

Layered metal phosphonates containing pyridyl groups: Syntheses and characterization of $\text{Mn}_2(2\text{-C}_5\text{H}_4\text{NPO}_3)_2(\text{H}_2\text{O})$ and $\text{Zn}(6\text{-Me-}2\text{-C}_5\text{H}_4\text{NPO}_3)$

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Abstract

This paper reports the syntheses and characterization of two phosphonate compounds with layered structures, namely, $\text{Mn}_2(2\text{-C}_5\text{H}_4\text{NPO}_3)_2(\text{H}_2\text{O})$ (**1**) and $\text{Zn}(6\text{-Me-}2\text{-C}_5\text{H}_4\text{NPO}_3)$ (**2**). In compound **1**, double chains are found in which the $\{\text{Mn}_2\text{O}_2\}$ dimers are linked by both aqua and O-P-O bridges. These double chains are connected through corner-sharing of $\{\text{MnO}_5\text{N}\}$ octahedra and $\{\text{CPO}_3\}$ tetrahedra, forming an inorganic layer. The pyridyl groups fill the inter-layer spaces. In compound **2**, each $\{\text{ZnO}_3\text{N}\}$ tetrahedron is vertex-shared with three $\{\text{CPO}_3\}$ tetrahedra and vice versa, hence forming an inorganic honeycomb layer. The pyridyl groups reside between the layers. Magnetic studies show that weak antiferromagnetic interactions are mediated between the manganese ions in compound **1**. Crystal data for **1**: monoclinic, space group $C2/c$, $a = 29.611(7)\text{Å}$, $b = 5.307(1)\text{Å}$, $c = 9.844(2)\text{Å}$, $\beta = 107.3(1)^\circ$. For **2**: orthorhombic, space group $Pbca$, $a = 10.305(2)\text{Å}$, $b = 9.493(2)\text{Å}$, $c = 15.603(3)\text{Å}$.

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1. Introduction

The chemistry of metal phosphonates has received an increasing attention in recent years. Great efforts have been devoted to the preparation of metal phosphonate compounds with new architectures and properties in searching for new materials with potential applications in catalysis, ion exchange, proton conductivity and magnetic materials etc. [1]. It has been well known that the monophosphonic acids RPO_3H_2 , where R represents an alkyl or aryl group, prefer to form layered structures with transition metal ions [2]. By introducing other functional groups such as amino [3], carboxylate [4], macrocycle [5] and a second phospho-

nate groups [6], compounds with new structures and properties can be obtained.

There are some metal phosphonate compounds reported during the past several years which contain pyridyl groups. Based on 3/4-pyridylphosphonate ligands, compound $\text{Zn}(4\text{-C}_5\text{H}_4\text{NHPO}_3)(\text{Br})$ with a ladder-like chain structure, $\text{Co}(4\text{-C}_5\text{H}_4\text{NPO}_3)(\text{H}_2\text{O})_3$, $\text{Cu}_2(4\text{-C}_5\text{H}_4\text{NPO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(3\text{-C}_5\text{H}_4\text{NPO}_3\text{H})_2 \cdot \text{DMSO}$, $\text{Cd}(4\text{-C}_5\text{H}_4\text{NPO}_3\text{H})_2$ and $\text{Cd}(4\text{-C}_5\text{H}_4\text{NPO}_3\text{Et})_2$ with layer or framework structures have been obtained [7]. By using hydroxy(2/3/4-pyridyl)methylphosphonate ligands, a number of compounds have been prepared including $[\text{Zn}_7\{(2\text{-C}_5\text{H}_4\text{N})\text{CH}(\text{OH})\text{PO}_3\}_6(\text{H}_2\text{O})_6]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ with a drum-like cluster structure [8], $\text{Gd}\{(4\text{-C}_5\text{H}_4\text{N})\text{CH}(\text{OH})\text{P}(\text{OH})\text{O}_2\}_3 \cdot 6\text{H}_2\text{O}$ with a chain structure, $M\{(4\text{-C}_5\text{H}_4\text{N})\text{CH}(\text{OH})\text{PO}_3\}(\text{H}_2\text{O})$ ($M = \text{Mn, Fe, Co, Cd}$) with a layer structure containing inorganic double chains, $\text{Ni}\{(4\text{-C}_5\text{H}_4\text{N})\text{CH}(\text{OH})\text{PO}_3\}$

