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Article

Synthesis and Characterization of Four Metal–Organophosphonates with One-, Two-, and Three-Dimensional Structures

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A series of metal-organic hybrid compounds were synthesized using two new phosphonic acids, pyridyl-4-phosphonic acid and *p*-xylylenediphosphonic acid ($H_2O_3PCH_2C_6H_4CH_2PO_3H_2$). The phosphonic acid ligands have been synthesized from their corresponding bromides following two different types of reactions. The reaction of pyridyl-4-phosphonic acid with three different divalent metal salts results in the formation of molecular structures of different dimensionality. The reaction of Cu(II) with the phosphonic acid under hydrothermal conditions yields a three-dimensional (3D) open framework structure having the molecular formula $[Cu_4(NC_5H_4–PO_3)_4(H_2O)_{10}]$ (**1**). The reactions with Mn(II) and Zn(II) salts with the same phosphonic acid resulted in a two-dimensional layered and a dinuclear compound with molecular formulas $[Mn_3(NC_5H_4–PO_3)_4(H_2O)_6(ClO_4)_2]$ (**2**) and $[Zn_2(NHC_5H_4–PO_3H)_2Cl_4]$ (**3**), respectively. Compound **1** crystallizes in the triclinic crystal system having space group $P\bar{1}$ with structural parameters $a = 7.4564(15)$ Å, $b = 9.1845(19)$ Å, $c = 11.582(2)$ Å, $\alpha = 100.842(3)°$, $\beta = 104.303(3)°$, $\gamma = 94.774(3)°$, and $Z = 1$. Compound **2** crystallizes in the triclinic crystal system, space group $P\bar{1}$, with structural parameters $a = 7.6871(14)$ Å, $b = 10.576(2)$ Å, $c = 14.470(3)$ Å, $\alpha = 81.340(3)°$, $\beta = 81.561(3)°$, $\gamma = 68.757(3)°$, and $Z = 2$, whereas compound **3** crystallizes in a monoclinic crystal system with space group $P2(1)/n$. The structural parameters are as follows: $a = 8.4969\ (5)$ Å, $b = 9.3911\ (5)$ Å, $c = 12.3779\ (6)$ Å, $\beta = 90.860(17)°$, and $Z = 4$. The pyridylphosphonate ligand shows different ligation behavior toward the three divalent metal ions. On the other hand, *p*-xylylenediphosphonic acid on reaction with Co(II) formed a 3D compound $[Co_2(O_3PCH_2C_6H_4CH_2PO_3)_2(H_2O)_2]$ (**4**) with a layered and pillared structure. Compound **4** crystallizes in an orthorhombic crystal system with space group *Pnma*. The structural parameters are $a = 21.744(4)$ Å, $b = 5.6744(10)$ Å, $c = 4.7927(9)$ Å, and $Z = 4$.

Introduction

After the discovery of crystalline zirconium phosphates[1] in the 1960s and layered organophosphonates[2] in the 1970s, the field of metal–organophosphonate chemistry expanded exponentially.[3–10] Phosphonates are a class of ligand that are widely known for forming layered and pillared-layer materials.[5–6] The numerous compounds of di-, tri-, tetra-, penta-, and hexavalent metals with a variety of organophosphonic ligands have been extensively studied due to their catalytic, ion exchange, sensor, and nonlinear optical properties.[7–9] Magnetic properties have also been described for transition-metal phosphonates.[10] Layered metal phosphonates with monophosphonates are polymeric species that

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contain alternating hydrophilic and hydrophobic regions. In these compounds, the oxygen-bridged metal atoms form the central two-dimensional (2D) layers that are separated on either side by the pendant organic moieties of the phosphonate group. These clay-type compounds are interesting for their use as hosts for intercalation reactions. Recently, a large number of organomonophosphonate ligands with a second functional group added (including phosphonate) to extend the dimensionality of the compound or to functionalize the material have been reported.[4a,5b,9b,11] In such ligands, the nature of the organic moiety may be designed to confer specific properties and/or different networks on the products. In this Article, we report the syntheses and characterization of a series of four organophosphonate-divalent metal complexes having molecular formulas $[Cu_4(NC_5H_4{-}PO_3)_4(H_2O)_{10}]$ (**1**), $[Mn_3(NC_5H_4{-}PO_3H)_4(H_2O)_6(ClO_4)_2]$ (**2**), $[Zn_2(NHC_5H_4{-}PO_3H)_2(Cl)_4]$ (**3**), and $[Co_2(O_3PCH_2C_6H_4CH_2PO_3)(H_2O)_2]$ (**4**) ($NC_5H_4{-}PO_3H_2$ = pyridyl-4-phosphonic acid and $H_2O_3PCH_2C_6H_4CH_2PO_3H_2$ = *p*-xylylenediphosphonic acid). The X-ray single-crystal structures of the compounds **1**, **2**, and **3** show that they are of three-dimensional (3D), 2D-layered, and dimeric structures, respectively, whereas compound **4** forms a pillared-layered 3D structure with perpendicular channels running through the *b* and *c* axes.

