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Synthesis and X-ray Powder Structures of Two Lamellar Copper Arylenebis(phosphonates)

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Reaction of copper salts with 1,4-phenylenebis(phosphonic acid) yielded a conventional layered compound, $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$, while a similar reaction with 4,4′-biphenylenebis(phosphonic acid) resulted in a new lamellar structure with composition $Cu[HO_3P(C_6H_4)_2PO_3H]$. The structures of these compounds were solved *ab initio* by using X-ray powder diffraction data. The crystals of the phenylenebis(phosphonate) compound are monoclinic, space group $C2/c$, with $a = 18.8892(4)$ Å, $b = 7.6222(2)$ Å, $c = 7.4641(2)$ Å, $\beta = 90.402(2)°$, and $Z = 4$. The layer structure in this case is similar to that in copper phenylphosphonate, $Cu[O_3PC_6H_5]$. The metal atoms display a distorted square pyramidal geometry where four of the coordination sites are occupied by the phosphonate oxygens. The remaining site is filled by an oxygen atom of the water molecule. Adjacent metal−O_3PC layers are covalently pillared by the phenyl group of the phosphonates to create a 3-dimensional structure. $Cu[HO_3P(C_6H_4)_2PO_3H]$ is triclinic, space group $P\bar{1}$, with $a = 4.856(2)$ Å, $b = 14.225(5)$ Å, $c = 4.788(2)$ Å, $\alpha = 97.85(1)°$, $\beta = 110.14(1)°$, $\gamma = 89.38(1)°$, and $Z = 1$. The structure in this case, ideally consists of linear chains of copper atoms. The copper atoms are bridged by centrosymmetrically related phosphonate groups utilizing two of their oxygen atoms. This binding mode leads to square planar geometry for the copper atoms. The third oxygen atom of the phosphonate is protonated and is involved in linking adjacent linear chains through hydrogen bonds. At the same time, these hydroxyl oxygens interact weakly (Cu−O = 3.14 Å) with the copper atoms of the adjacent chain. Considering these long Cu−O interactions, the geometry of the copper atom may be described as distorted square bipyramidal. As in the phenylphosphonate structure, the biphenyl groups covalently link the Cu−O_3PC networks in the perpendicular direction.

Introduction

The increased activity in the field of metal phosphonate chemistry is primarily due to their potential application in the areas of sorption and ion exchange,[1] catalysis,[2,3] sensors,[4,5] and nonlinear optics.[4,6,7] Originally work in this area was directed toward the study of the layered compounds of four-valent compounds largely due to their high stability.[8,9] Subsequent studies revealed that the quadrivalent metal ions are also capable of forming new structural types apart from the conventional layered structures.[10] Recent studies have shown that a variety of other metal ions including divalent and trivalent metals, alkaline earth metals, uranyl ions, etc. can form similar layered compounds.[4,11,12] In the case of the conventional 4-valent layered compound $[Zr(HPO)_2]\cdot H_2O$[10] and $[Zr(PO_4)(H_2PO_4)]\cdot 2H_2O$[13] the metal atoms are in octahedral coordination and the phosphonate and/or phosphate oxygens are involved only in binding to a single metal atom. However, in other types of metal phosphonates, due to the coordination requirements of the metal atoms and the deficiency of oxygen atoms, the oxygen atoms also take part in chelation and bridging modes of binding. This chelation-bridging type of bonding was found to be present in a variety of structural types[11,12,14,15] including porous structures.[16−19]

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The monophosphonic acids react with metal ions generally to yield layered compounds in which the metal−O_3PC networks are separated by the organic groups on either sides.[10] The van der Waals forces between the organic groups in the interlayer space hold the adjacent layers intact. By means of intercalation or pillaring reactions the layers can be expanded to any desired extent. The diphosphonic acids, on the other hand, provide compounds where the adjacent metal−O_3PC layers are covalently pillared. These cross-linked structures, either as prepared or as modified by introducing spacers like phosphite or phosphate groups during synthesis, could provide porous structures. Dines et al.[3,20] have prepared such cross-linked compounds using a mixture of diphosphonic acid and a smaller group such as phosphate or phosphite to produce porous materials with high surface areas. The compounds however showed a broad distribution of pore sizes possibly due to the nonuniformity of pores as a result of clustering or segregation of pillars and spacers.[21] On the other hand, by the proper choice of substitution on the diphosphonate, Alberti et al. have succeeded in positioning the spacer groups in a uniform manner adjacent to each pillaring diphosphonate.[16c] Using the cross-linking agent 3,3′,5,5′-tetramethylbiphenylenebis(phosphonic acid) and phosphite as spacers they were able to obtain compounds with uniform micropores of 5−6 Å. Recently Soghomonian et al. have reported a series of vanadium pillared layered structures containing the diphosphonates.[22]

The zirconium arylenebis(phosphonate) compounds prepared so far yielded only poorly crystalline samples primarily due to their low solubility. Interlayer spacings from powder patterns and electron diffraction studies indicate that the zirconium phenylenebis(phosphonate) compound formed a layer structure similar to its phenylphosphonate analog.[23] Since the divalent metal phosphonates have higher solubility than the zirconium compounds, it is possible to prepare the former compounds in reasonably crystalline form suitable for the determination of their structures by X-ray powder diffraction methods. Recently we were able to solve the structures of zinc phenylenebis(phosphonate) and zinc biphenylenebis(phosphonate) from their powder diffraction data.[24] In this paper we report the synthesis and the X-ray powder structures of copper phenylenebis(phosphonate) and copper biphenylenebis(phosphonate) compounds.

Experimental Section

Materials and Methods. Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification. Thermogravimetric analyses (TGA) were carried out under an oxygen atmosphere with a Du Pont Model No. 951 unit, at a rate of 10 °C/min. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr disk method.

