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Three-, Two-, and One-Dimensional Metal Phosphonates Based on [Hydroxy(4-pyridyl)methyl]phosphonate: M$\{$(4-C_5H_4N)CH(OH)$PO_3\}$(H_2O) (M = Ni, Cd) and Gd$\{$(4-C_5H_4N)CH(OH)P(OH)$O_2\}_3\cdot 6H_2O$

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Based on the [hydroxy(4-pyridyl)methyl]phosphonate ligand, three compounds with formula Ni$\{$(4-C_5H_4N)CH(OH)-$PO_3\}$(H_2O) (**1**), Cd$\{$(4-C_5H_4N)CH(OH)$PO_3\}$(H_2O) (**2**), and Gd$\{$(4-C_5H_4N)CH(OH)P(OH)$O_2\}_3\cdot 6H_2O$ (**3**) have been synthesized under hydrothermal conditions. The crystal data for **1** are as follows: orthorhombic, space group *Pbca*, $a = 8.7980(13)$ Å, $b = 10.1982(15)$ Å, and $c = 17.945(3)$ Å. For **2** the crystal data are as follows: monoclinic, space group *C*2/*c*, $a = 23.344(6)$ Å, $b = 5.2745(14)$ Å, $c = 16.571(4)$ Å, and $\beta = 121.576(4)°$. The crystal data for **3** are as follows: rhombohedral, space group $R\bar{3}$, $a = 22.2714(16)$ Å, $b = 22.2714(16)$ Å, and $c = 9.8838(11)$ Å. Compound **1** adopts a three-dimensional pillared layered structure in which the inorganic layers made up of corner-sharing $\{NiO_5N\}$ octahedra and $\{CPO_3\}$ tetrahedra are connected by pyridyl groups. A two-dimensional layer structure is found in compound **2**, which contains alternating inorganic double chains and pyridyl rings. Compound **3** has a one-dimensional chain structure where the Gd atoms are triply bridged by O–P–O linkages. The pyridyl nitrogen atom in **3** remains uncoordinated and is involved in the interchain hydrogen bonds. Magnetic susceptibility studies of **1** and **3** reveal that weak ferromagnetic interactions are mediated between Ni(II) centers in compound **1**. For compound **3**, the behavior is principally paramagnetic.

Introduction

Metal phosphonates are a class of hybrid materials that can integrate organic and inorganic characteristics within a single molecular composite, thus providing unique chemical and physical properties.[1−3] The organic moieties of the phosphonate ligand RPO_3^{2-} can be modified by other functional groups such as hydroxy,[4] amino,[5] carboxylate,[6] and pyridyl.[7] The introduction of these functional groups may not only result in new structure types of metal phosphonates, but also bring interesting functionalities. In many cases, however, the functional groups participate in the coordination to metal ions by using part or all of their binding sites at the cost of their functionalities. To prepare materials with new structure types especially porous structures while maintaining useful functionalities, one approach is to increase the number of functional groups in the phosphonate anion. This is the case for the phosphonate compounds containing amino acid groups where amino groups are frequently found to be protonated and not coordinated with metal ions.[8] Another approach is to employ suitable metal ion that can selectively coordinate with particular donor sites.

It is well-known that the transition metal ions with different electronic configurations could show different coordination modes toward the same ligand. The lanthanide ions, due to their unique $4f^n$ electronic configuration, bond preferentially to fluoride and oxygen donor ligands. In this article, we choose Ni(II), Cd(II), and Gd(III) with $3d^8$, $3d^{10}$, and $4f^7$

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electronic configurations, respectively, to react with [hydroxy(4-pyridyl)methyl]phosphonic acid under hydrothermal conditions. Three compounds with three-dimensional (3-D), two-dimensional (2-D), and one-dimensional (1-D) structures, respectively, have been obtained, namely Ni{(4-C_5H_4N)CH(OH)PO_3}(H_2O) (**1**), Cd{(4-C_5H_4N)CH(OH)PO_3}(H_2O) (**2**), and Gd{(4-C_5H_4N)CH(OH)P(OH)O_2}$_3$·6H_2O (**3**). The pyridyl nitrogen atom serves as a coordination donor in compounds **1** and **2**, while remaining "free" in compound **3**.

Experimental Section

[Hydroxy(4-pyridyl)methyl]phosphonic acid (4-hpmpH_2) was synthesized according to the literature.[9] All other starting materials were of reagent quality and were obtained from commercial sources without further purification.