Experimental Section

Materials and Methods. The starting materials $Cu(NO_3)_2\cdot 2.5H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$, $Co(ClO_4)_2\cdot H_2O$, $Mn(ClO_4)_2\cdot 2H_2O$, $ZnCl_2$, 4-bromopyridine hydrochloride, triethylamine, diethyl phosphite, and α,α′-dibromo-*p*-xylene were obtained from Aldrich. ^{1}H, ^{31}P, and ^{13}C NMR spectra in solution were recorded on a Bruker Avance DRX 300 Hz instrument. Chemical shifts (δ) are given in ppm. Thermogravimetric (TGA) analyses were carried out with a TGA Q 500 from TA Instruments, at a heating rate of 10 °C/min under a nitrogen atmosphere. Elemental analyses were done by Robertson Microlit Laboratories, Madison, New Jersey. IR spectra were measured as KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer with a spectral resolution of 2.00 cm^{-1}. Fourier-transform IR (FT-IR) frequencies are given in cm^{-1}. Magnetic susceptibility and magnetization measurements were carried out on a Quantum Design SQUID magnetometer MPMS-XL. Magnetic measurements of dc type were performed with an applied field of 1000 G in the 2−300 K temperature range. Diamagnetic corrections were made from the Pascal constants.[12]

X-ray Crystallography. Data collection of the compounds was performed at 110 K on a Bruker Smart CCD-1000 diffractometer with Mo Kα (λ=0.71073 Å) radiation using a cold nitrogen stream (Oxford). Data reduction and cell refinement were performed with the *SAINT* program,[13] and the absorption correction program *SADABS*[14] was employed to correct the data for absorption effects. Crystal structures were solved by direct methods and refined with full-matrix least-squares treatment (*SHELXTL-97*)[15] with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The crystallographic data are summarized in Table 1. All bond distances and angles for the four compounds are deposited as Supporting Information. The *SHELXTL*, *Mercury*, and *Diamond* software programs were used to visualize the structures.

A. Synthesis of the Ligands. A1. Diethyl Pyridyl-4-phosphonate. 4-Bromopyridine [obtained after neutralizing 4-bromopyridine

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Table 1. Crystal Data and Structure Refinement for Complexes **1**−**4**

	1	2	3	4
formula	$C_{20}H_{36}Cu_4N_4O_{22}P_4$	$C_{20}H_{32}Cl_2Mn_3N_4O_{26}P_4$	$C_5H_6Cl_2NO_3PZn$	$C_8O_8H_{12}P_2Co_2$
mol wt (g)	1062.32	1103.84	295.34	415.88
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	*Pnma*
a (Å)	7.4564(15)	7.687(11)	8.4969(5)	21.744(4)
b (Å)	9.1845(19)	10.576(2)	9.3911(5)	5.6744(10)
c (Å)	11.582(2)	14.470(3)	12.378(6)	4.7927(9)
α (deg)	100.842(3)	81.340(3)	90.00	90.00
β (deg)	104.303(3)	81.561(3)	90.860(11)	90.00
γ (deg)	94.774(3)	68.757(3)	90.00	90.00
Z	1	2	4	4
V (Å^3)	747.8(3)	1078.5(4)	987.59(9)	591.34(19)
density (gm/cm^3)	2.538	2.161	1.986	2.595
measured reflns	6165	7115	4363	3348
unique reflns	3166 [R(int) = 0.0303]	3278 [R(int)= 0.0251]	1491 [R(int) = 0.0672]	745 [R(int) = 0.0575]
R1 > 2$\sigma(I)$, wR2	0.0635, 0.1675	0.0977, 0.2818	0.0727, 0.2028	0.0791, 0.2108
GOF	1.095	1.112	1.128	1.216

hydrochloride (3.11 g, 16 mmol) with sodium carbonate (1.9 g, 18.0 mmol) in water (7 mL) and extracted using toluene (10 and 5 mL); finally, the combined extracts were dried with anhydrous potassium carbonate], diethyl phosphite (2.4 mL, 18.0 mmol), and triethylamine (2.5 mL, 18.0 mmol) were coupled using Pd-$[(C_6H_5)_3P]_4$ (0.93 g, 0.81 mmol), at 80 °C under argon for 40 h, according to the general procedure of Hirao et al.[16] A precipitate of triethylamine hydrobromide was formed during the course of the reaction. At the end of the reaction, a mixture of toluene (15 mL) and water (10 mL) was added. The product was separated in toluene from a water−toluene mixture using a separating funnel and dried with anhydrous potassium carbonate. Then toluene was removed, and the residue was subjected to column chromatography (silica gel for flash chromatography, ethyl acetate) affording an oil (1.83 g, 53%): $R_f = 0.065$ (silica gel on TLC-PET foils with fluorescent indicator 254 nm, ethyl acetate, UV lamp); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, $J = 6.59$ Hz, 6H, $POCCH_3$), 4.02−4.22 (m, 4H, $POCH_2C$), 7.59−7.66 (m, 2H, C_5H_2N), 8.72−8.75 (m, 2H, C_5H_2N); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 16.28, s.

A2. Pyridyl-4-phosphonic Acid (hydrolysis of the ester according to the Redmore procedure):[17] Diethyl pyridyl-4-phosphonate (1.83 g, 8.50 mmol), concentrated HCl (10 mL), and water (10 mL) were refluxed for 8 h. The hydrolyzed solution was evaporated to dryness under a water aspirator. The residue as oil was treated with ethanol (96%, 10 cm^3) and was evaporated to obtain a solid residue, which was washed with ethanol (96%) and dried in air to give pure pyridyl-4-phosphonic acid: 1.29 g, 95%; ^{1}H NMR (300 MHz, D_2O) δ 8.13−8.21 (m, 2H, C_5H_2N) and 8.71−8.77 (m, 2H, C_5H_2N); $^{31}P\{^1H\}$ NMR (121 MHz, D_2O) δ 5.65, s; $^{13}C\ \{^1H\}$ NMR (75 MHz, D_2O) δ 128.58 (d, $J = 8.75$ Hz, C-3), 141.02 (d, $J = 11.62$ Hz, C-2) and 156.46 (d, $J = 164.22$ Hz, C-4).