Synthesis Procedures. The phenylene and biphenylenebis(phosphonic acids) were prepared according to the reported procedure[25] with certain modifications.[23] In the first step the phosphonate esters, *p*-phenylenebis(diethyl phosphonate) and *p,p*′-biphenylenebis(diethyl phosphonate) were prepared by the reaction of their respective dibromo derivatives with triethyl phosphite in presence of 1,3-diisopropylbenzene and anhydrous $NiCl_2$ as a catalyst. The reactions were carried out under a N_2 atmosphere at around 180 °C. These esters were then converted to phenylene and biphenylenebis(phosphonic acids by reacting them with concentrated HCl. The yield was 96 and 78% for the phenylene- and biphenylenebis(phosphonic acids, respectively.

Copper 1,4-phenylenebis(diphosphonate) monohydrate was prepared by refluxing 10 mmol (2.50 g) of $CuSO_4 \cdot 5H_2O$ (MCB Manufacturing Chemist, Inc., reagent grade) and 2.5 mmol (0.60 g) of 1,4-phenylenebis(phosphonic acid) in water at 60 °C. After about 24 h a blue precipitate was formed which was filtered, washed, and dried at room temperature (yield = 0.88 g, 89% based on the phosphonic acid).

Copper biphenylenebis(phosphonate) was prepared by mixing 0.66 g (2.1 mmol) of 4,4′-biphenylenebis(phosphonic acid) and 1.02 g (4.4 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ (Baker Inc.) in 60 mL of water. The resulting solution was milky blue. The mixture was stirred thoroughly and placed into a steel pressure vessel fitted with a Teflon liner that was then sealed and placed in an oven at 150 °C for 12 days. The blue precipitate formed was filtered, washed, and dried at 50 °C (yield = 0.4 g, 51% based upon the phosphonic acid). Anal. Calcd for $Cu[HO_3P(C_6H_4)_2PO_3H]$: C, 38.35; H, 2.66; H_2O, 4.79. Found: C, 38.41; H, 2.66; H_2O(TGA), 4.9.

X-ray Data Collection. Step scanned X-ray powder data for the samples (side-loaded into a flat aluminum sample holder) were collected on the finely ground sample using a Rigaku computer automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data for the phenylenebis(phosphonate) compound were collected between 6 and 85° in 2θ with a step size of 0.01° in 2θ and a count time of 15 s per step. For the biphenylenebis(phosphonate) compound, the same step size and time constant were used, but the 2θ range was 4−80°. Data were mathematically stripped of the $K\alpha_2$ contribution, and peak picking was conducted by a modification of the double-derivative method.[26] The powder pattern was indexed by Ito methods[27] on the basis of the first 20 observed lines. The best solution (FOM = 76), which indexed all the peaks of the phenylenebis(phosphonate) compound, indicated a *C*-centered monoclinic cell with lattice parameters $a = 18.89$ Å, $b = 7.62$ Å, $c = 7.46$ Å, and $\beta = 90.4°$. The systematic absences were consistent with the space group *Cc* or *C*2/*c*. In the case of the biphenylenebis(phosphonate) compound, the best solution (FOM = 88) corresponded to a triclinic cell with $a = 4.866$ Å, $b = 14.25$ Å, $c = 4.81$ Å, $\alpha = 97.9°$, $\beta = 110.0°$, and $\gamma = 89.4°$. The initial selection of the centric space groups $C2/c$ and $P\bar{1}$ for the phenylenebis(phosphonate) and biphenylenebis(phosphonate) compounds, respectively, were found to be correct from the successful solution and refinement of the structures.

Structure Solution and Refinement of the Compound $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$. Integrated intensities were extracted from the profile over the range 7° < 2θ < 85° by decomposition methods as described earlier.[28] Least-squares procedures yielded 58 single indexed peaks up to a 2θ limit of 60°. There were also 20 strong peaks with two or three contributors which were included in the data set by dividing the peak intensities equally between the number of contributing reflections. A Patterson map was computed using this data set in the

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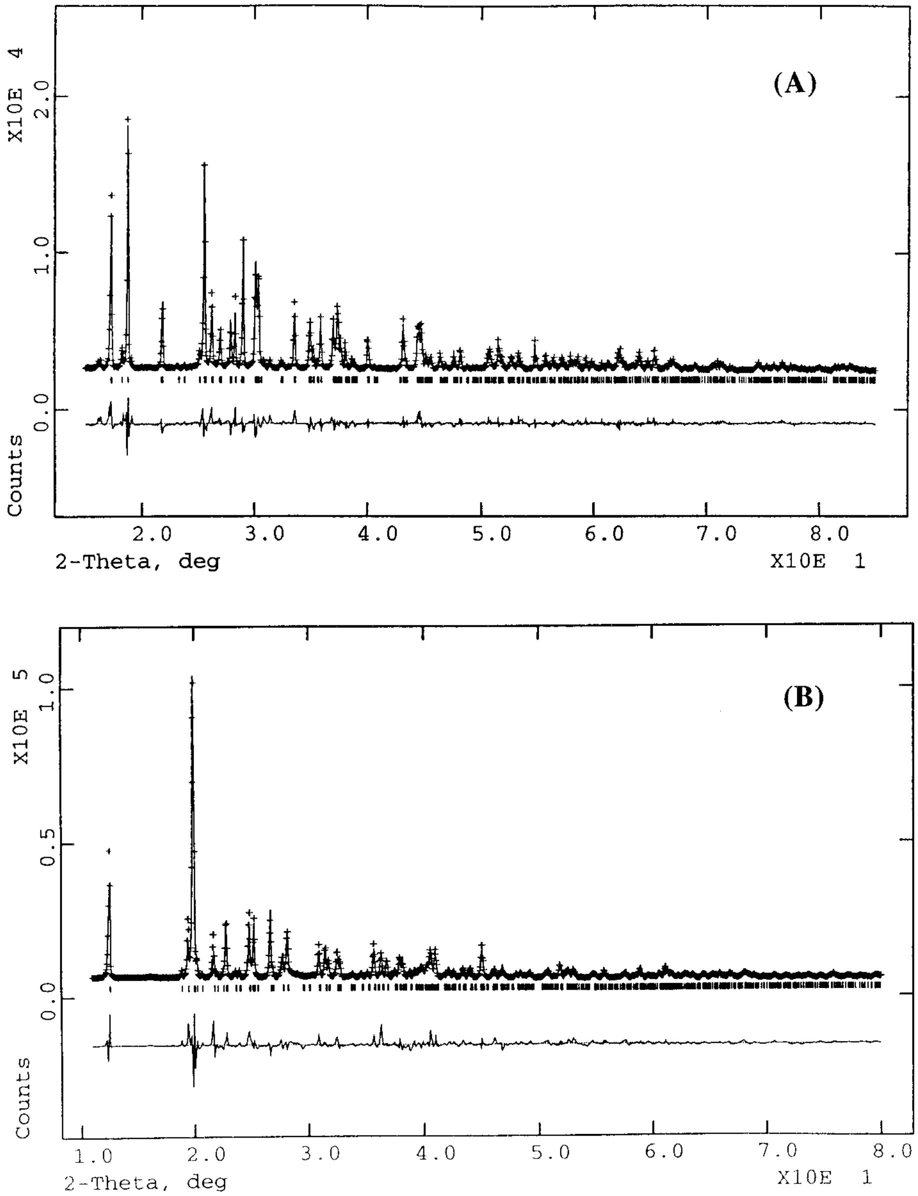

