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Synthesis, Crystal Structures, and Coordination Intercalation Behavior of Two Copper Phosphonates

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Two copper phosphonates, $Cu(O_3PCH_3)\cdot H_2O$ and $Cu(O_3PC_6H_5)\cdot H_2O$, have been synthesized and their structures determined. $Cu(O_3PCH_3)\cdot H_2O$ is monoclinic: space group $P2_1/c$, $a = 8.495\ (4)$ Å, $b = 7.580\ (4)$ Å, $c = 7.289\ (4)$ Å, $\beta = 90.08\ (4)°$, $Z = 4$, $V = 469.4\ (7)$ Å^3. Refinement with 683 observed reflections for which $I \geq 3\sigma(I)$ gave $R = 0.030$ and $R_w = 0.041$. The structure is layered as formed by unusual 5-coordinate distorted tetragonal pyramidal copper atoms. One oxygen of each phosphonate bonds to two copper atoms forming a chain, while the other two phosphonate oxygens bond to two copper atoms in an adjacent chain. The base of the pyramid thus consists of three phosphonate oxygens and the coordinated water molecule. All hydrogen bonds are of the intralayer type, so only van der Waals forces exist between adjacent layers. Amines are coordinatively intercalated with layer expansion. $Cu(O_3PC_6H_5)\cdot H_2O$ is orthorhombic: space group $Pbca$, $a = 7.5547\ (4)$ Å, $b = 7.4478\ (6)$ Å, $c = 27.982\ (1)$ Å, $Z = 8$, $V = 1574.4\ (2)$ Å^3. Refinement using 952 reflections for which $I \geq 3\sigma(I)$ gave $R = 0.037$ and $R_w = 0.043$. The coordination about the copper atoms and the layer structure are identical to those of the methylphosphonate compound. However, the phenyl rings in the interlamellar space are oriented at a 98° angle to each other in adjacent rows. These structures are compared to those of other layered divalent phosphonates and copper phosphites.

Introduction

Interest in metal phosphonate chemistry has accelerated in recent years. Among the newly synthesized compounds are examples of monomolecular coordination complexes,[1,2] one-dimensional (linear) complexes,[3,4] and layered compounds.[5,6] Our interest was originally focused on the layered compounds of group 4 and 14 elements because of their similarity to the inorganic phosphates of these metals.[7] More recently it has been demonstrated that divalent[6,8] and trivalent[9,10] elements form layered phosphonates and our preliminary studies indicate that certain penta- and hexavalent metals also form such compounds.[11] Just as the group 4 and 14 phosphonates have their structural counterparts among the inorganic phosphates of the α-zirconium phosphate type so do certain of the divalent elements form phosphonates with layer structures similar to that of NH_4FePO_4.[12,13] Among the vanadium phosphonates, it has been suggested that $VO(O_3PC_6H_5)\cdot 2H_2O$ conforms to the Newberyite structure,[14] while the monohydrate has features similar to those of β-$VOPO_4$.[14,15] These inorganic compounds exhibit interesting magnetic and electronic properties.[13,15,16] In the inorganic compounds, the metals are bridged within layers by phosphate groups with ions occupying the interlayer space. In the phosphonates, the metal–oxygen layers are similar to their inorganic counterparts but are separated by insulating alkyl or aryl groups. Thus, it may be possible to control interlayer interactions through choice of the organic phosphonate and thus modulate electronic and magnetic properties within the layers.

Another feature of these layered phosphonates is the inclusion of functional groups; these may be already present on the organic moiety,[17] or they may be incorporated by postsynthesis reactions.[18,19] This feature opens up a wealth of potential chemistry which can be exploited to prepare catalysts, ion exchangers, and sorbents. These layered phosphonates can also undergo both Bronsted and Lewis acid[20] intercalative chemistry, which can be used to modify optical or electronic properties of the host. It is therefore of interest to establish the structure of the prototype layered compounds so as to better understand the nature of the functionalized or intercalated products. In this paper we describe the synthesis and structure of two copper phosphonates, $Cu(O_3PCH_3)\cdot H_2O$ and $Cu(O_3PC_6H_5)\cdot H_2O$.

Experimental Section

Materials and Methods. Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification. X-ray powder diffraction patterns were obtained on a Rigaku AFC-5 diffractometer with monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) and a rotating anode generator. Thermogravimetric analyses (TGA) were carried out with a Du Pont thermal analysis unit, Model No. 951, at a rate of 10 °C/min. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr disk method.

Preparation of Copper Phosphonates. A 1.02-g sample of $H_2PO_3CH_3$ (Aldrich) and 2.61 g of $CuSO_4\cdot 5H_2O$ (MCB reagent) were dissolved in 100 mL of deionized water. To the resulting clear blue solution (pH = 1.8) was added 0.95 g of urea and the pH raised to 2.8 with 0.1 M NaOH. The solution was kept at 65 °C in an oil bath for a period of 5 days. Under these conditions, the urea slowly hydrolyses with release of NH_3, thereby raising the pH in a homogeneous manner. An 0.88-g amount of blue platelike crystals of $Cu(O_3PCH_3)\cdot H_2O$ was obtained (48% yield) after filtration, washing with deionized water, and air-drying. The single crystals of $Cu(O_3PC_6H_5)\cdot H_2O$ were obtained similarly using phenylphosphonic acid, except that NaOH was not added.

Crystallographic Study. A blue platelike crystal of $Cu(O_3PCH_3)\cdot H_2O$ having approximate dimensions 0.3 × 0.2 × 0.03 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator at room temperature. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 randomly oriented reflections in the range $10° \leq 2\theta \leq 35°$, corresponded to a monoclinic cell. Since

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(1) Clark, E. T.; Rudolf, P. R.; Martell, A. E.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *164*, 59.

