

$\{M(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (M = Mn, Fe, Co): layered compounds based on [hydroxy(4-pyridyl)methyl]phosphonate

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This paper describes the syntheses and characterization of three novel phosphonate compounds $M\{(C_5H_4N)CH(OH)PO_3\}(H_2O)$ [M = Mn (**1**), Fe (**2**), Co (**3**)] with isomorphous layered structures. Each $\{MO_4N\}$ trigonal bipyramid in the structure is corner-shared with three $\{CPO_3\}$ tetrahedra from three equivalent [hydroxy-(4-pyridyl)methyl]phosphonate ligands, forming a one-dimensional inorganic double chain. These inorganic chains are linked together *via* the organic groups of the ligand, leading to a two-dimensional layer structure. The layers are further connected to each other through extensive hydrogen bonds, thus generating a three-dimensional supramolecular network. The magnetic properties show that weak antiferromagnetic interactions are mediated between the metal centers in all three compounds.

During the past two decades, metal phosphonate chemistry has expanded significantly due to its potential applications in catalysis, molecular recognition, ion exchange, non-linear optics and sensors.¹⁻⁷ Great efforts have been devoted to the syntheses of novel inorganic-organic hybrid materials based on metal phosphonates.⁸⁻⁹ A number of compounds with one-, two- or three-dimensional structures have been reported, some of which show interesting microporous, catalytic and/or magnetic properties.¹⁰⁻¹⁶ The metal phosphonate compounds containing chiral or other functional groups such as carboxylato, amino and crown ether, however, are still quite limited in number.^{8,17-20} We have been interested in exploring novel metal phosphonate compounds with open framework structures based on 1-hydroxyethylidenediphosphonate.^{21,22} The work has been extended to [hydroxy(4-pyridyl)methyl]phosphonate²³ chemistry, where both a chiral carbon atom center and a functional pyridyl group are incorporated in the same ligand. In this paper we report the syntheses and characterizations of three new compounds, namely $\{Mn(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**1**), $\{Fe(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**2**) and $\{Co(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**3**).

Experimental

[Hydroxy(4-pyridyl)methyl]phosphonic acid was synthesized according to the literature.²⁴ Pyridine-4-carboxyaldehyde and other starting materials were obtained from commercial sources and were used without further purification. The elemental analyses were performed using a PE240C elemental analyzer. The infrared spectra were recorded on a Nicolet IFS66v spectrometer with pressed KBr pellets. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples (8.8 mg for **1**, 14.9 mg for **2** and 17.6 mg for **3**) from 2 to 300 K in a magnetic field of 5 kOe using a Quantum Design SQUID magnetometer. Diamagnetic corrections were obtained from Pascal's constants.²⁵

Synthesis of $\{Mn(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**1**)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.0906 g, 0.46 mmol) and [hydroxy(4-pyridyl)methyl]phosphonic acid (0.0941 g, 0.50 mmol) was thoroughly mixed with water (8 cm³) and ethanol

(2 cm³) in a Teflon-lined autoclave. The autoclave was sealed and placed inside an oven at 140 °C for 14 h. After slow cooling to room temperature, the colorless, tiny, needle-like crystals of **1** were collected as a monophasic material, as judged by the powder X-ray diffraction pattern. Yield: 11% based on Mn. Anal. calc. for $C_6H_8NO_5PMn$: C, 27.71; H, 3.10; N, 5.39. Found: C, 29.66; H, 4.10; N, 5.21%. IR (KBr, cm⁻¹): 3332(br), 2919(vw), 1655(w), 1612(m), 1557(w), 1501(w), 1425(m), 1347(w), 1288(w), 1192(m), 1126(s), 1094(vs), 1076(m), 1018(m), 986(s), 867(w), 840(m), 774(w), 738(w), 650(w), 575(m), 550(m), 475(w), 428(vw). The same product can be obtained when the molar ratio of Mn : ligand is 1 : 2 with a lower yield (7%). When the molar ratio of Mn : ligand is 1 : 3, a mixture results containing both the product and the unreacted ligand. In this case, however, single crystals suitable for the structural determination were obtained.