Figure 1. Observed (+) and calculated (−) profiles for the Rietveld refinement for (A) copper phenylenebis(phosphonate) and (B) copper biphenylenebis(diphosphonate). The difference plot is on the same intensity scale.

TEXSAN[29] series of single crystal programs. The positions of the Cu atoms were located from the vectors in the Patterson map. Constrained refinements and subsequent difference Fourier maps revealed the positions of the P atom and the oxygen atoms of the phosphonate group.

These atomic positions were used for Rietveld refinement in the GSAS[30] program package. For this purpose, the data from both Kα_1 and Kα_2 were used. After the initial refinement of scale, background, and unit cell parameters, a difference Fourier map was calculated which revealed the position of the water molecule coordinated to the Cu atom and that of a carbon atom bonded directly to the P atom. Successive difference Fourier maps allowed the location of the remaining carbon atoms of the phenyl group. The structure was then refined with soft constraints for the Cu and P polyhedra and also for the phenyl group. (A weight factor, F^{30} of 100, was initially applied for the soft constraints and was gradually reduced to 50 in the final cycles of refinement). Since the polyhedron about the Cu atom is not regular, a relatively large error limit was applied for the bond and non-bonded distances. The P−O and P−C bond distances were held at 1.53(1) and 1.80(1) Å, respectively. The tetrahedral geometry about the P atom was obtained by constraining the O- - -O and O- - -C nonbonded distances to 2.55(1) and 2.73(1) Å, respectively. The C−C bond lengths in the phenyl group were constrained to a value of 1.39 Å with an error limit of 0.01 Å. The distance between two carbon atoms bonded to a carbon atom whose angle was to be constrained to 120° was held to a value of 2.39(1) Å. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. A correction was made for preferred orientation effect by using the March−Dollase method[30b] in the GSAS suite of programs. The diffraction vector in the present case is along the a^*-axis. The refined parameter was the ratio of the effect along this axis to that along the perpendicular plane. No corrections were made for anomalous dispersion and absorption effects. A final Rietveld refinement plot is given in Figure 1A.

Structure Solution and Refinement of Compound Cu[$HO_3P(C_6H_4)_2PO_3H$]. The sample in this case is slightly less crystalline than that of the copper phenylenebis(phosphonate) and the data are severely affected by preferred orientation. The pattern decomposition in this case produced a total of 57 singly indexed peaks up to 64° in 2θ. The structure was solved by the Patterson method. The Cu

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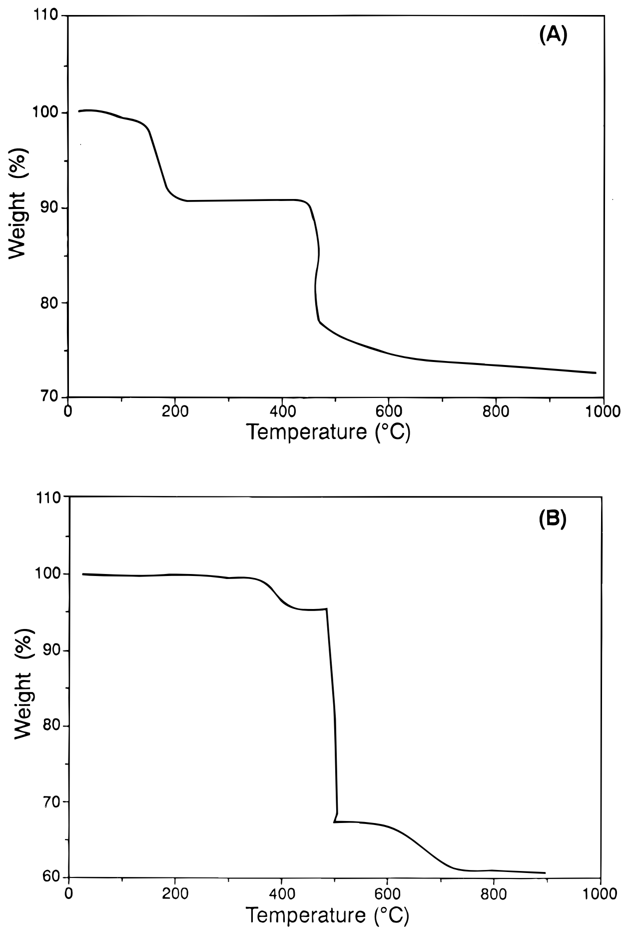

Figure 2. TGA curves for (A) copper phenylenebis(phosphonate) and (B) copper biphenylenebis(phosphonate).

atom was located at the origin and the position of the P atom was found from the Cu−P vector in the Patterson map. Difference Fourier maps using this data set yielded the positions of all the oxygen atoms of the phosphonate group. The positions of the these atoms were used as a starting model for Rietveld refinement.