(2) Rudolf, P. R.; Clark, E. T.; Martell, A. E.; Clearfield, A. *J. Coord. Chem.* **1985**, *14*, 139.

(3) Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chem. Mater.* **1990**, *2*, 582.

(4) Glowiak, T.; Sawka-Doborwolska, W.; Jezowska-Trzebratowska, B.; Antonow, A. *J. Cryst. Mol. Struct.* **1980**, *10*, 1.

(5) Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990**, *2*, 91.

(6) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781.

(7) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(8) Martin, K.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 7.

(9) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112.

(10) Wang, R.-C.; Zhang, Y. P.; Squattrito, P. J.; Hu, H-L.; Frausto, R. R.; Clearfield, A. *Chem. Mater.*, submitted.

(11) Zhang, Y-P.; Clearfield, A.; work in progress.

(12) Durif, A.; Averbuch-Pouchat, M. T. *Bull. Soc. Fr. Mineral Crystallogr.* **1968**, *91*, 495; Tranqui, D.; Durif, A.; Guitel, J. C.; Averbuch-Pouchat, M. T. *Bull. Soc. Fr. Mineral Crystallogr.* **1968**, *91*, 10.

(13) Janov, Yu. A.; Egorov-Tismenko, Yu. K.; Simonov, M. A.; Belov, N. V. *Sov. Phys. Crystallogr.* **1975**, *19*, 665.

(14) Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990**, *2*, 91.

(15) Gopal, R.; Calvo, C. J. *J. Solid State Chem.* **1972**, *5*, 432.

(16) Greedan, J. E.; Reubenbauer, K.; Birchall, T.; Ehlert, M.; Corbin, D. R.; Subramanian, M. A. *J. Solid State Chem.* **1988**, *77*, 376.

(17) Alberti, G.; Costantino, U.; Kornyei, J.; Luciani-Giavagnotti, M. L. *React. Poly.* **1985**, *4*, 1.

(18) Yang, C.-Y.; Clearfield, A. *React. Poly.* **1987**, *5*, 13.

(19) Alberti, G.; Costantino, U. *J. Mol. Catal.* **1984**, *27*, 235.

(20) (a) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434; (b) Frink, K. J.; Wang, R.-C.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438.

0020-1669/92/1331-2821$03.00/0

Table I. Crystallographic Data for $Cu(O_3PCH_3){\cdot}H_2O$ and $Cu(O_3PC_6H_5){\cdot}H_2O$

	$Cu(O_3PCH_3){\cdot}H_2O$	$Cu(O_3PC_6H_5){\cdot}H_2O$
empirical formula	$CuPO_4CH_5$	$CuPO_4C_6H_7$
fw	175.57	237.64
a, Å	8.495 (4)	7.5547 (4)
b, Å	7.580 (4)	7.4478 (6)
c, Å	7.289 (4)	27.982 (1)
β, deg	90.08 (4)	
V, Å^3	469.4 (7)	1574.4 (2)
Z	4	8
space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
D_c, g/cm^3	2.484	2.005
T, °C	23 ± 1	23 ± 1
λ(Mo Kα), Å	0.7107	0.7107
F(000)	348	952
μ, cm^{-1}	48.97	29.48
transm coeff	0.458–1.00	0.92–1.03
R	0.030	0.037
R_w	0.041	0.043
goodness of fit	1.48	1.47

the β angle was close to 90°, axial photographs were taken to confirm the monoclinic symmetry. On the basis of the systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$. The data were collected out to 50° in 2θ using the ω–2θ scan technique at a speed of 16°/min in ω.[21] A total of 961 reflections were measured, of which 924 were unique (R_{int} for averaging equivalent reflections is 0.013). The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection. An empirical absorption correction based on the ψ scan measurements was applied, and the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[22] The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located from ΔF maps and refined with fixed thermal parameters. The final cycle of full-matrix least-squares refinement was based on 683 observed reflections ($I \geq 3\sigma(I)$) and 79 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.030$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2} = 0.041$, where $w = 4F_o^2/(\sigma(F_o^2))^2$.

Crystallographic data for $Cu(O_3PCH_3){\cdot}H_2O$ and $Cu(O_3PC_6H_5){\cdot}H_2O$ are listed in Table I.

$Cu(O_3PC_6H_5){\cdot}H_2O$. The data were collected on a blue platelet of approximate dimensions 0.2 × 0.2 × 0.04 mm^3. Orthorhombic lattice parameters and an orientation matrix for data collection were obtained from a least-squares refinement using 25 carefully centered reflections in the range $17.7° \leq 2\theta \leq 28.07°$. On the basis of the systematic absences and successful refinement of the structure, the space group was determined to be $Pbca$. The data were collected out to 50° in 2θ by using the ω scan technique with a scan width of $(1.13 + 0.3 \tan \theta)°$ at a speed 16°/min in ω. A total of 3258 reflections were collected, of which 1665 were unique (R for averaging equivalent reflections is 0.038). Three representative reflections were measured every 150 reflections to monitor instrument and crystal stability. An empirical absorption correction, using the program DIFABS,[23] was applied, and the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and then the hydrogen atoms were located from the ΔF map and refined with fixed thermal parameters. The final cycle of full-matrix least-squares refinement was based on 997 observed reflections ($I \geq 3\sigma(I)$) and 130 variable parameters and converged (maximum $|\Delta/\sigma|$ is 0.28) with unweighted agreement factors of $R = 0.037$ and $R_w = 0.043$. Neutral-atom scattering factors were taken from Cromer and Waber,[24] and anomalous dispersion corrections were taken from Cromer and Liberman.[25]