Ni{(4-C_5H_4N)CH(OH)PO_3}(H_2O) (1). A mixture of $NiSO_4$·6H_2O (0.17 mmol, 0.0447 g) and 4-hpmpH_2 (0.25 mmol, 0.0473 g) in 8 mL of H_2O and 2 mL of C_2H_5OH, adjusted to pH 3−4 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 12 h. After slow cooling to room temperature, green blocky crystals were obtained together with a small amount of green powder. The green crystals were manually collected which were further used for single-crystal analysis and physical measurements. Yield: 0.011 g (25% based on Ni). Anal. found (calcd) for $C_6H_8NO_5PNi$: C, 27.08 (27.29); H, 3.05 (3.03); N, 5.03 (5.31) %; IR (KBr, cm^{-1}): 3039(s,br), 1615(m), 1561(m), 1501(w), 1426(m), 1400(m), 1358(w), 1243(w), 1216(w), 1199(m), 1070(s), 102(s), 971(s), 868(w), 830(m), 753(w), 707(w), 668(w), 643(w), 577(s), 556(m), 531(m), 481(m), 427(w).

Cd{(4-C_5H_4N)CH(OH)PO_3}(H_2O) (2) was prepared similarly to **1** except $CdSO_4$·2.7H_2O was used instead of $NiSO_4$·6H_2O, and pH was adjusted to 2.5−3.5. Colorless needlelike crystals were collected as a monophasic material based on the powder X-ray diffraction pattern. Yield: 0.015 g (28% based on Cd). Anal. found (calcd) for $C_6H_8NO_5PCd$: C, 22.62 (22.68); H, 2.42 (2.52); N, 4.31 (4.41) %. IR (KBr, cm^{-1}): 3286(s,br), 1612(m), 1557(w), 1501(w), 1428(m), 1404(w), 1347(w), 1291(w), 1198(m), 1089(s), 1075(s), 1020(m), 979(s), 868(m), 840(m), 774(w), 734(w), 651(w), 572(m), 548(m), 473(w).

Gd{(4-C_5H_4N)CH(OH)P(OH)O_2}$_3$·6H_2O (3) was initially synthesized following a procedure similar to those for **1** and **2**, but microcrystalline materials were obtained together with a small amount of impurities. A pure phase of **3** was obtained by the hydrothermal treatment of a mixture of Gd(NO_3)$_3$·6H_2O (0.1 mmol, 0.0451 g), NaN_3 (0.3 mmol, 0.0195 g), and 4-hpmpH_2 (0.3 mmol, 0.0568 g) in 8 mL of H_2O and 2 mL of C_2H_5OH, adjusted to pH 3.0 with 1 M NaOH, at 140 °C for 24 h. Colorless needlelike crystals were collected and used for physical measurements. Yield: 0.016 g (19% based on Gd). Anal. found (calcd) for $C_{18}H_{33}N_3O_{18}P_3Gd$: C, 27.58 (27.69); H, 4.29 (4.23); N, 5.24 (5.38) %; IR (KBr, cm^{-1}): 3278 (s,br), 3100(w), 2142(w), 2045(w), 1639(m), 1501(m), 1422(w), 1250(w), 1217(w), 1186(m), 1114(s), 1098(s), 1044(s), 972(s), 855(m), 715(m), 644(m), 566(m), 492(w), 465(w), 440(w).

Physical Measurements. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Variable temperature magnetic susceptibility data were obtained on microcrystalline samples (1.73 mg for **1**, 7.68 mg for **3**) from 1.8 to 300 K in a magnetic field of 2 kOe, using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants.[10]

X-ray Crystallographic Studies. Single crystals of dimensions 0.05 × 0.05 × 0.05 mm for **1**, 0.08 × 0.05 × 0.05 mm for **2**, and 0.10 × 0.04 × 0.04 mm for **3** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature. A hemisphere of data was collected in the θ range 2.27−25.00° for **1**, 2.05−28.04° for **2**, and 1.83−25.99° for **3** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. Numbers of observed and unique [$I > 2\sigma(I)$] reflections are 7385 and 1415 ($R_{\mathrm{int}} = 0.1062$) for **1**, 4535 and 1963 ($R_{\mathrm{int}} = 0.0614$) for **2**, and 7268 and 1856 ($R_{\mathrm{int}} = 0.0225$) for **3**, respectively. The data were integrated using the Siemens SAINT program,[11] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL.[12] All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters

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Table 1. Crystallographic Data and Refinement Parameters for **1**−**3**

compound	**1**	**2**	**3**
empirical formula	$C_6H_8NO_5PNi$	$C_6H_8NO_5PCd$	$C_{18}H_{33}N_3O_{18}P_3Gd$
fw	263.82	317.50	829.63
crystal system	orthorhombic	monoclinic	rhombohedral
space group	Pbca	*C*2/*c*	$R\bar{3}$
a (Å)	8.7980(13)	23.344(6)	22.2714(16)
b (Å)	10.1982(15)	5.2745(14)	22.2714(16)
c (Å)	17.945(3)	16.571(4)	9.8838(11)
β (deg)		121.576(4)	
V (Å^3)	1610.1(4)	1738.3(8)	4245.7(6)
Z	8	8	6
ρ_{calcd} (g cm^{-3})	2.177	2.426	1.947
F(000)	1072	1232	2490
μ(Mo Kα) (cm^{-1})	26.02	26.90	26.00
goodness of fit on F^2	0.919	1.218	0.995
R1, wR2[a] [$I > 2\sigma(I)$]	0.0541, 0.0834	0.0715, 0.1120	0.0516, 0.1502
R1, wR2[a] (all data)	0.1099, 0.0958	0.0953, 0.1192	0.0627, 0.1532
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	1.017, −1.250	1.079, −2.046	0.93, −0.76

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**[a]

Ni(1)−O(1W)	2.041(5)	Ni(1)−O(4)	2.210(5)
Ni(1)−O(1)	2.059(5)	P(1)−O(2)	1.513(5)
Ni(1)−O(3A)	2.067(4)	P(1)−O(1)	1.526(4)
Ni(1)−O(2B)	2.071(5)	P(1)−O(3)	1.516(5)
Ni(1)−N(1C)	2.075(5)	P(1)−C(6)	1.815(8)
O(1W)−Ni(1)−O(1)	177.83(18)	O(1)−Ni(1)−O(4)	81.70(19)
O(1W)−Ni(1)−O(3A)	85.72(19)	O(3A)−Ni(1)−O(4)	87.94(18)
O(1)−Ni(1)−O(3A)	93.66(18)	O(2B)−Ni(1)−O(4)	87.84(19)
O(1W)−Ni(1)−O(2B)	89.5(2)	N(1C)−Ni(1)−O(4)	172.8(2)
O(1)−Ni(1)−O(2B)	90.96(19)	P(1)−O(1)−Ni(1)	122.9(3)
O(3A)−Ni(1)−O(2B)	173.24(19)	P(1)−O(2)−Ni(1D)	137.8(3)
O(1W)−Ni(1)−N(1C)	89.6(2)	P(1)−O(3)−Ni(1E)	133.4(3)
O(1)−Ni(1)−N(1C)	92.4(2)	C(6)−O(4)−Ni(1)	111.9(4)
O(3A)−Ni(1)−N(1C)	88.3(2)	C(5)−N(1)−Ni(1F)	121.4(5)
O(2B)−Ni(1)−N(1C)	96.5(2)	C(1)−N(1)−Ni(1F)	121.6(5)
O(1W)−Ni(1)−O(4)	96.20(19)		

[a] Symmetry codes: A: $x - 1/2, y, -z + 3/2$; B: $-x + 1, y + 1/2, -z + 3/2$; C: $x, -y + 1/2, z + 1/2$; D: $-x + 1, y - 1/2, -z + 3/2$; E: $x + 1/2, y, -z + 3/2$; F: $x, -y + 1/2, z - 1/2$.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**[a]