Refinement of the profile was carried out using the program GSAS. Initially parameters such as zero point error, scale factor, lattice parameters, terms for background and peak shape functions were refined. The positional parameters were then refined with soft constraints. The phosphonate groups were constrained to the tetrahedral geometry as described above. A series of difference Fourier maps revealed the approximate positions of all the carbon atoms of the biphenyl group. The refinement of the phenyl groups was carried out with constraints for C−C bond lengths and C- - -C nonbonded distances as in the case of the phenylphosphonate compound. The C−C bond connecting the two phenyl groups was held at a distance of 1.47(1) Å. As the refinement progressed the weights for the soft constraints (*F*)[30] were reduced (from an initial value of 100 to 50) but they could not be removed without distorting the structure, particularly the geometry of the organic group. All the atoms were refined isotropically. Corrections were made for preferred orientation effects as described above. The diffraction vector in the present case is along the *b**-axis. A final difference Rietveld plot is given in Figure 1B.

Results

TGA and Spectral Characterization of the Compounds. The release of the coordinated water molecule in copper phenylenebis(phosphonate) begins at around 100 °C and the process is complete at about 225 °C (Figure 2A). The observed weight loss of 9.5%, corresponding to the release of two water molecules, agrees well with the calculated value of 9.07%. The removal of the phenyl group takes place in a single step starting at 437 °C. The calculated and observed weight loss for the removal of the organic group are 19.14% and 18.3%, respectively. The biphenylenebis(phosphonate) compound shows no weight loss up to about 340 °C indicating that no water molecules are present as such in the structure (Figure 2B). The weight loss due to the condensation of the hydroxyl groups of the phosphonate occurs in the temperature range 347−433 °C. The calculated weight loss of 4.78% is close to that observed (4.9%) in the TGA. The compound begins to lose its organic component at 480 °C. About 70% of the organic is lost up to 515 °C and the process continues even beyond 800 °C. The TGA data for these compounds resemble, very closely, those of their corresponding zinc arylenebis(phosphonates) except for the fact that the zinc compounds start losing their organic at a higher temperature (550−570 °C).

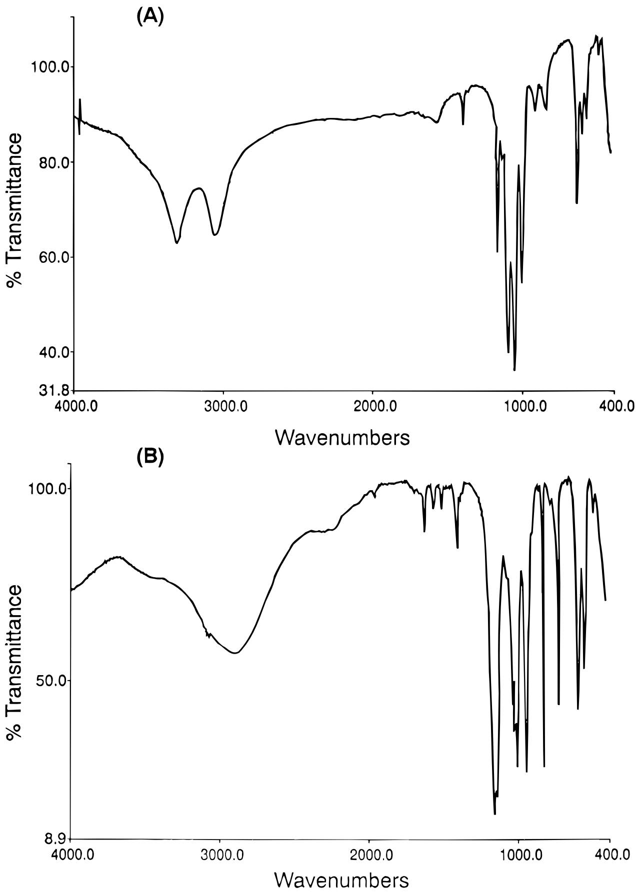

Figure 3. IR spectra for (A) copper phenylenebis(phosphonate) and (B) copper biphenylenebis(phosphonate).

The O−H stretching bands of the water molecules in the phenylenebis(phosphonate) are seen at 3299 and 3043 cm^{-1}. The IR spectrum (Figure 3A) also shows the corresponding deformation band at 1568 cm^{-1}. These bands are clearly absent in the biphenylenebis(phosphonate) compound (Figure 3B) since it does not contain any water molecules. The presence of strongly hydrogen bonded hydroxyl groups, in this compound, can be seen as broad band at 2892 cm^{-1}. The spectra of both compounds contain characteristic P−O_3 vibration frequencies and C−C stretching frequencies of the phenyl group as well as the out of the plane vibrations of the para-substituted phenyl groups at 828 and 816 cm^{-1} for the monophenyl and biphenyl derivatives, respectively.