Synthesis of $\{Fe(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**2**)

A mixture of $FeSO_4 \cdot 7H_2O$ (0.0701 g, 0.25 mmol) and [hydroxy(4-pyridyl)methyl]phosphonic acid (0.0943 g, 0.50 mmol) was thoroughly mixed with water (8 cm³) and ethanol (2 cm³) in a Teflon-lined autoclave. The autoclave was sealed and placed inside an oven at 140 °C for 12 h. On cooling down to room temperature, yellow needle-like crystals of **2** were collected as a monophasic material, as judged by the powder X-ray diffraction pattern. Yield: 57% based on Fe. Anal. calc. for $C_6H_8NO_5PFe$: C, 27.62; H, 3.09; N, 5.37. Found: C, 29.03; H, 3.32; N, 5.63%. IR (KBr, cm⁻¹): 3382(br), 1638(w), 1613(m), 1557(w), 1502(w), 1424(s), 1347(w), 1287(w), 1187(m), 1127(s), 1097(s), 1020(m), 990(s), 867(w), 841(m), 739(w), 652(w), 572(s), 476(m), 433(w). The same product can be obtained when the molar ratio of Fe : ligand is 1 : 1 or 1 : 3, with yields of 33 and 40%, respectively.

Synthesis of $\{Co(C_5H_4N)CH(OH)PO_3\}(H_2O)$ (**3**)

A mixture of $Co(en)_3Cl_3$ (0.0856 g, 0.25 mmol) and [hydroxy-(4-pyridyl)methyl]phosphonic acid (0.1384 g, 0.73 mmol) was thoroughly mixed with water (8 cm³) and ethanol (2 cm³) in a Teflon-lined autoclave. The autoclave was sealed and placed inside an oven at 140 °C for 12 h. Purple needle-like single crystals of **3** were collected as monophasic material, as judged

Table 1 Crystallographic data for compounds 1–3

Compound	1	2	3
Formula	MnC ₆ H ₈ O ₅ NP	FeC ₆ H ₈ O ₅ NP	CoC ₆ H ₈ O ₅ NP
<i>M</i>	260.04	264.95	264.03
<i>T</i> /K	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /Å	23.060(4)	22.851(5)	22.737(4)
<i>b</i> /Å	5.2330(10)	5.1891(12)	5.1613(8)
<i>c</i> /Å	16.412(3)	16.381(4)	16.318(2)
β /°	121.555(3)	121.721(4)	121.818(2)
<i>V</i> /Å ³	1687.6(6)	1652.2(7)	1627.2(4)
<i>Z</i>	8	8	8
<i>D</i> _f /g cm ⁻³	2.047	2.098	2.156
<i>F</i> (000)	1048	1056	1064
Goodness-of-fit on <i>F</i> ²	1.031	1.024	1.114
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0387, 0.0721	0.0474, 0.0681	0.0305, 0.0753
<i>R</i> ₁ , <i>wR</i> ₂ ^a (all data)	0.0633, 0.0775	0.0956, 0.0770	0.0365, 0.0774
(Δρ) _{max} , (Δρ) _{min} /e Å ⁻³	0.547, -0.390	0.579, -0.411	0.741, -0.285

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

by the powder X-ray diffraction pattern. Yield: 57% based on Co. Anal. calc. for C₆H₈NO₅PCo: C, 27.29; H, 3.05; N, 5.31. Found: C, 28.36; H, 3.35; N, 5.33%. IR (KBr, cm⁻¹): 3423(br), 1655(w), 1614(s), 1558(w), 1503(w), 1426(m), 1347(vw), 1290(w), 1189(m), 1138(s), 1093(s), 1023(m), 988(s), 866(w), 843(m), 775(w), 737(w), 654(w), 574(s), 551(m), 476(m), 436(w). The same product can be obtained when the molar ratio of Co : ligand is 1 : 1 or 1 : 2, but the yields are significantly lower (ca. 25%). It is worth noting that a Co(II) compound was formed although the synthesis was started with a Co(III) material. The reducing agent during the hydro(solvo)-thermal reaction could be either the phosphonate ligand or the ethylenediamine in Co(en)₃Cl₃. With Co(en)₃Cl₃ substituted by CoCl₂·6H₂O, a similar reaction but in a solution of H₂O (5 cm³) and ethanol (3 cm³) resulted in very tiny crystals of the same compound with a yield of up to 56% for the case of Co : ligand = 1 : 2.