Cd(1)−O(3A)	2.155(6)	P(1)−O(3)	1.505(7)
Cd(1)−O(2B)	2.202(6)	P(1)−O(1)	1.511(6)
Cd(1)−O(1C)	2.261(6)	P(1)−O(2)	1.520(6)
Cd(1)−N(1)	2.283(6)	P(1)−C(6)	1.835(8)
Cd(1)−O(1W)	2.327(6)		
O(3A)−Cd(1)−O(2B)	137.4(2)	O(1C)−Cd(1)−O(1W)	167.6(2)
O(3A)−Cd(1)−O(1C)	88.3(2)	N(1)−Cd(1)−O(1W)	88.1(2)
O(2B)−Cd(1)−O(1C)	101.9(2)	P(1)−O(1)−Cd(1A)	124.5(3)
O(3A)−Cd(1)−N(1)	108.9(3)	P(1)−O(2)−Cd(1D)	112.5(3)
O(2B)−Cd(1)−N(1)	112.1(2)	P(1)−O(3)−Cd(1C)	164.3(4)
O(1C)−Cd(1)−N(1)	91.1(2)	C(5)−N(1)−Cd(1)	121.3(5)
O(3A)−Cd(1)−O(1W)	80.3(2)	C(1)−N(1)−Cd(1)	120.7(6)
O(2B)−Cd(1)−O(1W)	89.8(2)		

[a] Symmetry codes: A: $-x + 1/2, y-1/2, -z + 1/2$; B: $x - 1/2, -y + 3/2, z - 1/2$; C: $-x + 1/2, y + 1/2, -z + 1/2$; D: $x + 1/2, -y + 3/2, z + 1/2$.

related to the non-H atom to which they are bonded. Crystallographic and refinement details of **1**−**3** are listed in Table 1. Selected bond lengths and angles are given in Tables 2, 3, and 4 for **1**, **2** and **3**, respectively.

Results and Discussion

Syntheses. Compounds **1**−**3** were prepared under similar experimental conditions. For compounds **1** and **2**, the M:ligand ratio is 1:1. For **3**, the ratio is 1:3. To study the influence of the molar ratio of the starting materials on the composition of the final products, a systematic work was carried out under similar hydrothermal conditions at 140 °C for 12 h with the initial pH values of the reactants being ca. 3.0. It was found that compounds **1** and **2** could be obtained when the molar ratio of Ni(Cd):ligand was 1:1, 1:2, 1:3, 2:1, or 3:1. However, with the presence of excess ligand, additional peaks can be clearly seen from the X-ray diffraction (XRD) patterns and the product was not a pure phase. Compound **3** could be prepared only when the Gd:ligand ratio was 1:1, 1:2, or 1:3. The presence of excess $Gd(NO_3)_3 \cdot 6H_2O$ (Gd:ligand = 2:1, 3:1) resulted in either a colloidal material or a clear solution. NaN_3 was added to improve the crystallization of the product. Compounds **1**−**3** can be prepared with or without it.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for **3**[a]

Gd(1)−O(2)	2.273(4)	P(1)−O(1)	1.543(5)
Gd(2)−O(1)	2.293(4)	P(1)−O(3)	1.513(5)
P(1)−C(6)	1.803(7)	P(1)−O(2)	1.520(5)
O(2B)−Gd(1)−O(2)	91.92(15)	O(1F)−Gd(2)−O(1)	86.98(15)
O(2C)−Gd(1)−O(2)	88.08(15)	O(1E)−Gd(2)−O(1)	93.02(15)
P(1)−O(2)−Gd(1)	152.5(3)	P(1)−O(1)−Gd(2)	136.3(3)

[a] Symmetry codes: B: $-x + y, -x, z$; C: $x - y, x, -z$; E: $-y, x - y, z$; F: $y, -x + y, -z + 1$.

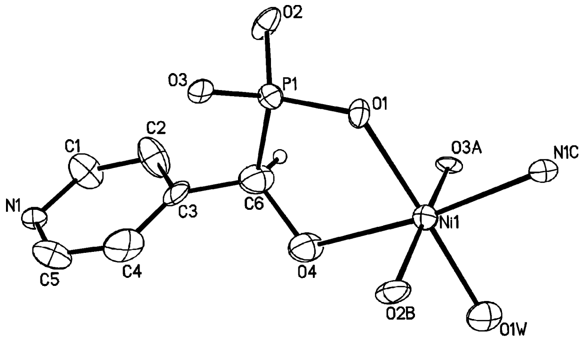

Figure 1. Building unit of compound **1** with atomic labeling scheme (50% probability). All H atoms except H6A are omitted for clarity. Symmetry codes: A: $x - 1/2, y, -z + 3/2$; B: $-x + 1, y + 1/2, -z + 3/2$; C: $x, -y + 1/2, z + 1/2$.