Structure of $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$. Crystallographic data are given in Table 1. Positional and thermal parameters are listed in Table 2 while selected bond parameters are presented in Table 3. The arrangement of the metal−phos-

Table 1. Crystallographic Data

	$Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$	$Cu[HO_3P(C_6H_4)_2PO_3H]$
formula	$C_6H_8O_8P_2Cu_2$	$C_{12}H_{10}O_6P_2Cu$
fw	397.1	375.7
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	18.8892(4)	4.856(2)
b (Å)	7.6222(2)	14.225(5)
c (Å)	7.4641(2)	4.788(2)
α (deg)	90.0	97.85(1)
β (deg)	90.402(2)	110.14(1)
γ (deg)	90.0	89.38(1)
V (Å^3)	1074.6(1)	307.3(3)
Z	4	1
λ (Å), (Kα_1 + Kα_2)	1.5406, 1.5444	1.5406, 1.5444
T (K)	296	296
d_{calcd} (g/cm^3)	2.45	2.03
μ (cm^{-1})	80.69	52.58
pattern range (2*θ*) (deg)	15−85	11−80
step size (2*θ*) (deg)	0.01	0.01
step scan time (s)	15	15
no. of unique reflcns	375	360
no. of structural params	36	41
no. of geometric observns	21	30
R_{wp}[a]	0.045	0.089
R_p[a]	0.029	0.061
R_F[a]	0.073	0.117

[a] See ref 29 for definitions.

Table 2. Positional Parameters and U_{iso} Values for $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$

atom	*x*	*y*	*z*	U_{iso}[a]
Cu1	0.2675(1)	0.0573(4)	0.0632(4)	0.096(2)
P1	0.1665(1)	0.2016(7)	0.3276(7)	0.029(2)
O1	0.2102(3)	0.2400(11)	0.1636(9)	0.012(3)
O2	0.1838(3)	0.0205(8)	0.4121(11)	0.007(3)
O3	0.1744(3)	0.3501(9)	0.4721(10)	0.036(4)
O4	0.3467(3)	0.1813(11)	0.1743(13)	0.015(3)
C1	0.0737(8)	0.1995(11)	0.2602(12)	0.062(5)
C2	0.0354(2)	0.0440(11)	0.2794(16)	0.054(7)
C3	0.0369(1)	0.3597(11)	0.2553(17)	0.044(7)

[a] $U_{iso} = B_{iso}/8\pi^2$.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$[b]

Cu1−O1	1.920(7)	Cu1−O1	2.332(7)
Cu1−O2	2.025(6)	Cu1−O3	1.943(7)
Cu1−O4	1.949(5)	P1−O1	1.510(5)
P1−O2	1.552(5)	P1−O3	1.569(5)
P1−C1	1.819(3)	C1−C2	1.397(3)
C1−C3	1.406(3)	C2−C2′	1.403(3)
C3−C3′	1.397(3)		
O1−Cu1−O1a	84.7(2)	O1−Cu1−O2	89.4(3)
O1−Cu1−O3	164.5(3)	O1−Cu1−O4	85.2(3)
O1[a]−Cu1−O2	86.2(3)	O1[a]−Cu1−O3	109.6(4)
O1[a]−Cu1−O4	81.1(3)	O2−Cu1−O3	97.3(3)
O2−Cu1−O4	166.6(4)	O3−Cu1−O4	91.1(3)
O1−P1−O2	112.8(4)	O1−P1−O3	111.6(4)
O1−P1−C1	107.9(4)	O2−P1−O3	110.1(4)
O2−P1−C1	107.7(3)	O3−P1−C1	106.4(3)
P1−C1−C2	118.6(3)	P1−C1−C3	118.3(3)
C2−C1−C3	118.9(2)	C1−C2−C2′	117.5(4)
C1−C3−C3′	119.7(1)		

[a] *C*-center related position of oxygen atom, O1, with the longer Cu−O bond. [b] Primes indicate centrosymmetrically related atoms.

phonate network within the layer along with atom labeling is shown in Figure 4A while the bridging of the layers by the phenyl groups in depicted in Figure 4B.

The copper atoms have a distorted square pyramidal coordination. Four of the coordination sites are provided by the oxygen atoms (O1, O1a, O2, and O3) of the phosphonate groups while the fifth site is occupied by the oxygen atom (O4) of the water molecule. The basal plane of the polyhedron is defined by the atoms O1, O2, O3, and O4. The Cu−O bond distances involving these oxygens are in the range 1.92−2.03(1) Å. The axial site is occupied by the symmetry related position of O1 (O1a) at a longer distance of 2.33(1) Å. This O1 atom is also involved in bridging an adjacent Cu atom within the layer (Figure 4A). The arrangement thus leads to four membered rings (Cu−O−Cu−O) with a Cu- - -Cu distance of 3.15(1) Å. The other two oxygen atoms, O2 and O3, bridge copper atoms of the neighboring 4-membered rings. This connectivity creates 8-membered rings between adjacent 4-membered rings (−O3a−Cu1−O1−P1−O2- -; O3−P1−O1−Cu1a- - etc.). The basal plane is slightly distorted. The cis-bond angles vary between 85.2(3) and 97.3(3)° while the average of two trans-angles is 165.6(4)°. The axial Cu−O1a bond is tilted closer to the O1 atom in the base since O1a occupies the basal site of the adjacent Cu atom (Cu1a) to which O1 acts as an axial site. As a result of these constraints, the bond angles involving the axial site and the basal sites vary between 81.1(3) and 109.6(4)°.