Results

Structure of $Cu(O_3PCH_3){\cdot}H_2O$. Positional and thermal parameters of the atoms in this structure are given in Table II, and selected bond distances and angles are listed in Table III. Figure

Table II. Positional and Thermal Parameters for the Atoms of $Cu(O_3PCH_3){\cdot}H_2O$

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	0.45019 (8)	0.19023 (8)	0.05974 (9)	1.16 (3)
P(1)	0.3167 (2)	0.5503 (2)	0.1556 (2)	0.98 (6)
O(1)	0.3226 (5)	0.3969 (5)	0.0193 (5)	1.4 (2)
O(2)	0.4188 (5)	0.5084 (5)	0.3210 (5)	1.3 (2)
O(3)	0.3628 (5)	0.7240 (5)	0.0653 (5)	1.5 (2)
O(4)	0.2642 (6)	0.0656 (6)	0.1635 (6)	1.6 (2)
C(1)	0.1180 (8)	0.573 (1)	0.231 (1)	2.1 (3)
H(1)	0.29 (1)	−0.03 (1)	0.13 (1)	3.0
H(2)	0.28 (1)	0.07 (1)	0.27 (1)	3.0
H(3)	0.039 (9)	0.602 (8)	0.12 (1)	3.0
H(4)	0.103 (9)	0.66 (1)	0.31 (1)	3.0
H(5)	0.06 (1)	0.48 (1)	0.30 (1)	3.0

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}A_i{\cdot}A_j$.

Table III. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cu(O_3PCH_3){\cdot}H_2O$

Cu(1)–O(1)	1.928 (4)	Cu(1)–O(2)A[a]	1.973 (4)
Cu(1)–O(3)A[c]	1.945 (4)	Cu(1)–O(4)	1.991 (5)
Cu(1)–O(2)B[b]	2.316 (4)	P(1)–O(1)	1.530 (4)
P(1)–O(2)	1.518 (4)	P(1)–O(3)	1.523 (4)
P(1)–C(1)	1.783 (7)		
O(1)–Cu(1)–O(3)[c]	96.7 (2)	O(1)–Cu(1)–O(2)[a]	162.2 (2)
O(1)–Cu(1)–O(4)	89.8 (2)	O(1)–Cu(1)–O(2)[b]	110.4 (2)
O(3)[c]–Cu(1)–O(2)[a]	88.8 (2)	O(3)[c]–Cu(1)–O(4)	170.4 (2)
O(3)[c]–Cu(1)–O(2)[b]	87.6 (2)	O(2)[a]–Cu(1)–O(4)	87.1 (2)
O(2)[a]–Cu(1)–O(2)[b]	86.6 (2)	O(4)–Cu(1)–O(2)[b]	83.5 (2)
O(1)–P(1)–O(2)	109.7 (2)	O(1)–P(1)–O(3)	111.6 (2)
O(1)–P(1)–C(1)	107.7 (3)	O(2)–P(1)–O(3)	112.1 (2)
O(2)–P(1)–C(1)	108.5 (3)	O(3)–P(1)–C(1)	107.1 (3)

Hydrogen-Bond Parameters

	D···A	H···A	∠DHA
O(4)[b]–H(2)···O(1)	2.655 (6)	1.86 (7)	173 (7)
O(4)[c]–H(1)···O(3)	2.815 (6)	2.06 (8)	173 (8)

[a] Atom related by $1 - x$, $y - {}^1/_2$, ${}^1/_2 - z$. [b] Atom related by x, ${}^1/_2 - y$, $z - {}^1/_2$. [c] Atom related by x, $1 + y$, z.

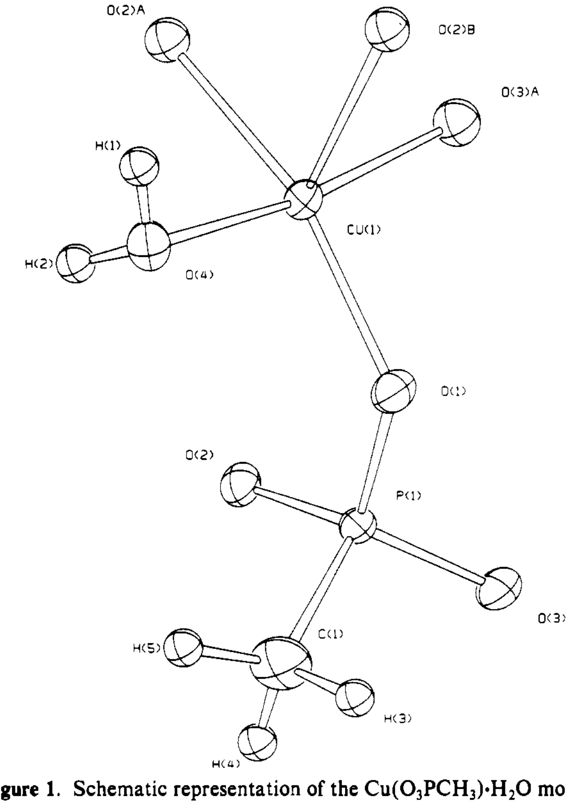

Figure 1. Schematic representation of the $Cu(O_3PCH_3){\cdot}H_2O$ molecule showing the coordination about the copper atom and the numbering scheme used in the tables. Thermal ellipsoids are at the 50% probability level.