B. Synthesis of *p*-Xylylenediphosphonic Acid. Tetraethyl *p*-xylylenediphosphonate was obtained according to the procedure reported in the literature.[18] α,α′-Dibromo-*p*-xylene (5.2794 g, 0.02 mol) was suspended in deaerated triethyl phosphite (7.6 mL, 0.044 mol), and the mixture was heated to reflux at 155 °C with stirring for 1 h. The unreacted triethyl phosphite was removed in vacuo at 80 °C. Crystalline tetraethyl *p*-xylylene-α,α′-diphosphonate was obtained by crystallization of the yellow oil from hexane (yield 6.156 g, 87%, mp 75−77 °C). Six grams (16.56 mmol) of tetraethyl *p*-xylylenediphosphonate was then dissolved in HCl (40 mL, 6 M) and heated at reflux overnight. The pure phosphonic acid was obtained by removing hydrochloric acid with a rotary evaporator. Yield: 4.4 g, 100%; ^{1}H NMR (DMSO-d_6, TMS) δ 2.90 (d, 2H), 7.14 (s, 2 H_{arom}); ^{31}P NMR (DMSO-d_6, H_3PO_4) δ 22.57.

Synthesis of $[Cu_4(NC_5H_4{-}PO_3)_4(H_2O)_{10}]$ (1). A 0.072 g portion (0.5 mmol) of pyridyl-4-phosphonic acid was mixed with 0.116 g of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.5 mmol) in 3 mL of deionized distilled water, and the mixture was heated in a Teflon-lined steel vessel (volume ∼20 mL) at 170 °C for 4 days. The vessel was cooled to room temperature, and X-ray-diffraction-quality greenish-blue single crystals were collected from the Teflon liner by filtration (yield ∼90% based on Cu). Anal. Calcd for $C_{20}H_{36}Cu_4N_4O_{22}P_4$: C, 22.70; H, 2.96; N, 5.25. Found: C, 23.21, H, 2.04; N, 5.29. FTIR frequencies (KBr) above 1000 cm^{-1}: 2949 s, 2918 s, 2851 s, 1653 w, 1606 w, 1455 m, 1404 w, 1377 m,1131 m, 1112 m, 1077 s.

Synthesis of $[Mn_3(NC_5H_4{-}PO_3H)_4(H_2O)_6(ClO_4)_2]$ (2). A 0.072 g portion (0.5 mmol) of pyridyl-4-phosphonic acid was mixed with 0.181 g of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol) in 3 mL of deionized distilled water, and the mixture was heated in a Teflon-lined steel vessel (volume ∼20 mL) at 170 °C for 4 days. The vessel was cooled to room temperature, and the colorless solution was kept at room temperature for slow evaporation. The tiny platelike colorless crystals good for X-ray diffraction were collected after a few days by filtration (yield ∼35% based on Mn). Anal. Calcd for $C_{20}H_{32}Cl_2Mn_3N_4O_{26}P_4$: C, 23.21; H, 3.09; N, 5.41. Found: C, 22.98; H, 3.25; N, 5.31. FTIR frequencies (KBr) above 1000 cm^{-1}: 2952 s, 2916 s, 2852 s, 1632 m, 1499 w, 1462 w, 1374 w, 1375 w,1131 m, 1223 w, 1096 m.

Synthesis of $[Zn_2(NHC_5H_4{-}PO_3H)_2Cl_4]$ (3). A 0.072 g portion (0.5 mmol) of pyridyl-4-phosphonic acid was mixed with 0.068 g of $ZnCl_2$ (0.5 mmol) in 3 mL of deionized distilled water, and the mixture was heated in Teflon-lined steel vessel (volume ∼20 mL) at 170 °C for 4 days. The vessel was cooled to room temperature, and the colorless solution was kept at room temperature for slow evaporation. The X-ray-diffraction-quality colorless crystals were collected after a few days by filtration (yield ∼43% based on Zn). Anal. Calcd for $C_5H_6Cl_2NO_3PZn$: C, 20.87; H, 2.87; N, 4.87. Found: C, 20.21; H, 2.55; N, 4.78. FTIR frequencies (KBr) above 1000 cm^{-1}: 2952 s, 2916 s, 2852 s, 1632 m, 1499 w, 1462 w, 1374 w, 1375 w,1131 m, 1223 w, 1096 m.

Synthesis of $[Co_2(O_3PCH_2C_6H_4CH_2PO_3)(H_2O)_2]$ (4). A 0.137 g portion (0.5 mmol) of *p*-xylylenediphosphonic acid was mixed with 0.366 g of $Co(ClO_4)_2{\cdot}6H_2O$ (1.0 mmol) in 3 mL of deionized distilled water, and the mixture was heated in a Teflon-lined steel vessel (volume ∼20 mL) at 160 °C for 4 days. The vessel was

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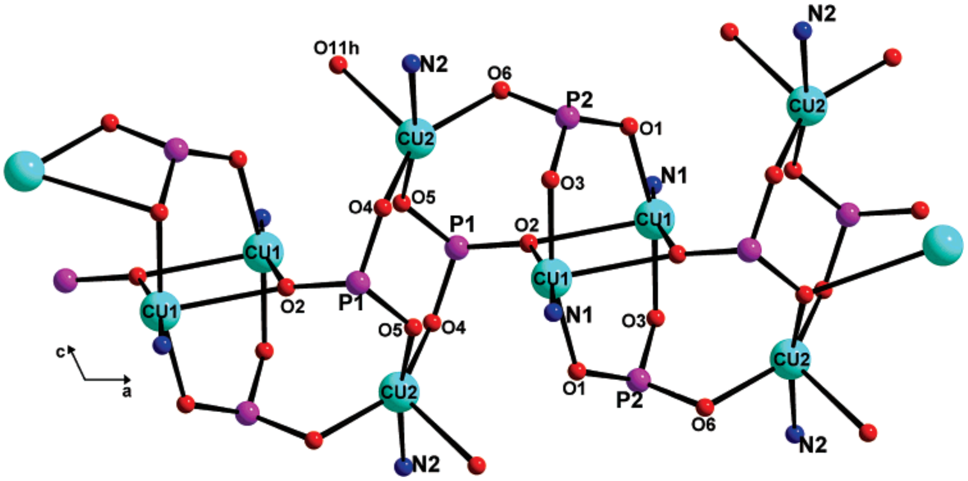