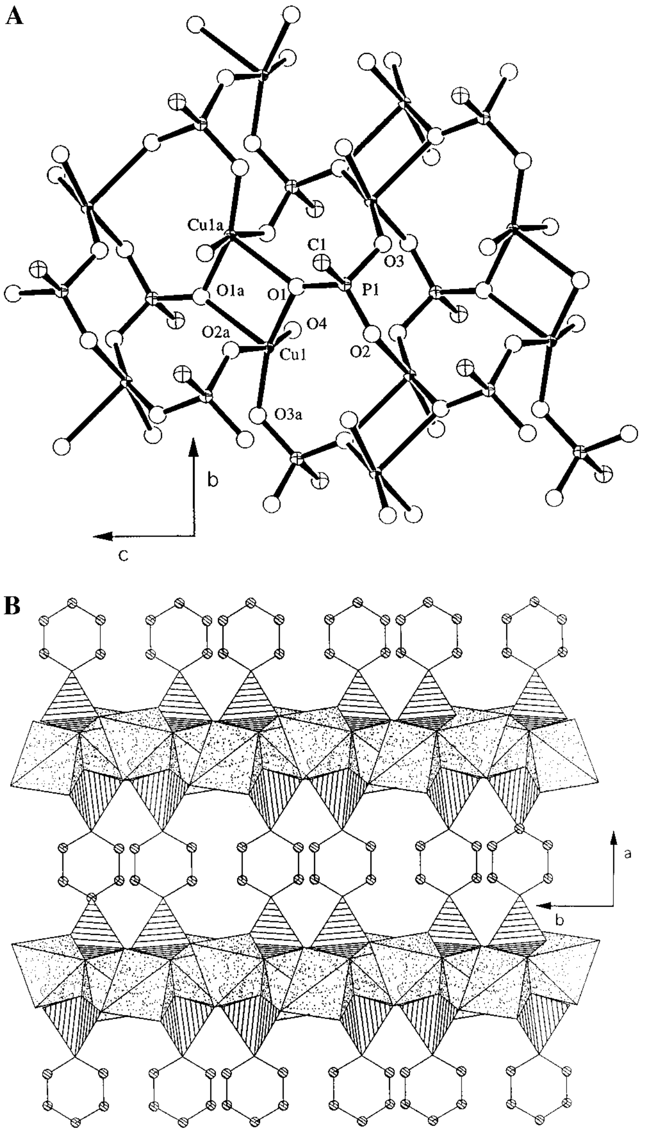

Figure 4. (A) Layer arrangement in the structure of copper phenyldiphosphonate along with atom labeling. All the atoms are isotropic, but they are represented by different ellipsoid types for distinction. (B) Polyhedral representation of the structure of copper phenylenebis(phosphonate) showing the bridging of the M−O$_3$PC layers by the phenyl group.

Table 4. Positional Parameters and U_{iso} Values for $Cu[HO_3P(C_6H_4)_2PO_3H]$

atom	x	y	z	U_{iso}
Cu1	0	0	0	0.108(1)
P1	0.489(2)	0.1372(4)	−0.020(2)	0.028(1)
O1	0.269(3)	0.1245(6)	−0.369(2)	0.031(1)
O2	0.379(3)	0.0828(6)	0.174(3)	0.063(1)
O3	0.788(2)	0.1111(5)	−0.030(3)	0.013(1)
C1	0.498(3)	0.2652(4)	0.085(3)	0.020(1)
C2	0.224(3)	0.3064(7)	−0.060(5)	0.147(1)
C3	0.226(3)	0.4050(8)	−0.054(6)	0.195(2)
C4	0.504(3)	0.4528(5)	0.051(4)	0.200(2)
C5	0.732(3)	0.4004(7)	−0.005(6)	0.161(1)
C6	0.714(3)	0.3040(7)	−0.030(6)	0.108(1)

Table 5. Bond Lengths (Å) and Bond Angles (deg) for $Cu[HO_3P(C_6H_4)_2PO_3H]$[a]

Cu1−O2	2.05(1) 2×	Cu1−O3	1.87(1) 2×
Cu1−O1	3.14(1) 2×		
P1−O1	1.63(1)	P1−O2	1.51(1)
P1−O3	1.51(1)	P1−C1	1.82(1)
C1−C2	1.44(1)	C1−C6	1.49(1)
C2−C3	1.40(1)	C3−C4	1.41(1)
C4−C5	1.41(1)	C5−C6	1.36(1)
C4−C4′	1.49(1)		
O2−Cu1−O2′	180.0	O2−Cu1−O3	88.6(3) 2×
O2−Cu1−O3	91.5(3) 2×	O3−Cu1−O3′	180.0
O1−Cu1−O1′	180	O1−Cu1−O2	50.5(3) 2×
O1−Cu1−O2	129.5(3) 2×	O1−Cu1−O3	74.7(3) 2×
O1−Cu1−O3	105.3(3) 2×		
O1−P1−O2	112.6(6)	O1−P1−O3	105.8(6)
O1−P1−C1	101.6(5)	O2−P1−O3	115.3(6)
O2−P1−C1	113.1(5)	O3−P1−C1	107.3(5)
P1−C1−C2	113(1)	P1−C1−C6	106(1)
C2−C1−C6	106(1)	C1−C2−C3	117(1)
C2−C3−C4	117(1)	C3−C4−C5	113(2)
C4−C5−C6	119(1)	C5−C6−C1	115(1)
C3−C4−C4′	113(2)	C5−C4−C4′	110(1)

[a] Primes indicate centrosymmetrically related atoms.

The metal-phosphate network forms two dimensional layers in the bc-plane whose mean plane is located at $x \sim 0.25$ and 0.75 with a basal spacing of 9.44 Å or half the *a*-axis length, β being very close to 90°. These layers are bridged by the phenyl groups of the phosphonate (Figure 4B) to form a 3-dimensional structure. The phenyl groups are almost parallel to the *ab*-plane. The two phosphonate groups at the ends of the phenyl ring are related by a 2-fold axis at (0, *y*, $^1/_4$) in such a way that the 2-fold axis is in the plane of the phenyl group. Adjacent phenyl groups are well separated both along the *b*- and *c*-directions. The closeness of two rings as seen in Figure 4B is due to the *C*-centering of the lattice. They are actually separated by 3.73 Å along the projection axis. The water molecule, apart from binding to the metal, is also involved in hydrogen bonding with the oxygens from within the layer. There are two hydrogen bonds, one with O2 (2.73(1) Å) and the other with O3 (2.68(1) Å) with an O2- - -O4- - -O3 angle of 106.6(4)°.

Structure of $Cu[HO_3P(C_6H_4)_2PO_3H]$. Positional and thermal parameters for this compound are given in Table 4 and bond distances and angles in Table 5. Metal coordination along with the bridging nature of the phosphonate groups is shown in Figure 5A and the packing of the molecules down the *a*- and *c*-axes are given in parts B and C of Figure 5, respectively.