Crystallographic studies

Single crystals of dimensions 0.25 × 0.1 × 0.1 mm for **1**, 0.3 × 0.1 × 0.1 mm for **2**, and 0.3 × 0.1 × 0.1 mm for **3** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data was collected in the θ range 2.07–26.03° for **1**, 2.10–26.09° for **2**, and 2.11–26.12° for **3** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s per frame. The number of measured and observed reflections [*I* > 2σ(*I*)] are 4566 and 1189 (*R*_{int} = 0.0455) for **1**, 4508 and 950 (*R*_{int} = 0.0662) for **2**, and 4413 and 1319 (*R*_{int} = 0.0286) for **3**, respectively. The data were integrated using the Siemens SAINT program,²⁶ with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The structure was solved by direct methods and refined on *F*² by full-matrix least squares using SHELXTL.²⁷ All non-hydrogen atoms in compounds **1**, **2** and **3** were refined anisotropically except O4 which is disordered over two sites. The disordered O4 was refined isotropically. The H4 and H6 atoms were located from the Fourier maps and were treated as riding atoms having isotropic displacement parameters related to the atom to which they are bonded. Crystallographic and refinement details are listed in Table 1. The selected bond lengths and angles are given in Table 2.

CCDC reference numbers 196086–196088.

See <http://www.rsc.org/suppdata/dt/b2/b210491a/> for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structures of compounds 1–3

Compounds **1–3** are isomorphous. All crystallize in space group *C2/c*. Fig. 1 shows the asymmetric building unit of compound **1**, which consists of one manganese atom, one water molecule and one [hydroxy(4-pyridyl)methyl]phosphonate group. Each metal atom has a distorted trigonal bipyramidal geometry. The basal plane is defined by the N1, O2B and O3A atoms from three equivalent [hydroxy(4-pyridyl)methyl]phosphonate ligands. The Mn atom deviates from this plane by 0.1265 Å. The O–Mn–O(N) bond angles are in the range 107.78(12)–139.14(11)°. The Mn1–N1, Mn1–O2B and Mn1–O3A bond lengths are 2.214(3), 2.085(2) and 2.033(2) Å, respectively. Two axial sites are provided by O1w from the water molecule and a phosphonate oxygen (O1C) from the fourth equivalent phosphonate ligand at distances of 2.219(3) and 2.149(2) Å, respectively. The bond angle of O1C–Mn1–O1w is 171.39(9)°. Each distorted {MnO₄N} trigonal bipyramid is corner-shared by three {CPO₃} tetrahedra from three equivalent phosphonate ligands, generating ‘staircase’ chains containing four-membered rings, with composition {MnO₄N}{CPO₃} (Fig. 2). An inversion center locates in the middle of each four-membered ring. The pyridyl nitrogens from the ‘tails’ of each chain are further coordinated to the Mn atoms from its neighbors, thus connecting the chains into a two-dimensional layer (Fig. 2). Within the layer, the centroid-to-centroid distance between the adjacent pyridyl rings is 4.776 Å.