Figure 1. 1D chain of the compound **1** propagating along the *a* axis

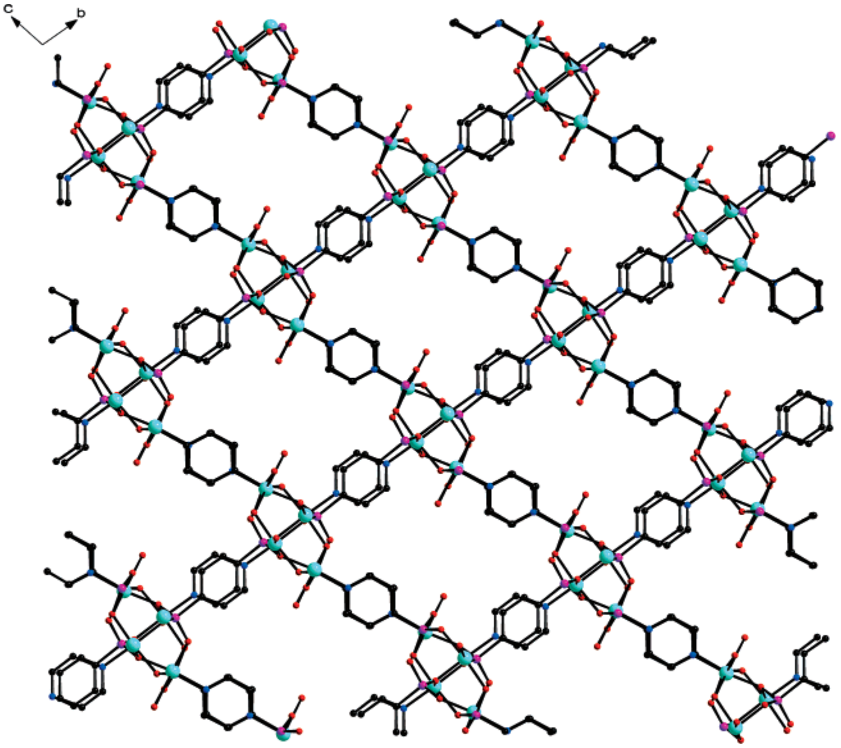

Figure 2. View of **1** along the *a* axis. Color code: green, copper; purple, phosphorus; red, oxygen; black, carbon; blue, nitrogen.

cooled to room temperature, and X-ray-diffraction-quality pink single crystals were collected from the Teflon liner by filtration. (yield ~47% based on Co). Anal. Calcd for $Co_2C_8O_8H_{12}P_2$: C, 23.08; H, 2.88. Found: C, 23.01; H, 2.83. FTIR frequencies (KBr) above 1000 cm^{-1}: 2959 s, 2923 s, 2862 s, 1499 w, 1462 w, 1374 w, 1367 w, 1212 w, 1082 m.

Results and Discussion

Structure of 1. The X-ray analysis reveals that there are two types of crystallographically distinct Cu(II) ions (Cu1 and Cu2) connected by phosphonate groups. A symmetry-related Cu(II) pair (Cu1) alternates with another pair of Cu(II) (Cu2), thereby forming a one-dimensional (1D) metal−phosphonate chain (Figure 1). A pair of μ_2-O atoms (O2) coming from a phosphonate ligand and two O−P−O (O1−P2−O3) bridges connect two Cu1 centers in the dimeric unit. Two well-separated Cu2 ions are connected with a pair of O−P−O bonds (O4−P1−O5) in a chain conformation. In addition to phosphonate oxygens, each Cu atom is further connected by a nitrogen atom of the ligand of which the phosphonate group is involved, binding to the neighboring chain of the framework. The nitrogen atoms bonded to Cu1-(N1) and Cu2(N2) are coming from the ligands whose phosphonate groups extend the dimensionality of the framework in the *b*- and *c*-axis directions, respectively, and thereby form a 3D framework with three interpenetrated channels along the three crystallographic axes (Figure 2). There are two cross-linking trapezoidal channels parallel to the crystallographic *a* and *b* axes with dimensions ~11.6 × 7.5 Å^2 and ~9.2 × 3.5 Å^2 (Figure 3), and the channel along the *c* axis having dimensions ~6.3 × 3.5 Å^2 further intersects both