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(21) MSC/AFC Diffractometer Control Software, Molecular Structure Corp.; The Woodlands, TX 1988 (revised).

(22) "TEXSAN, Texray Structural Analysis Package"; Molecular Structure Corp.; The Woodlands, TX, 1987 (revised).

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(24) Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(25) Cromer, D. T.; Lieberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

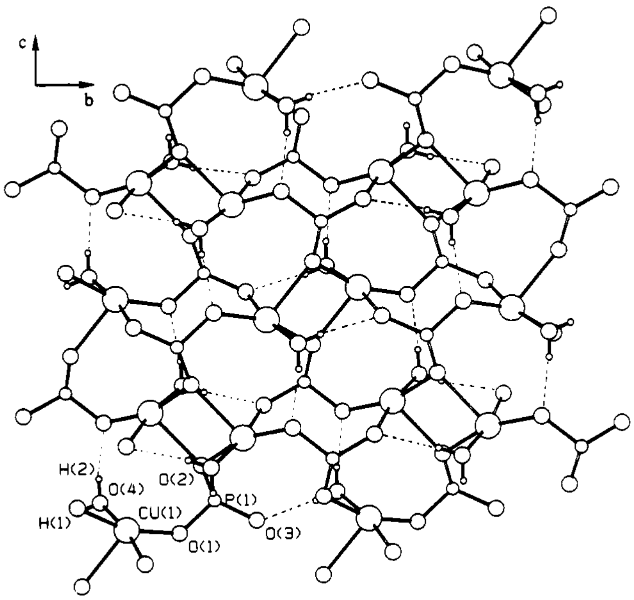

Figure 2. Schematic representation of a $Cu(O_3PCH_3)\cdot H_2O$ layer as seen perpendicular to the *a*-axis. Dashed lines represent hydrogen bonds. Methyl groups were omitted for clarity.

Table IV. Least-Squares Planes and Atom Deviations (Å) from the Planes

Plane No. 1—$Cu(O_3PCH_3)\cdot H_2O$			
$1.8948X + 3.7155Y + 6.1395Z = 1.9394$			
Cu(1)	−0.0128 (6)	O(3)A[b]	−0.108 (4)
O(1)	0.265 (4)	O(4)	−0.191 (5)
O(2)A[a]	0.292 (4)		
$\chi^2 = 14758$; mean deviation = 0.174 Å			
Plane No. 2—$Cu(O_3PC_6H_5)\cdot H_2O$			
$3.8502X + 6.1188Y - 7.1510Z = 2.7858$			
Cu(1)	0.0120 (7)	O(3)A[c]	−0.248 (4)
O(1)	0.192 (4)	O(4)A[d]	−0.225 (4)
O(2)	0.163 (4)		
$\chi^2 = 12768$; mean deviation = 0.168 Å			

[a] Atom related by $1 - x, y - 1/2, 1/2 - z$. [b] Atom related by $x, 1 + y, z$. [c] Atom related by $1 - x, \bar{y}, \bar{z}$. [d] Atom related by $3/2 - x, y - 1/2, z$.

1 shows the coordination environment of the Cu atom in $Cu(O_3PCH_3)\cdot H_2O$ and the numbering scheme used in the tables. Each Cu atom has a distorted tetragonal pyramidal coordination. The four coplanar oxygen atoms (three phosphonate oxygens, O(1), O(2)A, O(3)A, and one water oxygen) have bond distances in the range 1.928 (4)–1.991 (5) Å. The fifth oxygen atom, O(2)B, related to O(2) by $x, 1/2 - y, z - 1/2$) is nearly perpendicular to the plane and has a bond length of 2.316 (4) Å, which is about 16% longer than the average of the four equatorial bond lengths. There are no other oxygen atoms at a distance shorter than 3.5 Å to the Cu atom. The three oxygens of the phosphonate group are all bonded to Cu atoms. One of them, O(2), bridges two Cu atoms which are 3.129 (2) Å apart. This bridging oxygen forms a short (1.973 (4) Å) and a long (2.316 (4) Å) bond to the adjacent copper atoms. These same two copper atoms are bridged by a second O(2) atom from another phosphonate group forming a 4-membered parallelogram-shaped ring. The remaining two oxygen atoms of each phosphonate group then bridge across copper atoms in adjacent rows to form 8-membered puckered rings (Figure 2) of the type Cu–O(1)–P–O(3)–Cu–O(1)′–P–O(3)′. In the process a second more circular 8-membered ring structure is formed. The layer then consists of rows of circular 8-membered rings running in the *b*-axis direction and alternating in the *c*-axis direction with rows consisting of alternating 4-membered rectangular rings and 8-membered puckered rings.

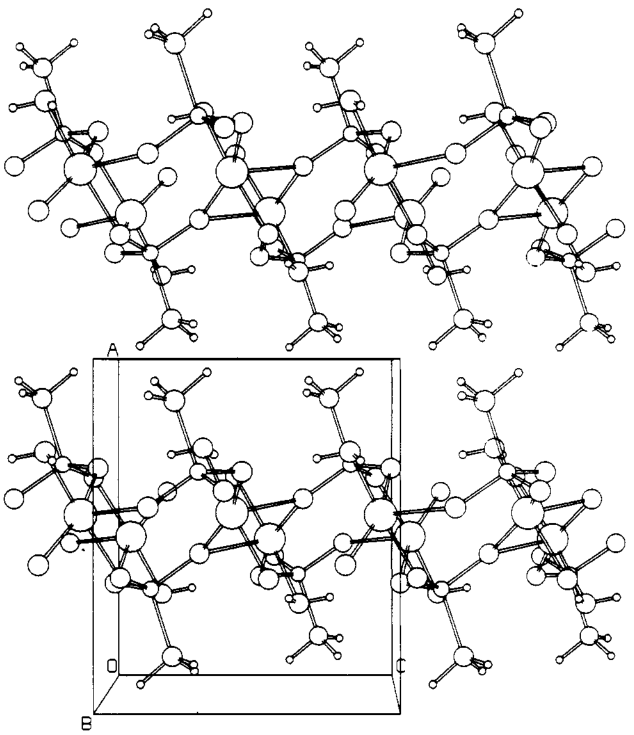

Figure 3. Layer arrangement in $Cu(O_3PCH_3)\cdot H_2O$ as viewed down the *b*-axis.