The phosphonate groups in this compound exist as monohydrogen phosphonates. Oxygen atom, O1, is bonded to the proton as judged from the increased P−O1 bond length. Copper atoms are located at the centers of symmetry along the *a*-axis and are bridged by centrosymmetrically related phosphonate groups. Two of the oxygens of the phosphonate, O2 and O3, are involved in this bridging as shown in Figure 5A. The four

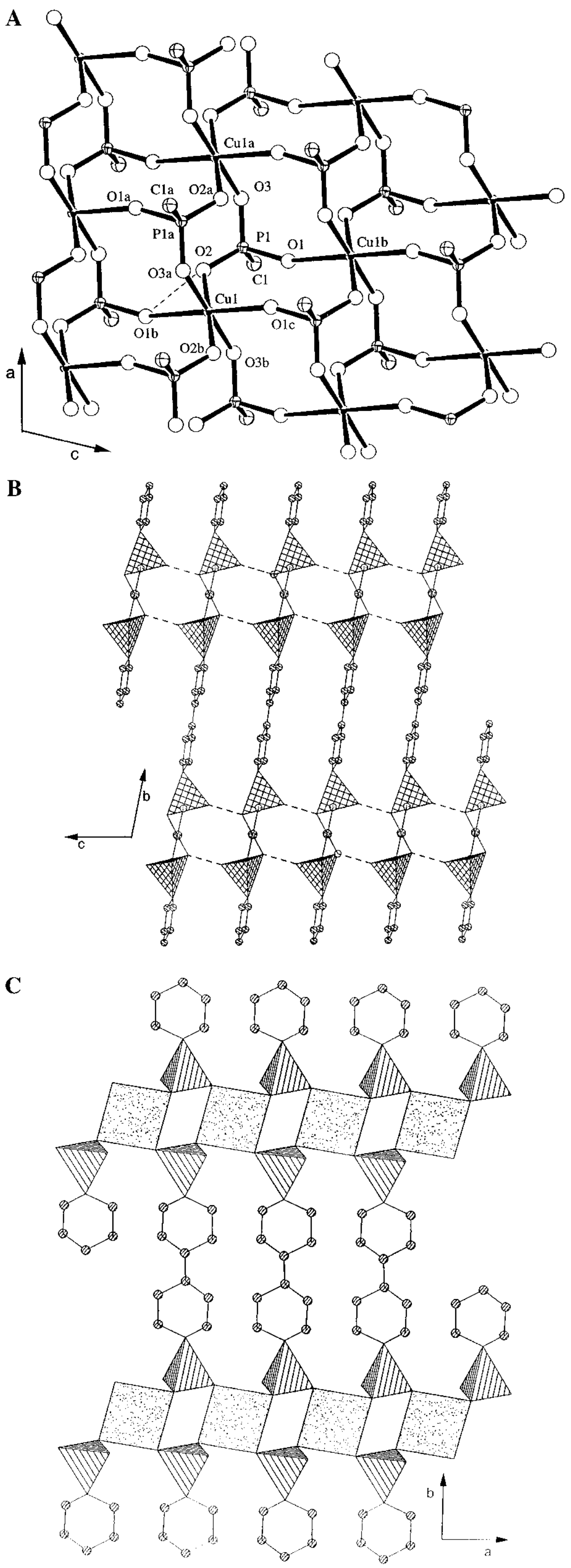

Figure 5. (A) Figure showing the metal coordination and the bridging nature of monophosphate groups in the structure of copper biphenylenebis(phosphonate). The dashed line indicates an O1 donor−O2 acceptor H-bond. All the atoms are isotropic but they are represented by different types for distinction. (B) Plot of the structure of copper biphenylenebis(phosphonate) as viewed down the *a*-axis. Hydrogen bonding between O1 and O2 is shown by dotted lines. The long axial Cu−O1 bonds are not shown. (C) Portion of the inorganic−organic sheet in the structure of copper biphenylenebis(phosphonate) in the *ab*-plane. The stippled squares represent the square-planar copper coordination. These sheets are connected to adjacent sheets through the long Cu−O1 bonds and O1- - -O2 hydrogen bonds in the *c*-direction.

oxygen atoms O2, O2b, O3a, and O3b thus define the basal plane of the copper polyhedra. The Cu−O2 and Cu−O3 distances are 2.05(1) and 1.87(1) Å, respectively. The average *cis* and *trans* angles in this plane are 90 and 180°, respectively indicating a square-planar type arrangement of atoms but with two sets of bond lengths. The third oxygen atom, O1 of the phosphonate, is protonated and is at 3.14(1) Å from the copper atom which is translated one unit cell along the *c*-axis. Considering these long Cu−O distances, the geometry of the copper atom can described as a highly distorted square bipyramidal geometry. The angles between O1 and the oxygens in the basal plane range between 50.5(3) and 129.5(3)° which again indicates the level of distortion of the polyhedron. The longer Cu−O bond and the angular distortion described above is primarily attributed to Jahn−Teller distortion; the effect in the present case being enhanced by the fact that the oxygen atom is protonated.

If the two long axial bonds are not considered, the structure can be described in terms of linear chains running parallel to the *a*-axis (Figures 5B and 5C). These chains are linked together in the *b*-axis direction into layers by the bis(phosphonate) groups as shown in Figure 5B. The distance between two neighboring copper atoms in the chain is 4.57 Å (*a*-axis dimension). Apart from the weak Cu−O1 bonds, these chains are also held together by hydrogen bonds involving the O1 hydroxyl group and the O2 atom of the adjacent chain. The O1- - -O2 distance of 2.42(1) Å and the P-O1- - -O2 angle of 129.5(8)° is a clear indication of the existence of hydrogen bonds[31] between the chains. Because of the O1−Cu bonds and the hydrogen bonding between the chains, the neighboring chains are about 4.47 Å apart (*c*-axis dimension).