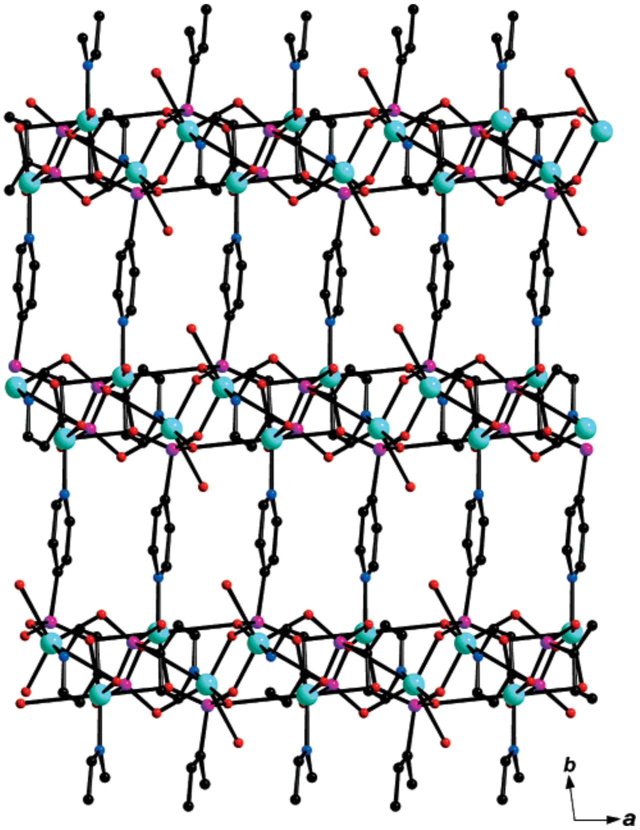

Figure 3. View of **1** along the *c* axis. Color code: green, copper; purple, phosphorus; red, oxygen; black, carbon; blue, nitrogen

channels along the *a* and *c* axes. The channels are filled with solvent water molecules. The number of water molecules in the channel is ∼10 per tetrameric molecular formula unit, but they are all disordered, and it is difficult to locate their exact position. The number of water molecules is confirmed by TGA, but removing those from the channels in high vacuum (at room temperature) results in a loss of crystallinity of the compound. The coordination geometry around each Cu1 atom is distorted-square pyramidal, with four O atoms of four different phosphonate groups [with Cu1−O1, 1.987(4) Å; a pair of symmetry-related O2 atoms at 1.961(5) Å and Cu1−O3 at 1.962(5) Å] and one pyridyl N (Cu1−N1 at 1.983(5) Å). The coordination geometry around each Cu2 atom is a distorted-trigonal bipyramid, with three O atoms of the phosphonate groups (Cu2−O4, 1.927(6) Å; Cu2−O5, 1.955(5) Å; Cu2−O6, 2.018(6) Å), a water molecule (Cu2−O11, 2.463(8) Å), and one pyridyl N (Cu2−N2) at 2.007(6) Å attached.

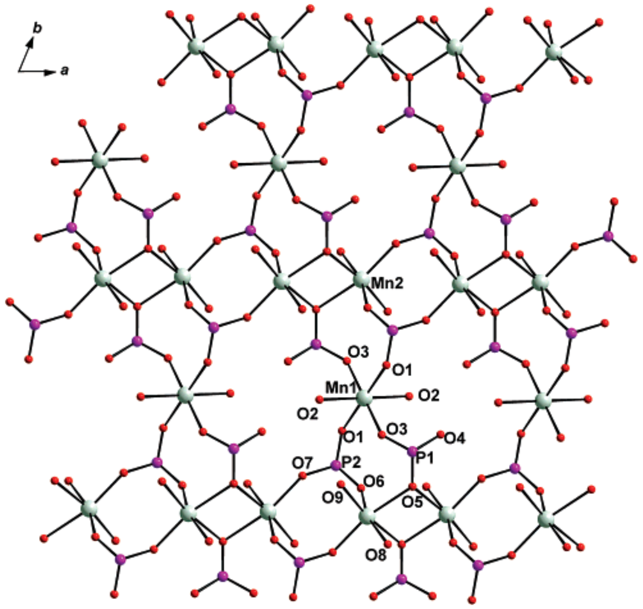

Figure 4. 2D view of **2** along the *c* axis. The pyridyl part of the ligand is omitted.

Structure of 2. The X-ray analysis reveals that there are two types of Mn(II) centers present in the compound. A six-coordinated octahedral Mn(II) (Mn1) and a pair of symmetry-related distorted octahedral Mn(II) (Mn2) share one edge and form a dimeric subunit (Figure 4). Mn1 is sited on a inversion center, and all four equatorial corners of the Mn1 octahedron are connected with oxygens from two pairs of symmetry-related phosphonate groups (Mn1−O1, 2.095(6) Å; Mn1−O3, 2.138(6) Å), a pair of which are further involved to share their remaining corners with two Mn2 octahedral units from two different dimeric subunits (O6, O7). Interestingly, the P−O distance for P2−O7 is 1.533(7) Å, which indicates that the O7 atom is possibly protonated and balances the charge of the molecule. The remaining pair of phosphonates share one of their oxygens (O5) with an edge of one of the dimeric subunit, and the third oxygen remains pendant (O4) with a significant longer P−O bond distance (1.558(7) Å) compared with those of the coordinated phosphonate oxygens. Two axial positions of the Mn1 are occupied by a pair of symmetry-related water molecules (Mn1−O2, 2.265(9) Å). Interestingly, these water molecules are involved in strong hydrogen bonding with the neighboring pendant oxygen of the phosphonate group (O4). There is a point of inversion on the shared edge of the dimeric subunit. Mn2−O5 and Mn2−O5_#1 (#1 = $-x$, $-y + 1$, $-z + 1$) distances are 2.196(5) and 2.343(5) Å. The remaining two positions of the Mn2 atom are occupied by two water molecules (Mn2−O8, 2.258(10) Å; and Mn2−O9 at 2.195(10) Å). According to the observed connectivity, there are two different types of phosphonates present in the molecule, one with 3.111 and another with 3.21 connectivity.[19] Finally, the 2D structure of the molecule could best be described as an edge-sharing Mn2 dimer connected to two other dimers through phosphonate groups in a linear fashion and thereby forming 1D chains. Such 1D chains are alternatively connected to each other through isolated Mn1 octahedral units in a lateral fashion and thereby form a 2D layered structure (Figure 5). The average Mn−Mn distance between the layers is 11.30 Å, whereas the average distance between the nitrogens of the hanging pyridines is 6.2 Å. There are two perchlorate anions per formula unit of the molecule. They are located between the layers, more precisely, between the pendant pyridyl parts of the phosphonate ligands.