Structure of Ni{(4-C_5H_4N)CH(OH)PO_3}(H_2O) (1). Compound **1** crystallizes in orthorhombic space group *Pbca*. The asymmetric unit consists of one Ni atom, one 4-hpmp^{2-} ligand, and one coordinated water molecule (Figure 1). Each Ni atom has a distorted octahedral environment. Three of its six binding sites are occupied by phosphonate oxygens (O1, O2B, O3A) from three phosphonate ligands. The remaining positions are filled with the hydroxy oxygen (O4), pyridyl nitrogen (N1C), and water oxygen (O1w). The Ni1−O(N) bond lengths range from 2.042(5) to 2.210(5) Å. The bond angles around the Ni atom are in the range of 85.72(17)−177.83(17)°.

The 4-hpmp^{2-} ligand serves as a pentadentate ligand. Besides the phosphonate oxygens, both the pyridyl nitrogen and the hydroxy group are involved in the coordinations to the Ni atom. Each {CPO_3} tetrahedron is corner-shared with three {NiO_5N} octahedra through three phosphonate oxygens and vice versa, thus forming an inorganic layer containing 12-membered rings of {−Ni−O−P−O−}$_3$ (Figure 2). The

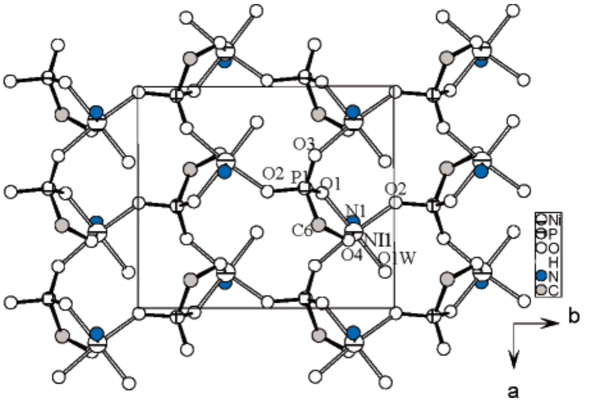

Figure 2. One inorganic layer of compound **1** viewed along *c*-axis. All H and C atoms except C6 are omitted for clarity.

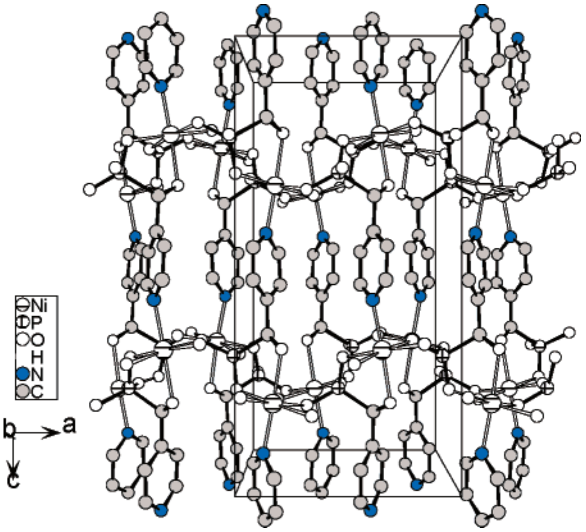

Figure 3. Structure **1** packed along *b*-axis.

layer is reminiscent of that in compound $Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$,[13] although it is remarkably different from those observed in other monophosphonate compounds such as $Ni(CH_3PO_3)(H_2O)$.[14] The coordinated water molecules point toward the middle of the cavities. The inorganic layers are covalently linked by pyridyl groups, resulting in a new type of pillared layered structure (Figure 3).

Structure of Cd{(4-C$_5$H$_4$N)CH(OH)PO$_3$}(H$_2$O) (2). Compound **2** crystallizes in monoclinic space group *C*2/*c*. Although it has the same composition as compound **1**, the two structures are significantly different. The Cd atom in **2** is five-coordinated and has a distorted trigonal bipyramidal geometry. The 4-hpmp^{2-} ligand acts as a tetradentate ligand, using three of its phosphonate oxygens and the pyridyl nitrogen atom. The hydroxy group is not coordinated. Consequently, each $\{CdO_4N\}$ trigonal bipyramid is corner-shared with three $\{CPO_3\}$ tetrahedra and vice versa, forming a "staircase" chain containing eight-membered rings of $\{-Cd-O-P-O-\}_2$. The chains are connected by pyridine rings through coordination, leading to a two-dimensional layer structure (Figure 4). Extensive hydrogen bonds are found between the layers. Compound **2** is isostructural to $M\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}$).[7b]