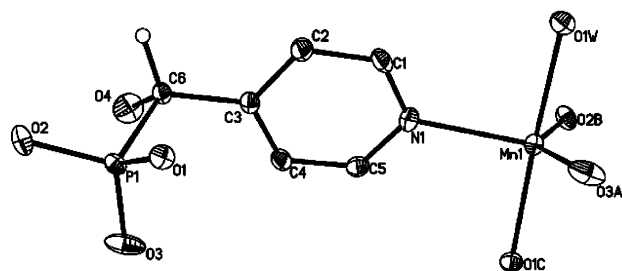


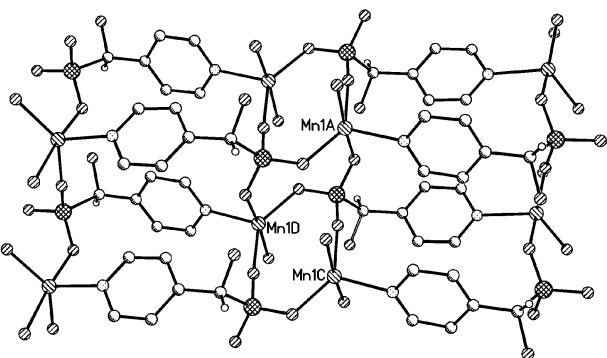
Fig. 1 Asymmetric building unit of compound **1**. Only one configuration of the disordered O4 is shown. Thermal ellipsoids are at the 50% probability level.

The phosphonate oxygens O1 and O2 of the [hydroxy(4-pyridyl)methyl]phosphonate also form two sets of intralayer hydrogen bonds, each with the hydroxy oxygen O4 and the coordinated water molecular (O1w). The O4...O1ⁱ and

Table 2 Selected bond lengths (Å) and bond angles (°) for compounds 1–3

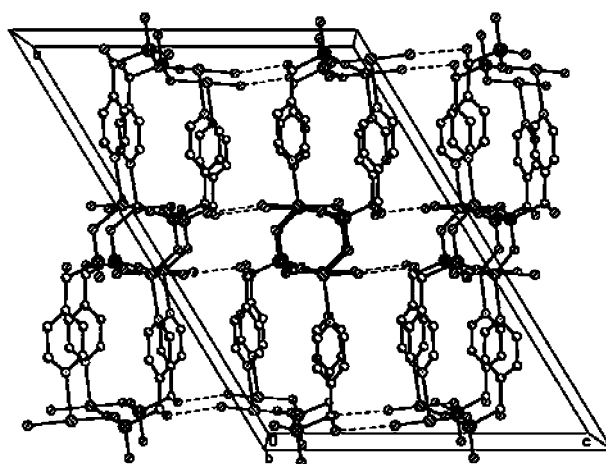
	1	2	3
M(1)–O(3A)	2.033(2)	1.972(3)	1.9538(19)
M(1)–O(2B)	2.085(2)	1.994(3)	1.9915(18)
M(1)–O(1C)	2.149(2)	2.158(3)	2.0675(19)
M(1)–N(1)	2.214(3)	2.128(4)	2.086(2)
M(1)–O(1w)	2.219(3)	2.215(4)	2.197(2)
P(1)–O(3)	1.498(2)	1.493(3)	1.497(2)
P(1)–O(1)	1.512(2)	1.509(4)	1.5134(18)
P(1)–O(2)	1.522(2)	1.523(3)	1.522(2)
P(1)–C(6)	1.833(4)	1.836(5)	1.835(3)
C(6)–O(4)	1.454(4)	1.437(6)	1.438(4)
O(3A)–M(1)–O(2B)	139.14(11)	141.22(14)	139.70(9)
O(3A)–M(1)–O(1C)	89.85(9)	89.93(13)	92.08(8)
O(2B)–M(1)–O(1C)	97.92(9)	95.93(12)	97.73(8)
O(3A)–M(1)–N(1)	107.78(12)	104.79(15)	105.35(9)
O(2B)–M(1)–N(1)	111.92(10)	113.16(14)	112.37(8)
O(1C)–M(1)–N(1)	92.05(10)	92.58(14)	95.61(8)
O(3A)–M(1)–O(1w)	81.69(10)	81.65(13)	80.07(8)
O(2B)–M(1)–O(1w)	89.60(10)	90.44(13)	86.86(8)
O(1C)–M(1)–O(1w)	171.39(9)	171.57(13)	171.77(7)
N(1)–M(1)–O(1w)	89.00(10)	89.97(15)	88.89(8)
P(1)–O(1)–M(1A)	128.67(14)	127.99(18)	128.10(11)
P(1)–O(2)–M(1D)	115.64(14)	121.9(2)	121.24(12)
P(1)–O(3)–M(1C)	166.35(18)	159.9(2)	157.76(15)
C(1)–N(1)–M(1)	122.0(2)	122.4(4)	120.29(18)
C(5)–N(1)–M(1)	121.4(2)	122.0(3)	121.93(19)

Symmetry transformations used to generate equivalent atoms: 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: $x + 1/2, -y + 3/2, z + 1/2$.