Structure of 3. The crystal structure of the compound shows that it is a dimeric Zn(II) molecule with a $Zn_2O_2Cl_2$

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[19] Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

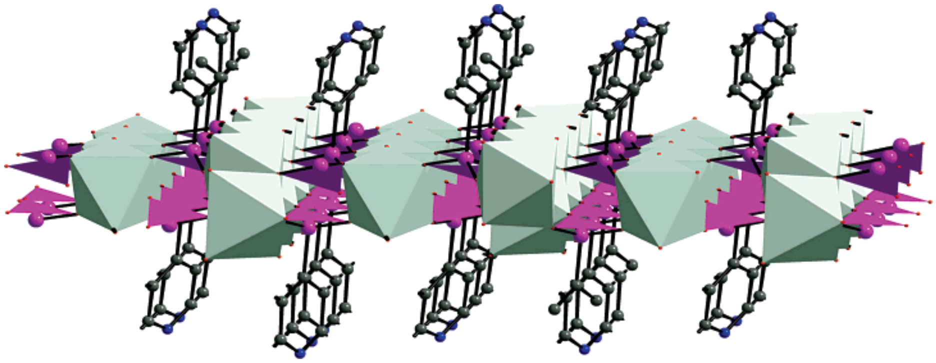

Figure 5. Polyhedral view of **2** along the *a* axis. Color code: purple, phosphorus; red, oxygen; black, carbon; blue, nitrogen

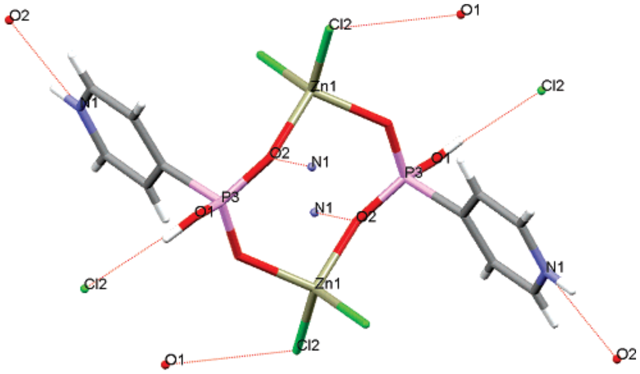

Figure 6. Stick representation of the crystal structure of **3** with atoms labeled. The intermolecular hydrogen bond interactions are schematically shown as dashed lines.

chromophore-formed 3D supramolecular network with extensive intermolecular hydrogen bonding. Each Zn(II) is bonded with two pendant Cl ions and two oxygen atoms from two different phosphonates. The second oxygen of each phosphonate is involved in bonding with the other Zn(II) unit, and the third one remains terminal with a longer bond distance (1.557(5) Å). The coordination environment of each Zn(II) atom is regular tetrahedral with a slightly high Cl−Zn−Cl bond angle (117.45°(6)) due to steric hindrance. The intramolecular Zn−Zn distance is 4.52 Å. The interesting feature of the compound is that for the sake of charge balance, the pyridine nitrogen of the phosphonic acid is protonated, which has been confirmed by the peaks at 3075 cm^{-1} in the IR spectra[20] for the N−H stretching frequency. As shown in Figure 6, in each individual molecule, the H atoms attached to the pendant oxygen of the phosphonates (O1) are involved in hydrogen bonding with the Cl2 atoms of the neighboring four molecules (Cl2···O1 distance 3.028 Å) and thereby form a 2D sheet along the *bc* diagonal. Interestingly, there is another hydrogen bond between the H atoms bonded with the pyridinium nitrogen and the phosphonate oxygen of the four neighboring dimeric units (N1···O2 distance 2.823 Å) bonded to Zn along the *ac* diagonal. These two interactions give rise to a 3D structure from a discrete dimeric molecule. Interestingly, both types of hydrogen bonding formations occur in linear chain motifs; the donors are always different than the acceptors. The eight-membered ring motif seen in Figure 6 is a common one in zinc phosphates and phosphonates. The compound $Zn[(O_3PCH_2NHC_{10}H_{20}O_4)NO_3]\cdot 0.5H_2O$ contains similar eight-membered rings that form a central ladder-type stem or chain from which the aza crown ethers are pendant groups alternately above and below the chains.[3e] Such rings are also present in similar cadmium compounds.[3i] The reason that the present zinc compound did not form a ladder-type chain is due to the fact that the two Cl atoms occupying the opposite corners of the eight-membered ring prevented further growth of the chain.

Structure of 4. In the asymmetric unit of the molecule, all the atoms except O1, C2, and C3 are located on mirror planes at $y = 0.25$ ($z = 4$). Due to this symmetry, the phenyl group has only three independent carbon atom positions, C2, C3, and C4. The C4 atom lies on a mirror plane, while C2 and C3 are in a general position. The *p*-xylene ligands are located in the *ac* plane primarily due to the small *b*-axis dimension (Figure 7). In the extended structure, the compound shows that there is one Co(II) ion in the asymmetric unit having a CoO6 chromophore, where the inorganic layers built by corner-sharing CoO6 units are pillared by the organic ligand and thereby form a 3D framework. The octahedral environment of each Co atom is fulfilled by five phosphonate oxygen atoms from four different completely deprotonated diphosphonate ligands, and the sixth position is occupied by a water molecule. Co−O (phosphonate) distances are 2.086(4) and 2.209(4) Å; the Co−O (water) distance is 2.146(4) Å. Each phosphonate group binds to four Co(II) ions through three oxygen atoms, of which one behaves as monocoordinating and other two as bicoordinating toward three Co(II) ions (Figure 8). So, each phosphonate shares three corners and an edge with a total of four CoO6 octahedra. As shown in Figure 7 (and in Figure 5 in the Supporting Information), the propagation of the *p*-xylylene ligand along the *a* and *b* directions creates two cross-linked 1D channels with dimensions ~10.5 × 4.7 Å^2 and ~10.80 × 5.6 Å^2. The metal centers within the inorganic layer are separated by 3.737 and 4.793 Å in both *b* and *c* directions, respectively. The metal centers across the layer are separated by ~12 Å. The inorganic layers are very similar to Mn, Co, and Zn phenylphosphonates with similar in-plane dimensions.[21] The main difference in the present study is that the position of the two phosphonic acid functions (parallel to each other) is favorable to the formation of a pillared-layered structure.