Table V. Positional and Thermal Parameters for the Atoms of $Cu(O_3PC_6H_5)\cdot H_2O$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.80872 (8)	−0.06378 (9)	−0.01038 (2)	1.08 (3)
P(1)	0.5460 (2)	0.1547 (2)	0.05684 (5)	0.93 (6)
O(1)	0.9271 (6)	−0.1746 (6)	−0.0666 (1)	1.3 (2)
O(2)	0.7264 (5)	0.0766 (5)	0.0443 (1)	1.4 (2)
O(3)	0.3991 (5)	0.0195 (5)	0.0481 (1)	1.1 (2)
O(4)	0.5072 (5)	0.3289 (5)	0.0300 (1)	1.0 (2)
C(1)	0.5440 (7)	0.2038 (8)	0.1197 (2)	1.3 (2)
C(2)	0.4202 (9)	0.321 (1)	0.1380 (2)	2.2 (3)
C(3)	0.412 (1)	0.352 (1)	0.1687 (3)	3.4 (4)
C(4)	0.525 (1)	0.267 (1)	0.2170 (2)	3.6 (4)
C(5)	0.648 (1)	0.149 (1)	0.1993 (3)	3.6 (4)
C(6)	0.660 (1)	0.116 (1)	0.1507 (2)	2.4 (3)
H(2)	0.336 (9)	0.38 (1)	0.118 (2)	4.0
H(3)	0.34 (1)	0.41 (1)	0.196 (3)	4.0
H(4)	0.52 (1)	0.30 (1)	0.247 (3)	4.0
H(5)	0.73 (1)	0.08 (1)	0.219 (2)	4.0
H(6)	0.74 (1)	0.05 (1)	0.139 (2)	4.0
H(7)	1.05 (1)	−0.15 (1)	−0.063 (2)	4.0
H(8)	0.92 (1)	−0.29 (1)	−0.062 (3)	4.0

[a] See Table II.

The base of the square pyramid is not very planar as seen by the data in Table IV. Two of the oxygens, O(1) and O(2)A, are out of the plane in the positive direction with an O(2)A–Cu–O(1) angle of 162.2 (2)° and O(3)A and O(4) are out of the plane in the opposite direction at an O(3)A–Cu–O(4) angle of 170.4 (2)°. The fifth atom, O(2)B, lies on the O(3), O(4) side.

The layers are situated perpendicular to the *a*-axis with an interlayer distance equal to *a* as shown in Figure 3. The phosphonate group forms an almost regular tetrahedron with the methyl groups extending into the interlamellar space above and below the CuO_3P inorganic portion of the layer. The P–C bond is inclined at an angle of 71° to the mean plane of the layer.

Both hydrogens of the water molecule form hydrogen bonds with adjacent oxygen atoms within the layer as indicated in Table III and by the dashed lines in Figure 2. Thus, the layers are held together by van der Waals attractions as all the hydrogen bonds lie within the layer.

Structure of $Cu(O_3PC_6H_5)\cdot H_2O$. Positional and thermal parameters for $Cu(O_3PC_6H_5)$ are listed in Table V while selected bond distances and angles are given in Table VI. This compound has a layered structure similar to that of the corresponding methylphosphonate with an interlayer distance of *c*/2 as shown in

Table VI. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cu(O_3PC_6H_5)\cdot H_2O$

Cu(1)–O(1)	1.990 (4)	Cu(1)–O(2)	1.956 (4)
Cu(1)–O(3)A^{c}	1.921 (4)	Cu(1)–O(4)B^{b}	2.369 (4)
Cu(1)–O(4)A^{a}	1.963 (4)	P(1)–O(2)	1.523 (4)
P(1)–O(3)	1.518 (4)	P(1)–O(4)	1.527 (4)
P(1)–C(1)	1.796 (6)	C(1)–C(2)	1.376 (8)
C(1)–C(6)	1.393 (8)	C(2)–C(3)	1.385 (9)
C(3)–C(4)	1.36 (1)	C(4)–C(5)	1.37 (1)
C(5)–C(6)	1.384 (9)		
O(1)–Cu(1)–O(2)	169.8 (2)	O(1)–Cu(1)–O(3)^{c}	90.2 (2)
O(1)–Cu(1)–O(4)^{b}	80.7 (2)	O(1)–Cu(1)–O(4)^{a}	88.2 (2)
O(2)–Cu(1)–O(3)^{a}	94.5 (2)	O(2)–Cu(1)–O(4)^{b}	89.3 (1)
O(2)–Cu(1)–O(4)^{a}	89.6 (2)	O(3)^{c}–Cu(1)–O(4)^{b}	105.3 (1)
O(3)^{a}–Cu(1)–O(4)^{a}	165.0 (2)	O(4)^{a}–Cu(1)–O(4)^{b}	89.2 (1)
O(2)–P(1)–O(3)	111.3 (2)	O(2)–P(1)–O(4)	112.5 (2)
O(2)–P(1)–C(1)	108.1 (2)	O(3)–P(1)–O(4)	110.1 (2)
O(3)–P(1)–C(1)	106.7 (2)	O(4)–P(1)–C(1)	107.9 (2)
P(1)–C(1)–C(2)	120.0 (5)	P(1)–C(1)–C(6)	120.6 (5)
C(2)–C(1)–C(6)	119.3 (6)	C(1)–C(2)–C(3)	120.2 (7)
C(2)–C(3)–C(4)	120.5 (7)	C(3)–C(4)–C(5)	120.6 (6)
C(1)–C(6)–C(5)	119.4 (7)		