**Fig. 2** One layer of compound 1 viewed approximately along c -axis. The O4' and all the H atoms except H6 are omitted for clarity. Symmetry codes: A: $-x + 1/2, y - 1/2, -z + 1/2$; C: $-x + 1/2, y + 1/2, -z + 1/2$; D: $x + 1/2, -y + 3/2, z + 1/2$.

O1w \cdots O2ⁱⁱ distances are 2.828(4) and 2.765(3) Å, respectively (symmetry codes: i: $x, y + 1, z$; ii: $x - 1/2, -y + 1/2, z - 1/2$). Between the layers, moderately strong hydrogen bonds are found between O4 and O1w atoms. The O1w \cdots O4ⁱⁱⁱ distance is 2.746(4) Å (symmetry code: iii: $-x + 1/2, -y + 3/2, -z$). Consequently, a three-dimensional supramolecular network structure is created (Fig. 3).

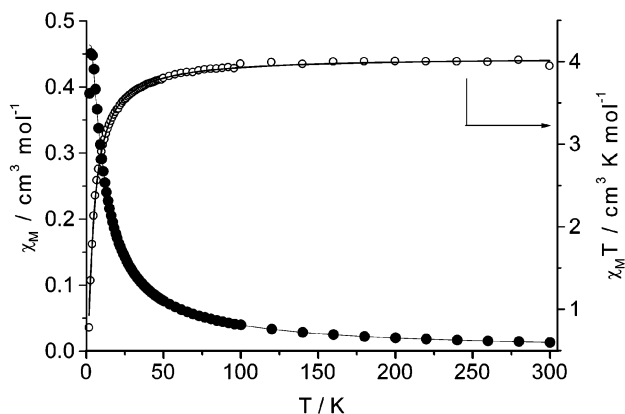
The structures of compounds 2 and 3 are identical to that of 1, except that the Mn atom in 1 is substituted by Fe in 2 or Co in 3. Accordingly, the cell volumes are reduced in the sequence 1 > 2 > 3. It is interesting to note that the overall structures of 1–3 are not chiral, although each [hydroxy(4-pyridyl)methyl]phosphonate ligand contains a chiral center at C6. From Fig. 2, it is clear that these chiral centers are symmetrically related to each other in the layer. The configuration of the C6 centers is (*R*) within one column, while it is (*S*) within the other column across the inorganic chain. Subsequently, racemic structures result as observed in 1–3.

**Fig. 3** Structure of compound 1 packed along the [010] direction. All the H atoms and the O4' are omitted for clarity.

Infrared spectra and magnetic properties

The infrared spectra of the three compounds exhibit a series of bands in the 950–1200 cm^{-1} range, corresponding to the characteristic stretching modes of PO_3 groups.²⁸ Broad bands at about 3350 cm^{-1} are due to the presence of extensive hydrogen bonds. The frequencies at about 1612 and 1426 cm^{-1} can be assigned to the characteristic C–C and C–N stretching in the pyridyl groups of the ligand.

The temperature dependent magnetic behaviors of compounds 1–3 were investigated in the temperature range 2 to 300 K. The effective magnetic moment (5.60 μ_B per Mn) at 300 K is in agreement with the theoretical value (5.92 μ_B) for an $S = 5/2$ ion, calculated from $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$. The Weiss constant, determined in the temperature range 80–300 K, is -0.95 K, suggesting a very weak antiferromagnetic exchange between the magnetic centers. This is further confirmed by the peak appearing in the χ_M versus T curve (*ca.* 3 K) and the continuing decrease of $\chi_M T$ on cooling from room temperature (Fig. 4).