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[20] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; New York: Wiley, 1963.

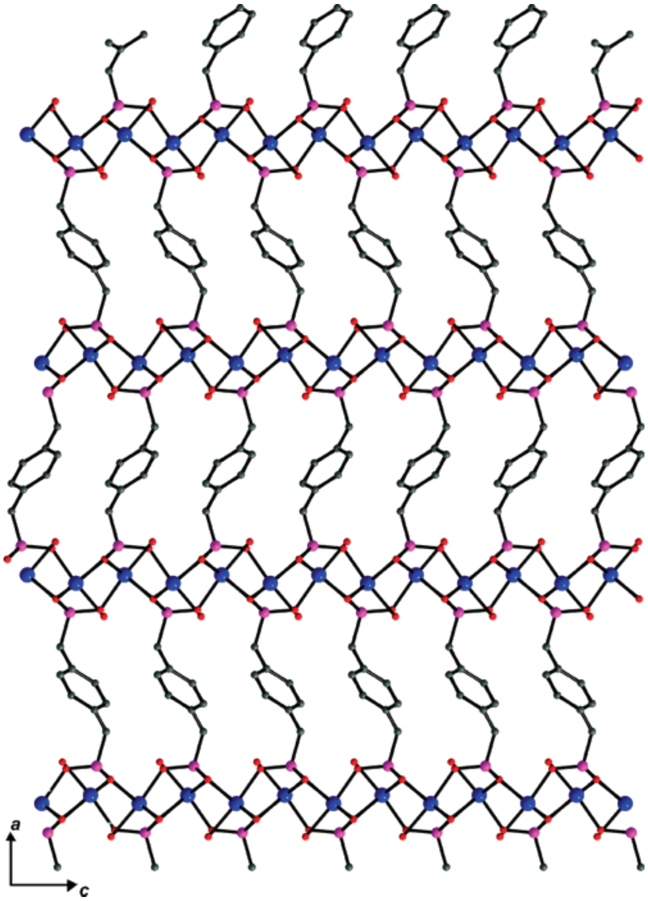

Figure 7. View of **4** along the *b* axis. Color code: blue, cobalt; purple, phosphorus; red, oxygen; gray, carbon.

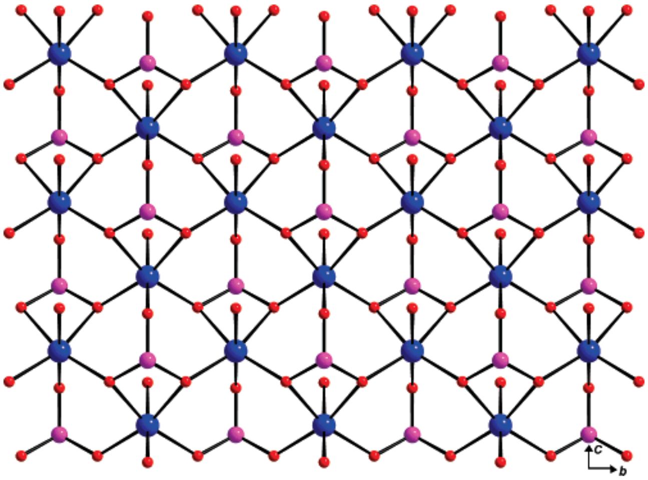

Figure 8. In-plane connectivity of **4** on *bc* plane. Organic part of the ligand is omitted. Color code: blue, cobalt; purple, phosphorus; red, oxygen.

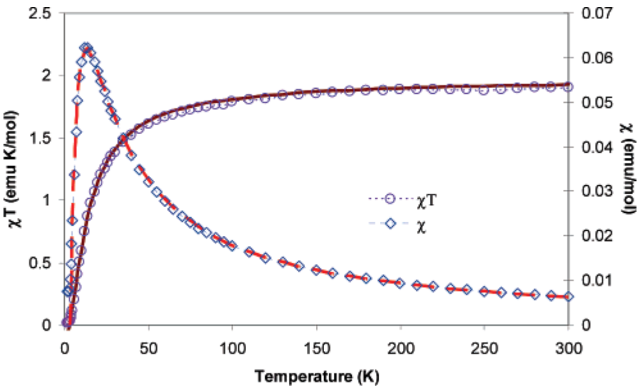

Figure 9. Plots of the temperature dependence (from 300 to 3 K) of $\chi_M T$ and χ_M in **1**. Solid lines represent the best theoretical fit (see text for parameters).

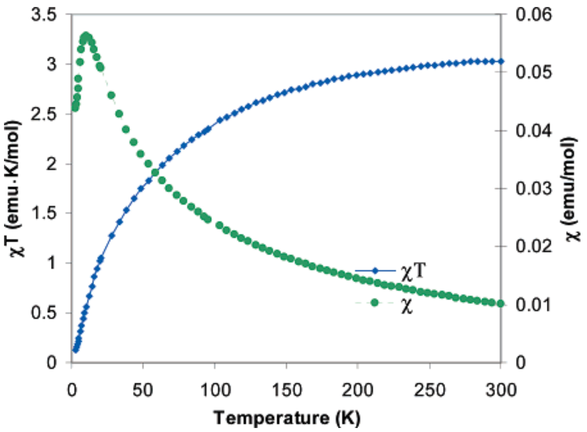

Figure 10. Plots of the temperature dependence (from 300 to 3 K) of $\chi_M T$ and χ_M in **4**.