Hydrogen-Bond Parameters

	D···A	H···A	∠DHA
O(1)–H(7)···O(2)^{e}	2.788 (6)	1.86 (7)	168 (6)
O(1)–H(8)···O(3)^{d}	2.629 (6)	1.80 (8)	175 (7)

[a] Atom related by $^3/_2 - x, y - ^1/_2, z$. [b] Atom related by $^1/_2 + x, ^1/_2 - y, \bar{z}$. [c] Atom related by $1 - x, \bar{y}, \bar{z}$. [d] Atom related by $^1/_2 + x, \bar{y} - ^1/_2, \bar{z}$. [e] Atom related by $2 - x, \bar{y}, \bar{z}$.

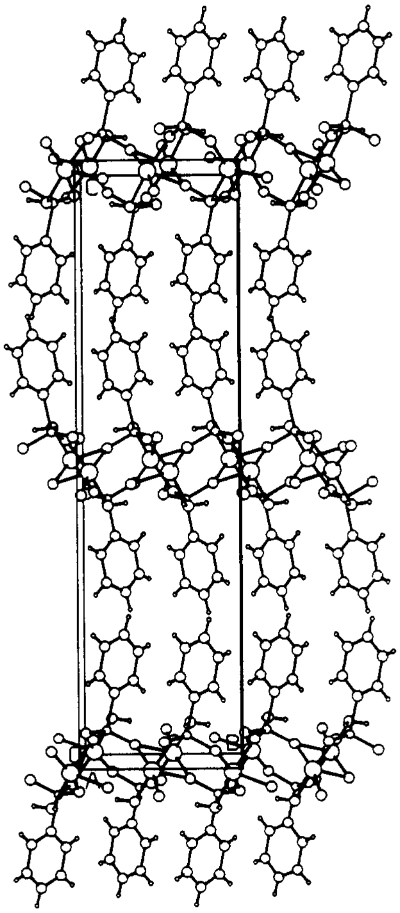

Figure 4. Layer arrangement in $Cu(O_3PC_6H_5)\cdot H_2O$ as viewed down the *a*-axis.

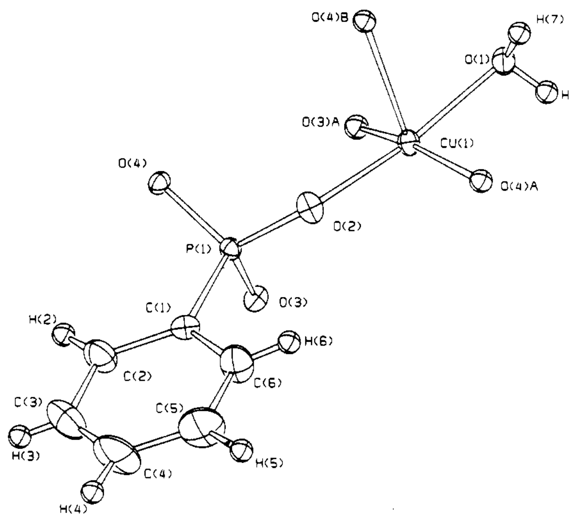

Figure 5. Molecular representation and atom numbering scheme for $Cu(O_3PC_6H_5)\cdot H_2O$.

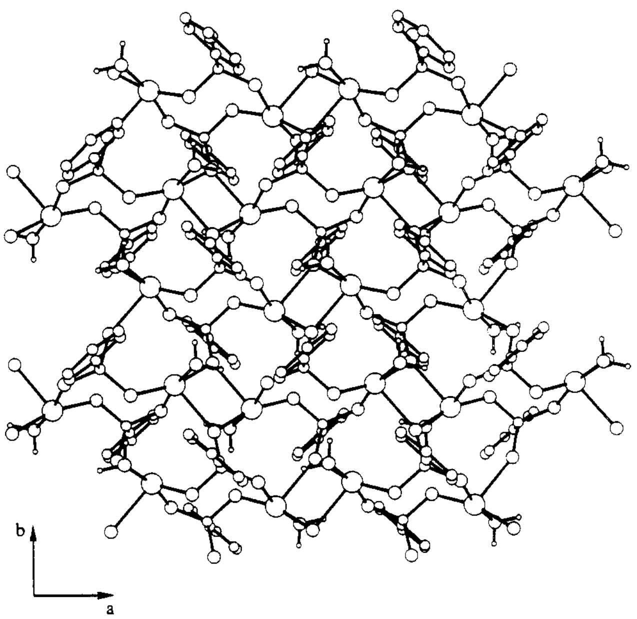

Figure 6. Schematic representation of a $Cu(O_3PC_6H_5)\cdot H_2O$ layer as viewed down the *c*-axis illustrating the arrangement of phenyl rings.