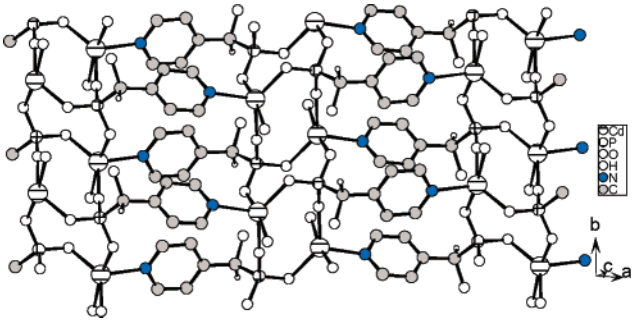

Figure 4. One layer of structure **2** viewed approximately along *c*-axis.

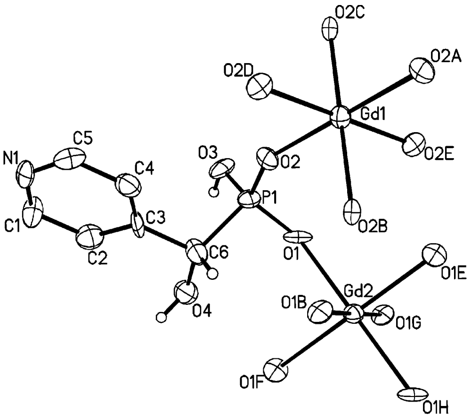

Figure 5. Building unit of structure **3** with atomic labeling scheme (50% probability). All H atoms except H6A, H4A, and H3B are omitted for clarity. Symmetry codes: A: $-x, -y, -z$; B: $-x + y, -x, z$; C: $x - y, x, -z$; D: $y, -x + y, -z$; E: $-y, x - y, z$; F: $y, -x + y, -z + 1$; G: $x - y, x, -z + 1$; H: $-x, -y, -z + 1$.

Structure of Gd{(4-C$_5$H$_4$N)CH(OH)P(OH)O$_2$}$_3$·6H$_2$O (3). Compound **3** crystallizes in rhombohedral space group $R\bar{3}$. Figure 5 shows the building unit of the structure. It contains two crystallographically independent Gd atoms, residing in special positions (0,0,0) and (0,0,0.5), respectively. Each Gd atom is six-coordinated and exhibits a distorted octahedral geometry. The Gd1 atom is surrounded by six equivalent O2 atoms, while the Gd2 atom is surrounded by six equivalent O1 atoms from phosphonate ligands. The Gd1−O2 and Gd2−O1 bond lengths are 2.273(4) and 2.293(4) Å, respectively. All atoms of the 4-hpmp^{2-} ligand locate in general positions in the structure. The ligand is bidentate and bridges the Gd1 and Gd2 atoms by using two of its three phosphonate oxygens (O1, O2), forming an infinite chain along the *c*-axis (Figure 6). The Gd1···Gd2 distance over the O−P−O bridge is 4.942 Å. The third phosphonate oxygen (O3) is protonated. Both the pyridyl nitrogen and the hydroxy group are not coordinated to the metal ion. Instead, they are involved in the interchain hydrogen bond interactions (O3···N1^{i}: 2.621 Å; symmetry code: i, $-x + y - 1/3, -x + 1/3, z + 1/3$), forming a three-dimensional open-network structure with triangular cavities generated along the *c*-axis (Figure 7). The lattice water molecules reside in these cavities with extensive hydrogen bond interactions.

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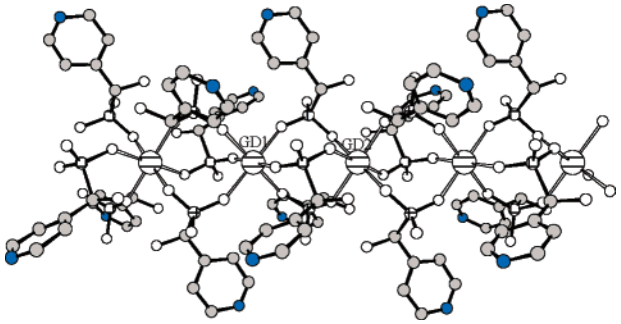

Figure 6. Fragment of chain in structure **3**. All H atoms are omitted for clarity.