The copper biphenylenebis(phosphonate) may also be considered as a loosely formed layer structure where the metal−O_3PC network is located in the ac-plane. These layers are bridged by the biphenyl groups of the diphosphonate, with a basal separation of 14.1 Å as shown in parts B and C of Figure 5. The center of the biphenyl group contains a center of symmetry which leads to the trans arrangement of the two end phosphate groups similar to that observed for the phenylenebis(phosphonate) structure. The biphenyl group is almost planar and its plane is perpendicular to the *c*-axis. Yet another and probably the best way of describing the copper biphenylenebis(phosphonate) structure is in terms of inorganic−organic sheets. A metal−phosphonate sheet formed by the bridging of copper chains (along the *a*-axis) by the biphenyl groups is shown in Figure 5C. These sheets extend in the *ab*-plane and are loosely connected to such sheets above and below by the hydrogen bonds and weak Cu−O bonds as described above.

Discussion

The layer structure of copper phenylenebis(phosphonate) presented here is basically similar to that observed for copper phenylphosphonate and copper methylphosphonate although the layers in the latter compounds are not covalently connected. The structures of copper phenylphosphonate, $Cu[O_3P(C_6H_5)H_2O]$, and copper methylphosphonate, $Cu[(O_3PCH_3)H_2O]$, were solved by single crystal methods.[12b] Copper phenylphosphonate is orthorhombic, space group *Pbca*, with $a = 7.5547(4)$ Å, $b = 7.4478(6)$ Å, and $c = 27.982(1)$ Å, and copper methylphosphonate crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.495(4)$ Å, $b = 7.580(4)$ Å, $c = 7.289(4)$ Å, and $\beta = 90.08°$. The layer dimensions (*a* and *b* in the phenylphosphonate and *b* and *c* in the methylphosphonate) in these compounds are very similar to that observed in $Cu_2[(O_3PC_6H_4PO_3)(H_2O)_2]$. In terms of symmetry, the bis(phosphonate) corresponds very closely to the methylphosphonate compound. However, in the bis(phosphonate) the layer axis is doubled and the lattice type is *C*-centered.

We were also able to obtain copper ethylenebis(phosphonate),[32] $Cu_2[(O_3PCH_2CH_2PO_3)(H_2O)_2]$, as a highly crystalline powder. Its structure has been solved using the powder diffraction data in a manner similar to the arylenebis(phosphonates) described above. The crystals are monoclinic, space group $P2_1/c$, with $a = 8.0756(1)$ Å, 7.5872(1) Å, $c = 7.4100(1)$ Å and $b = 116.319(1)°$. Again, the layer structure in this case is strikingly similar to the copper monophosphonates and copper phenylenebis(phosphonate). The crystal symmetry and unit cell dimensions are comparable to the copper methylphosphonate except for the monoclinic angle. An increase in the monoclinic angle in the ethylenebis(phosphonate) compound is necessary in order to bridge the adjacent layers by the P−C−C−P linkages. Details about this structure will be presented in a subsequent publication.

Recently we have investigated the structures of zinc phenylenebis(phosphonate) and zinc biphenylenebis(phosphonate).[24] As in the present case, the zinc phenylenebis(phosphonate) formed a cross-linked layer structure similar to zinc phenylphosphonate, $Zn(O_3PC_6H_5)\cdot H_2O$[12a] and its isomorphous compounds of Mn, Co,[11] and Cd.[33] However, in the presence of biphenylenebis(phosphonate) such a layer structure is not observed. Instead it formed a protonated compound $Zn[HO_3PC_6H_5PO_3H]$,[24] as in the copper biphenylenebis(phosphonate), but with a double chain structure cross-linked into layers. The phosphonate groups are singly protonated and use only two of the phosphonate oxygens for metal binding. The zinc atoms are tetrahedrally coordinated. The hydroxyl groups of the phosphonate are involved in linking the adjacent layers of double chains through hydrogen bonding. The situation is very similar to the copper compound, except for the fact that the copper compound formed single chains by utilizing two oxygen atoms from each of the phosphonate groups. The hydroxyl groups then link the adjacent chains through hydrogen bonds. These hydroxyl groups are also at a distance of 3.1 Å from the copper atoms in these adjacent chains. This distance is within the limits of allowed Cu−O axial bonds. The arrangement is therefore considered as a loosely formed layered compound. The commen feature of the Zn and Cu biphenylenebis(phosphonate), however, is that their phosphonate groups are singly protonated and that they did not form traditional layered compounds similar to their monophenyl counterparts.

We have found that at a pH of about 4.5, the reaction of a copper salt with biphenylenebis(phosphonic acid) resulted in a green compound which appears to contain a M−O_3PC layer structure similar to that in copper phenylenebis(phosphonate). The crystallinity of the compound, at present, is not high enough for us to solve its structure from the powder pattern. The interlayer spacing (14.0 Å) observed in the powder pattern is consistant with model calculations for a cross-linked layered structure. The TGA curve shows that the compound does not contain any water molecules and the weight loss (around 400 °C) corresponds to a Cu to phosphonate ratio of 2:1 similar to that observed for the phenylenebis(phosphonate) compound. In addition, the IR spectrum also shows no evidence for the presence of water molecules and hydroxyl groups in the structure. Since all the phosphonate oxygens are unprotonated

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and available for metal binding and no water oxygens are available, it is probable that more than one oxygen atom is involved in bridging metal atoms to form a layer. Such an arrangement was observed in the case of $Cu(C_2H_5PO_3]$.[34] In this compound the copper atoms have a trigonal bipyramidal coordination and all the coordination sites are occupied by the phosphonate oxygens. Unlike the hydrated structures, two of the three ethylphosphonate oxygens are involved in bridging the metal atoms and the third oxygen binds to only one copper atom.

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