Figure 4. The layers are stacked perpendicular to the *c*-axis, and adjacent layers are symmetrically related by the *c*-glide. Each Cu atom is 5-coordinate in a tetragonal pyramidal geometry very similar to that present in the methyl derivative. The four oxygen atoms forming the base of the pyramid have bond lengths in the range 1.921 (4)–1.990 (4) Å, with values identical to those of the corresponding bond lengths in the methyl derivative. This coordination geometry and the numbering scheme used in the tables is shown in Figure 5. The CuO_3P inorganic portion of the structure is thus very similar to its methylphosphonate counterpart. However, the phenyl rings show an ordered orientation (Figure 6). The phenyl rings adjacent to each other are oriented so that their mean planes are approximately perpendicular to each other. The actual dihedral angle is 98°. Thus, each phenyl ring is perpendicular to two others at a distance of 4.85 Å and two at 5.75 Å. Neither of these distances is long enough for two phenyl rings to sit edge to edge. Reference to Figure 4 shows that all the phenyl rings in any one row along the *b*-axis direction are oriented parallel to each other while the phenyl rings in an adjacent layer are oriented at 98° to the first. In this structure, the P–C bond is at an angle of 78° to the mean plane of the layer.

The hydrogen-bonding scheme is of the same type as exhibited by the methyl derivative. This tight hydrogen-bonding scheme results in high temperatures of dehydration. Thermogravimetric weight loss curves show the onset of water loss at 195 °C for the methyl compound and 160 °C for the phenyl derivative. A second contributing factor to the stability of the copper–water bond is the highly unfavorable coordination which results upon water loss. Either a highly distorted tetrahedral or trigonal pyramid would result, both being high-energy arrangements. It is interesting to note that the interlayer spacing of both copper compounds increases by 1.2 Å on dehydration. The powder patterns do not contain sufficient data, due to preferred orientation, to determine whether the dehydration is topotactic or not, but it is most likely so since the dehydration is readily reversible.

Intercalation of Amines. The 5-coordinate copper atoms described in these phosphonate structure would be expected to have a sixth coordination site available for interaction with electron donors. In addition by removal of the coordinated water molecule a second coordination site may become available. This was the case for the cobalt phosphonates where it was shown that amines or NH_3 could be intercalated between the layers at the coordination site vacated by a water molecule.[20] Therefore, two different experiments were carried out. In the first a small quantity of $Cu(O_3PCH_3)\cdot H_2O$ was added to neat butylamine. The light blue color of the compound was transformed to a deep blue almost immediately. After an hour of immersion, the solid was filtered off and an X-ray powder pattern immediately obtained. It showed a major peak at 14.8 Å and a doublet at 8.64 and 8.50 Å. These latter two reflections are those of the original copper phosphonate while the former is due to the expanded interlayer distance resulting from amine intercalation. On standing in air the intensity of the 14.8-Å peak diminished and finally disappeared.

In the second experiment, a quantity of $Cu(O_3PCH_3)\cdot H_2O$ was heated to remove the coordinated water and then immediately immersed in neat butylamine for 1 h. The X-ray powder pattern of the resultant deep blue solid in this case consisted of broad peaks at 15.1 Å (001), 7.54 Å (002), and 5.03 Å (003) with small but narrow reflections at 8.66 and 8.52 Å. From the shapes of the peaks it was evident that the interlayer spacing had increased to 15.1 Å and that the 7.54- and 5.03-Å peaks are higher orders of this reflection. Longer immersion in butylamine removed the reflections of the unintercalated solid. When fully intercalated, the compound contained only 1 mol of amine, and no loss of amine was observed on standing in air. Only when heated to about 120 °C does the compound begin to lose amine.

Corroborating evidence that amine intercalation has indeed occurred was derived from infrared spectra. The important vibrations of $Cu(O_3PCH_3)\cdot H_2O$ are as follows: 3242 cm^{-1} (s), O–H stretch of coordinated water; 1575 cm^{-1} (m), H_2O bend; 3011 (s) and 2982 cm^{-1} (m), methyl C–H stretch; 1420 (w) and 1304 cm^{-1} (ms) asymmetric and symmetric C–H deformation, respectively; four bands between 930 and 1200 cm^{-1} representing PO_3 vibrations. The butylamine intercalate showed additional vibrations at 3384 and 3124 cm^{-1} and a much broadened water bend vibration at 1585 cm^{-1} indicative of intercalated water, with 2960, 2924, and 2867 cm^{-1} observed for the methyl and methylene C–H stretches of the butyl group and 1464 (w) and 1379 cm^{-1} (w) observed for methylene bending and twisting. In the intercalate for which coordinated water was removed before exposure to butylamine all of the bands were very sharp. Bands at 3250, 3210, and 3125 cm^{-1} must be due to N–H vibrations of the amine coordinated to the copper. The phenylphosphonate was also found to intercalate amines. A full report of these intercalation reactions will be published subsequently.

Discussion

The structure for the copper phosphonates presented here differs from those of the zinc and manganese phosphonates. While these latter compounds have layered structures, the metal atoms are 6-coordinate.[6,8] This coordination is achieved by having the phosphonate group chelate a metal atom, and at the same time the two chelating oxygen atoms bond to metal atoms adjacent to the one chelated. The third phosphonate oxygen then bridges metal atoms in a direction roughly perpendicular to the chelate ring as shown in Figure 7. The sixth coordination site is occupied by a water molecule. Other divalent metals such as magnesium and cobalt phosphonates are thought to be isostructural. Because of the regularity of the octahedral coordination the P–C bond is directed almost perpendicular to the rings. In the copper phosphonates the unusual 5-coordination results in a tilting of the P–C bond away from the perpendicular.

