2] \cdot 2.8\text{H}_2\text{O}$ .

**Thermodiffraction.** The thermodiffraction pattern for compound **1** in the temperature range 25–315 °C is shown in Figure 9. It is seen that the X-ray pattern persists to 150 °C. At the next temperature of measurement, the pattern is that of an amorphous solid. This change of phase correlates with the loss of 4 mol of water for compound **1**. However, the pillars apparently do not collapse up to 315 °C. On cooling, the poorly crystalline phase persists to room temperature. Even contact with the water for 24 h does not restore the original crystalline compound. Compound **2** behaves in an almost identical fashion.

**Infrared Spectra.** The FT-IR spectra for the two subject compounds are shown in parts a and b of Figure 10, respectively. The broad bands centered at 3370 and 3364  $\text{cm}^{-1}$  for compounds **1** and **2**, respectively, correspond to the O–H stretch of the bound and free water. The corresponding water bending vibrations are at 1633 and 1630  $\text{cm}^{-1}$ . The asymmetric and symmetric C–H stretching vibrations as well as strong  $\text{CH}_2$  bending motions are prominently visible, as are the phosphonate P–O stretches. The IR spectrum of compound **2** heated at 205 °C for 2 h, soaked in water overnight, and rinsed with acetone to remove surface water showed that rehydration did not take place under these conditions.

The FT-IR spectrum of a sample of  $\text{Cu}_2(\text{O}_3\text{PC}_4\text{H}_8\text{PO}_3) \cdot 4\text{H}_2\text{O}$  exposed to ammonia vapor in a desiccator for 80

**Table 6. Unit Cell Dimensions (Å) and Space Groups of Copper Alkylene Phosphates,  $\text{Cu}_2[(\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3)(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$**

<i>n/x</i>	2/0	3/1	4/2	5/2.8
<i>a</i> (Å)	8.0756(1)	17.3181(8)	20.0305(6)	22.3773(2)
<i>b</i> (Å)	7.5872(1)	6.7624(3)	6.6713(2)	6.7633(2)
<i>c</i> (Å)	7.4100(1)	4.3276(2)	4.3966(1)	4.3529(1)
$\beta$ (deg)	116.319(1)	90.00	91.379	90.00
space group	<i>P</i> 2 <sub>1</sub> /c	<i>P</i> nc2	<i>C</i> 2/m	<i>P</i> mmn

min is shown in Figure 10d. The sample turned from a pale blue to a bright turquoise. The absence of the broad O–H stretch at 3370  $\text{cm}^{-1}$  and the presence of absorption bands at 3408, 3268, 3208, and 3121  $\text{cm}^{-1}$  is indicative of the absence of  $\text{H}_2\text{O}$  and its replacement by both free and bound  $\text{NH}_3$ .

## Discussion

It is of interest to compare the four compounds of the type  $\text{Cu}_2[(\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3)(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$ , with *n* = 2–5. The unit cell dimensions and space groups of these compounds are listed in Table 6. We rearranged the unit cell dimensions of the propylene derivative to accord with the *C*<sub>4</sub> and *C*<sub>5</sub> listings. The interlayer spacings are 7.238, 8.659, 10.012, and 11.189 Å for the 2, 3, 4, and 5 carbon chain compounds, respectively. The average increase in the interlayer spacing is 1.316 Å per carbon atom added to the chain. If the alkyl chains are situated perpendicular to the mean plane of the layers, then the increase should be 1.545 Å sin(109.5/2) or 1.27 Å, in reasonable agreement with the observed value. It should be remarked, however, that the *C*<sub>2</sub> and *C*<sub>3</sub> copper compounds are five-coordinate with distorted square-pyramidal  $\text{CuO}_5$  polyhedra. In the case of the *C*<sub>4</sub> and

$C_5$  compounds, the coordination is octahedral with edge sharing in the *b*-axis direction. There is only one water molecule in the square pyramid but two in the  $CuO_6$  octahedra. However, the effective ratio of coordinated water to Cu is still 1 because the coordinated water in the  $C_4$  and  $C_5$  compounds bridge across adjacent copper atoms.

The water content of the tunnels increases as the length of the carbon chain increases from zero to 2.8 for the four compounds listed in Table 6. This is undoubtedly the result of the increased volume accompanying the increase in alkyl chain length. Removal of the water by heating destroys the crystallinity without collapse of the layers. The process appears to be irreversible because 24 h immersion in water did not restore the crystallinity. It would be advantageous to do so because the anhydrous compounds have two open coordination sites on the copper atoms that might be used in catalytic reactions. In this connection, it is cogent to observe the results with similar lanthanide compounds of general composition<sup>4</sup>  $LnH(O_3P(O_3P(CH_2)_nPO_3)_2$ , with  $n = 2$  and 3. These compounds have structures similar to the disposition of the alkyl chains in the present compounds, as was already described in the Introduction, but are anhydrous. The bonding in the cross-linked compounds is similar to that in the non-cross-linked  $LnH(O_3PC_6H_5)_2$ .<sup>5</sup> The alkyl pillars in these lanthanides are  $\sim 5.3$ – $5.4$  Å apart in one direction and

4.2 Å apart in the perpendicular direction as compared to 6.7 and 4.3–4.5 Å in the copper compounds. This narrowing of the tunnels in the lanthanides is the result of the chelation–donation-type bonding. These tunnels are more hydrophobic, which may account for the absence of water in the tunnels. Apparently, once the copper compounds lose their water, the hydrophobic nature of the carbon chains mitigates against rehydration. The lanthanide phosphonates were prepared hydrothermally at 210 °C, and alternatively, this high temperature may be responsible for the lack of water in the tunnels. This temperature is greater than the dehydration temperature of the copper compounds. Thus, it may be possible to prepare the copper alkylene derivatives, water free, under similar synthesis conditions, to create open tunnels that will accept relatively nonpolar molecules.

**Acknowledgment.** This study was carried out with funds supplied by the R. A. Welch Foundation Grant A673 and the National Science Foundation Grants DMR-9707151 and DMR-0080040, for which grateful acknowledgment is made. We thank Dr. Aurelio Cabeza of the University of Malaga, Spain, for obtaining the thermodiffraction data.

CM010651+