The *p*-xylylene-α,α′-diphosphonate ligands have a bilayer arrangement in which the organic parts of the ligands are pointed away from either side of the inorganic layer into the interlayer space, not in a parallel fashion (Figure 7). But they are parallel in every other layer. The distance between the benzene rings is about 4.5 Å (along the *a*-axis), and their π−π interaction may hold them parallel. Due to disorder in the structure, it was not possible to determine the exact position of the *p*-xylene group along the *b*-axis direction (Figure 5 in the Supporting Information). Through indexing of all the spots during the determination of the unit cell of the compound, the possibility of having a supercell is excluded.

Magnetic Properties. The magnetic properties of complexes **1** and **4** in the form of $\chi_M T$ and χ_M versus T plots (χ_M is the molar magnetic susceptibility for four Cu(II) ions for **1** and one Co(II) for **4**) are shown in Figures 9 and 10. For **1**, the $\chi_M T$ value is 1.9029 cm^3 mol^{-1} K at 300 K for four magnetically quasi-isolated spin doublets (or 0.45 cm^3 mol^{-1} K per Cu(II) for $g = 2.3$), as expected. The $\chi_M T$ values slowly decrease from room temperature to 60 K (1.945 cm^3 mol^{-1} K) and then quickly decrease to 0.01497 cm^3 mol^{-1} K at 2 K. The global feature is characteristic of antiferromagnetic interactions.

Magnetic data were fitted (solid line in the Figure 9) excellently, using the alternating-chain model for the Cu(II) system.[22] The best-fitted parameters for complex **1** are $J = -7.6$ cm^{-1}, $g = 2.30$, and $\alpha = 0.6$, where J is the exchange integral between the two nearest-neighbor Cu((II) centers

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(21) (a) Frink, K. J.; Wang, R. C.; Col'on, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438. (b) Fanucci, G. E.; Krzystek, J.; Meisel, M. W.; Brunel, L.-C.; Talham, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 5469. (c) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781. (*d*) Mao, J.-G.; Wang, Z.; Clearfield, A. *Inorg. Chem.* **2002**, *41*, 2334. (e) Fredoueil, F.; Evain, M.; Massiot, D.; Bujoli-Doeuffb, M.; Bujoli, B. *J. Mater. Chem.* **2001**, *11*, 1106. (f) Penicaud, V.; Massiotb, D.; Gelbardc, G.; Odobela, F.; Bujoli, B. *J Mol. Struct.* **1998**, *470*, 31.

(Cu1) and αJ is the exchange integral between the two farthest-neighbor Cu(II) centers (Cu1 and Cu2, see the structural details above).

The magnetic properties of complex **4** in the form of the $\chi_M T$ versus T plot (χ_M is the molar magnetic susceptibility for the Co(II) ion) are shown in Figure 10. The value of $\chi_M T$ at 300 K is 3.043 cm^3 mol^{-1} K, which is larger than that expected for the spin-only case ($\chi_M T = 1.87$ cm^3 mol^{-1} K, $S = {}^3/_2$), which indicates that an important orbital contribution is involved. The $\chi_M T$ values continuously decrease from room temperature to 0.1316 cm^3 mol^{-1} K at 3 K. The global feature is characteristic of antiferromagnetic interactions between the metal centers. The χ_M curve is less indicative: it starts at 0.0101 cm^3 mol^{-1} at room temperature and increases in a uniform way to 0.0539 cm^3 mol^{-1} at 6 K and then decreases sharply to 0.043867 cm^3 mol^{-1} at 3 K. The presence of a maximum in this χ_M curve may indicate that the possible antiferromagnetic coupling is very strong. In the case of the data for **4**, using a simple model, no satisfactory fitting was obtained at this moment due to considerable orbital contribution to the magnetic moment.

Conclusions

In conclusion, the synthesis and characterization of two phosphonic acids and four metal−organophosphonate hybrid compounds prepared from those acids are described in this paper, together with a magnetic study of two of the compounds. Pyridyl-4-phosphonic acid played a versatile role toward different divalent metal ions to form compounds (**1**, **2**, and **3**) in different dimensionalities. The pyridyl nitrogen of the ligand, by binding to the two types of Cu in **1**, transformed the linear chains into a 3D structure. **2** is a layered compound with pendant hydrophobic organic pyridyl groups. It is possible to modify the hydrophobic/hydrophilic character of the ligand and make it potentially applicable as a host for intercalation reactions. So, by affixing different functional groups on the organic part of the ligand, we believe more interesting new inorganic−organic hybrid layered and porous compounds with potential material applications are possible. On the other hand, the 3D layered and pillared compound formed by *p*-xylylenediphosphonate and Co(II) has a bilayer arrangement of the ligands where the benzene rings of the ligands are involved in a $\pi-\pi$ interaction that makes them a potential hydrogen storage material. Although compound **1** has a 3D structure, magnetically it has been considered a 1D chain, and the data have been analyzed in terms of an alternating-chain Heisenberg-exchange model. Whereas the magnetic susceptibility of **4** is higher than that expected for a spin-only value, fittings using simple models did not yield satisfactory agreement.

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Supporting Information Available: X-ray crystallographic data in CIF format; tables giving bond lengths, bond angles, and hydrogen bonding; and additional structural drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033.