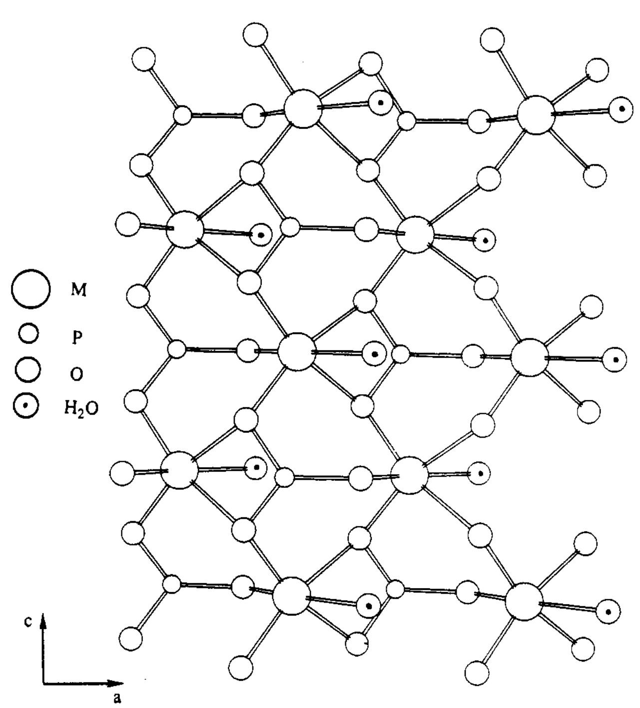

Figure 7. Representation of the layers in $M(O_3PR)\cdot H_2O$ compounds with M = Mn, Mg, Co, and Zn.

In the phenylphosphonates of Mn[6] and Zn,[8] the phenyl rings were found to be disordered about two orientations with one perpendicular to the other. This disorder undoubtedly arises from the closeness of the phenyl rings along both the *a*- and *c*-axis directions (5.63 and 4.83 Å, respectively in the zinc compound). Although the structures of the zinc and manganese phenylphosphonates were refined in the orthorhombic system, space group $Pmn2_1$, superlattice spots along both *a*- and *c*-axes were found suggesting that the true unit cell may be a *B*-centered monoclinic lattice[6] with a = 7.589 (3) Å, b = 14.930 (5) Å, c = 7.606 (3) Å, and β = 98.64 (3)°. Refinement in this larger cell has not been successful, but it is highly probable that the phenyl rings are canted toward each other as in the copper compounds. For example, the *a*- and *c*-axes in the monoclinic cell are almost equal to the *b*- and *c*-axis lengths in $Cu(O_3PCH_3)\cdot H_2O$ and the *a*- and *b*-axis lengths in $Cu(O_3PC_6H_5)\cdot H_2O$.

In the case of $Cu(HO_3PCH_2NH_2)_2$ the copper atom is 4-coordinate square planar.[4] The coordination arises from four different phosphonate groups, each of which bridges across two copper atoms. The third phosphonate oxygen is protonated and hence does not bond to a metal atom. This arrangement produces linear chains which are hydrogen bonded to each other through P–O–H- - -N– linkages.

It is instructive to compare the copper phosphonates to the copper phosphites. The structures of two such compounds, $Cu(O_3PH)\cdot 2H_2O$[26] and $Cu(HO_3PH)_2$,[27] have been reported. Both of these compounds have three-dimensional structures in which the copper atoms are reported to be 6-coordinate. The dihydrate has three oxygens from three different phosphite groups in the equitorial plane, and the fourth position is occupied by a water molecule (bond lengths 1.95 (1)–2.02 (1) Å). The second water molecule occupies an axial position at a distance of 2.35 Å and is thought to bridge to the underside of an adjacent copper atom, forming the second axial position at a distance of 3.03 (1) Å. This distance may be considered as too great to constitute a bond but serves to sterically hinder the sixth site. Thus, in many respects the copper coordination in the phosphite is close to that in the phosphonates. Unfortunately, no bond angles were provided in the paper. In this compound the phosphite group bridges three

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(26) Handlovic, M. *Acta Crystallogr.* **1969**, *B25*, 227.

(27) Sghyar, P. M.; Cot, L.; Rafiq, M. *Acta Crystallogr.* **1990**, *C46*, 1378.

copper atoms. In the copper phosphonates each phosphonate bridges four copper atoms forming alternating small and large rings.

In the copper monohydrogenphosphite the octahedral coordination is achieved by having six oxygens from six different phosphite groups bond to the metal atoms. The four equatorial oxygens are at average bond distances of 1.957 Å. The oxygens in the axial positions are respectively 2.343 (3) and 3.20 (6) Å from the copper atom. There are two kinds of $[HPO_3H]^-$ groups in terms of bonding modes. One of the phosphite groups uses two oxygen atoms to bridge three metal atoms while the third oxygen is bonded to a hydrogen atom. The other phosphite group uses all three oxygens to bridge across three copper atoms but the oxygen bearing a proton is the one which forms the very long bond distance with copper. If this distance of 3.201 Å is considered too long to represent a bond, then this compound also fits the 5-coordinate square pyramidal coordination type.

With two coordination sites available for Lewis acid type intercalative reactions, the layered copper phosphonates become interesting candidates for exhibiting unusual intercalation behavior controlled by choice of the alkyl- or arylphosphonate group. This possibility will be explored in a subsequent paper.

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Supplementary Material Available: For $Cu(O_3PCH_3)\cdot H_2O$ and $Cu(O_3PC_6H_5)\cdot H_2O$, Tables SI and SII, listing thermal parameters (1 page); Tables SIII and SIV, giving structure factors (12 pages). Ordering information is given on any current masthead page.