**Fig. 4** χ_M and $\chi_M T$ vs. T plots for compound 1.

The layer structure of compound 1 contains double chains of $\{\text{MnO}_4\text{N}\}\{\text{CPO}_3\}$ separated by the [hydroxy(4-pyridyl)methyl]phosphonate ligands. Since the Mn \cdots Mn distance over the organic bridge between the inorganic chains is 10.125 Å, the magnetic exchange through this pathway is expected to be very weak. Within the $\{\text{MnO}_4\text{N}\}\{\text{CPO}_3\}$ double chain, the Mn(II) ions are bridged by O–P–O groups (Fig. 2). Considering that the distance for Mn1C \cdots Mn1D (3.747 Å) is much shorter than those for Mn1A \cdots Mn1D (5.076 Å) and Mn1A \cdots Mn1C (5.233 Å), the observed antiferromagnetic interaction should mainly arise from the exchange between the

magnetic centers within 'Mn₂ dimers'. The susceptibility data were thus analyzed by an isotropic dimer model for two $S = 5/2$ ions based on the Heisenberg Hamiltonian $H = -JS_A \cdot S_B$.²⁵ The best fit, shown as solid lines in Fig. 4, leads to the parameters $g = 1.92$ and $J = -0.67 \text{ cm}^{-1}$. The inclusion of inter-dimer interactions using molecular field approximation does not improve the result much. We also tried to fit the data based on the isotropic chain model, using Fisher's expression,²⁵ which gives the parameters $g = 1.96$ and $J = -0.46 \text{ cm}^{-1}$.

Compounds **2** and **3** again show dominant antiferromagnetic exchange interactions between the metal ions, indicated by the maximum appearing in the χ_M versus T curves [4 K (**2**), 14 K (**3**)] and the negative Weiss constants [$\theta = -11.82$ K (**2**), -12.74 K (**3**)]. The effective magnetic moments at room temperature are $5.09 \mu_B/\text{Fe}$ for **2** and $4.84 \mu_B/\text{Co}$ for **3**. The latter is much greater than the spin-only value of $3.87 \mu_B$ for an $S = 3/2$ center, attributed to the orbital contribution of the high spin cobalt(II) ion. The magnetic susceptibility data of **2** were analyzed similarly by an isotropic dimer model for $S = 2$.²⁵ The best fit, shown as solid lines in Fig. 5, gives the parameters $g = 2.14$ and $J = -1.77 \text{ cm}^{-1}$. For compound **3**, theoretical fitting using an isotropic dimer model of $S = 3/2$ was not successful, possibly due to the significant orbital contribution of the Co(II) ion.

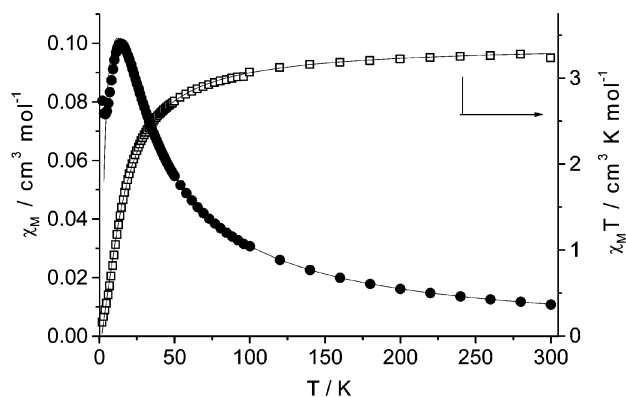


Fig. 5 χ_M and $\chi_M T$ vs. T plots for compound **2**.

Conclusion

This paper reports three novel isomorphous metal phosphonate compounds based on [hydroxy(4-pyridyl)methyl]phosphonate: $\{M(\text{C}_5\text{H}_4\text{N})\text{CH}(\text{OH})\text{PO}_3\}(\text{H}_2\text{O})$ ($M = \text{Mn}$, **1**; Fe , **2**; Co , **3**). All show two-dimensional layer structures, where inorganic 'staircase' chains of $\{\text{MO}_4\text{N}\}\{\text{CPO}_3\}$ are linked by the organic groups of the [hydroxy(4-pyridyl)methyl]phosphonate ligand. Weak antiferromagnetic interactions are found to be dominant in all three cases, which are propagated mainly through the O–P–O bridges within 'dimers' of the inorganic double chain.

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