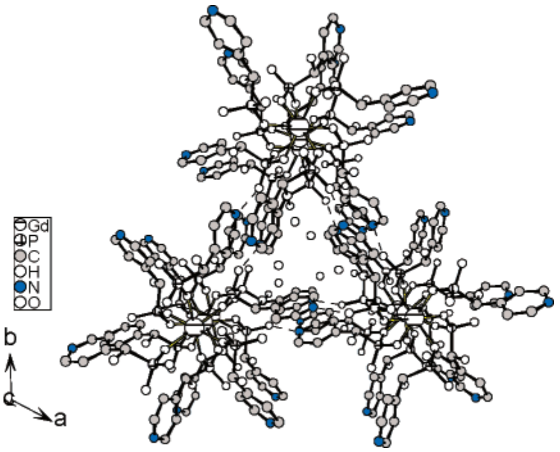

Figure 7. Structure **3** packed along *c*-axis, emphasizing cavity generated by interchain hydrogen bonds. The lattice water molecules within the cavity are shown as empty circles.

Clearly, when [hydroxy(4-pyridyl)methyl]phosphonic acid reacts with different metal ions under similar hydrothermal conditions, different structures can result. For the Ni(II) ion with d^8 configuration, a three-dimensional pillared layered structure with formula $Ni\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$ is formed in which the Ni atom has an octahedral coordination environment and the phosphonate ligand provides all five potential donor sites including the hydroxy group. For Cd(II) with d^{10} configuration, a two-dimensional layer structure with formula $Cd\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$ similar to **1** is obtained. In this case, each metal atom has a trigonal bipyramidal geometry and the hydroxy group of the ligand is not involved in the coordination to the metal ion. The reaction with the rare earth metal ion Gd(III) (f^7 configuration) leads to the formation of a one-dimensional chain structure with formula $Gd\{(4\text{-}C_5H_4N)CH(OH)P(OH)O_2\}_3\cdot 6H_2O$. The structure is unexpected because only two phosphonate oxygen atoms participate in the coordination with the Gd atoms, leaving one phosphonate oxygen, the hydroxy group, and the pyridyl nitrogen atoms "free" for coordination.

Although there are many factors that determine the crystal engineering of a special structure, the electronic nature of different metal ions in compounds **1**−**3** plays important roles. For Ni(II) ion, octahedral coordination as observed in compound **1** is generally the preferred state because of the ligand field stabilization effects (LFSE), although other configuration complexes are also known.[15] The spherically symmetric d^{10} configuration of Cd(II) affords no LFSE, so the preferred coordination is determined by other factors such as electrostatic forces, covalence, and size.[15] In the case of compound **2**, trigonal bipyramidal coordination is favored. The lanthanides behave as typical hard acids, bonding preferentially to fluoride and oxygen donor ligands.[15] Therefore, it is not a surprise that the pyridyl nitrogen atom is not coordinated to the Gd atom in compound **3**. The formation of a chain structure is still unprecedented, however, because three-dimensional structures were observed in the other rare earth monophosphonate compounds with additional carboxylate groups such as $Ln_4(H_2O)_7[O_2CC_5H_{10}NCH_2PO_3]_4(H_2O)_5$[6t] and $Pr[O_3P(CH_2)_2CO_2]$.[6j] It is interesting that the Mn(II), Fe(II), and Co(II) ions in compounds $M\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$[7b] also prefer a five-coordinated trigonal bipyramidal geometry, although octahedral geometries are commonly found for these ions.

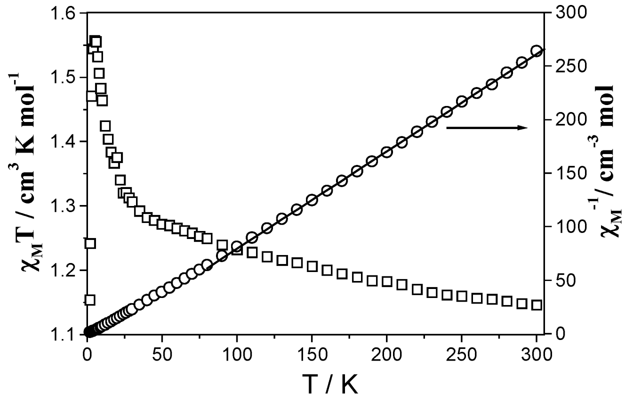

Figure 8. $\chi_M T$ and χ_M^{-1} vs T plots for **1**.

Magnetic Properties. Figure 8 shows the $\chi_M T$ and χ_M^{-1} vs T plots for compound **1**. The room temperature effective magnetic moment is 3.02 μ_B per Ni, close to the expected spin-only value for spin $S = 1$ (2.82 μ_B). Above 100 K, the magnetic behavior follows the Curie−Weiss law with the Weiss constant $\theta = +12.4$ K. The positive Weiss constant indicates a weak ferromagnetic interaction between Ni(II) centers. This is confirmed by the continuous increasing of $\chi_M T$ upon cooling. The decrease of $\chi_M T$ value below 5.0 K could be caused by the zero-field splitting of the ground state. The field-dependent magnetization, measured at 2.0 K, shows no evidence of hysteresis, indicating that no long-range magnetic ordering occurred above 2 K. The saturation magnetization at 70 kOe (1.99 μ_β) is close to the value of 2.0 μ_β anticipated for a spin value of $S = 1$ with $g = 2.0$ (see Supporting Information).

Ferromagnetic interactions have been found in a limited number of nickel phosphonates including $Ni_4(O_3PCH_2PO_3)_2(H_2O)_3$, $Ni_4(O_3PCH_2PO_3)_2(H_2O)_2$,[16] and $(enH_2)Ni(hedpH_2)_2\cdot 2H_2O$[17] [hedp = $CH_3C(OH)(PO_3)_2$]. Compound $Ni_4(O_3PCH_2$-

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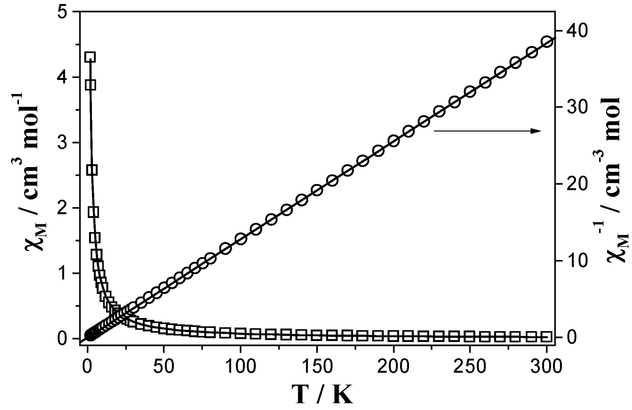

Figure 9. χ_M and χ_M^{-1} vs T plots for **3**.

$PO_3)_2(H_2O)_3$ has a layer structure built from sheets of trimeric edge-sharing units of Ni(II) octahedra on which Ni octahedra and diphosphonate groups are grafted. In compound $Ni_4(O_3PCH_2PO_3)_2(H_2O)_2$, one Ni(II) is jumped to a tetrahedral site, leading to the connection of the layers into a three-dimensional structure. Compound $(enH_2)Ni(hedpH_2)_2{\cdot}2H_2O$ has a chain structure where the Ni(II) ions are linked by O−P−O units. Compound **1** shows a pillared layered structure that is completely different from those of the above three compounds. The observed ferromagnetic interaction could be related to its structure where triangular units of $\{PO_3Ni_3\}$ are found in the inorganic layer. Ferromagnetic exchange was also found in $Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$[13] containing a similar triangular arrangement.

The magnetic behavior of **3** is given in Figure 9 in the forms of χ_M and χ_M^{-1} vs T plots. At 300 K, the effective magnetic moment per Gd (7.89 μ_B) agrees well with the spin-only value of 7.94 μ_B for $S = 7/2$. The magnetic behavior follows the Curie−Weiss law in the whole temperature range, leading to a very small Weiss constant $\theta = -0.086$ K which suggests that compound **3** is paramagnetic. Considering that this compound has a chain structure where the Gd(III) ions are triply linked by O−P−O units, the susceptibility data were also analyzed by Fisher's expression for a uniform chain, with the classical spins scaled to a real quantum spin $S = 7/2$.[10,18] A good fit was obtained, shown as the solid line in Figure 9, with parameters $g = 1.99$ and $J = -0.0016$ cm^{-1}. The very small $|J|$ value again confirms the paramagnetic nature of the system.

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Supporting Information Available: X-ray crystallographic files in CIF format and XRD patterns for the three compounds, and field-dependent magnetization for compound **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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