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(H₂O) and Zn{(3-C₅H₄N)CH(OH)PO₃} with a pillared layered structure, and Cu_{1/2}Cu^{II}{(3-C₅H₄N)CH(OH)PO₃}₂ with a framework structure [9–11]. When the pyridyl N-oxide functional group is involved, mononuclear compounds Er{(2-C₅H₄NO)CH₂PO₃H₂}₃{(2-C₅H₄NO)CH₂PO₃H₂} · 8H₂O and Er{(2-C₅H₄NO)CH(OH)PO₃H₂}₃{(2-C₅H₄NO)CH(OH)PO₃H₂} · 8H₂O [12], chain compound Cd{(2-C₅H₄NO)CH(OH)PO₃}₂(H₂O)₂ and layer compound Zn{(4-C₅H₄NO)CH(OH)PO₃} containing inorganic chains are isolated [13]. Mononuclear compounds are also formed when 6-phosphopyridine-2-carboxylic acid is allowed to react with metal salts [14]. Clearly, the formation of a particular structure is dependent not only on the properties of metal ions but also on the properties of ligands including the substitution position of pyridyl groups and the involvement of additional functional groups.

In this paper, we select 2-pyridylphosphonic (2-C₅H₄NPO₃H₂) and 6-Me-2-pyridylphosphonic acids (6-Me-2-C₅H₄NPO₃H₂) to react with manganese and zinc salts under hydrothermal conditions, and to investigate the effect of the additional Me group on the structures of the final products. Two compounds with formula Mn₂(2-C₅H₄NPO₃)₂(H₂O) (**1**) and Zn(6-Me-2-C₅H₄NPO₃) (**2**) are isolated and crystallographically characterized. It is worth noting that based on 2-pyridylphosphonic acid, three copper phosphonates with dimer and layer structures have been described by us [15]. There is no complex reported so far based on 6-Me-2-pyridylphosphonic acid, although the bonding properties of this acid with metal ions such as Zn²⁺, Cd²⁺, Ni²⁺ were studied in solution [16].

2. Experimental

2.1. Materials and methods

All the starting materials were reagent grade used as purchased. The 2-pyridylphosphonic and 6-methyl-2-pyridylphosphonic acids were prepared according to the literature [17]. Elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 10 °C/min on a TGA-DTA V1.1B TA Inst 2100 instrument. The magnetic susceptibility measurements for **1** were carried out on a polycrystalline sample using a Quantum Design MPMS-XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants [18].

2.2. Synthesis of Mn₂(2-C₅H₄NPO₃)₂(H₂O) (**1**)

Hydrothermal treatment of a mixture of MnSO₄ · H₂O (0.1 mmol, 0.0169 g), 2-C₅H₄NPO₃H₂ · H₂O (0.1 mmol, 0.0177 g), NaN₃ (0.2 mmol, 0.013 g) and H₂O (8 cm³) (pH = 4.33) at 140 °C for 48 h results in colorless sheet-like crystals of compound **1** as a single phase. Yield: 31%

based on Mn. Found: C, 27.13; H, 2.52; N, 6.34%. Calcd.: C, 27.17; H, 2.28; N, 6.34%. IR (KBr, cm⁻¹): 3447(m,br), 1590(w), 1560(w), 1464(w), 1423 (w), 1175(m), 1141(s), 1123(s), 1109(s), 1086(m), 1044(m), 1012(m), 975(m), 843(w), 763(m), 750(m), 635(w), 599(m), 549(w), 529(m), 444(m). Thermal analysis shows a one-step weight loss in the temperature range 200–280 °C with the weight loss (3.2%) slightly lower than the calculated value of 4.0% for the removal of one water molecule. The dehydrated compound is stable up to ca. 520 °C, above which the compound is completely decomposed.

2.3. Synthesis of Zn(6-Me-2-C₅H₄NPO₃) (**2**)

Hydrothermal treatment of a mixture of ZnSO₄ · 7H₂O (0.1 mmol, 0.0282 g), 6-Me-2-C₅H₄NPO₃H₂ · H₂O (0.1 mmol, 0.0191 g), NaN₃ (0.2 mmol, 0.013 g) and H₂O (8 cm³) (pH = 4.78) at 140 °C for 48 h results in colorless block-like crystals of compound **2** as a single phase. Yield: 66% based on Zn. Found: C, 30.29; H, 2.51; N, 5.80%. Calcd.: C, 30.47; H, 2.56; N, 5.92%. IR (KBr, cm⁻¹): 3446(m,br), 3070(w), 1599(m), 1567(w), 1464(m), 1384(w), 1265(w), 1183(m), 1168(m), 1117(s), 1024(s), 922(w), 877(w), 812(m), 746(w), 700(m), 614(m), 599(m), 565(m), 474(w), 431(w), 407(w).

2.4. Crystallographic studies

Single crystals with dimensions 0.28 × 0.26 × 0.10 mm³ for **1** and 0.32 × 0.28 × 0.24 mm³ for **2** were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite monochromatized MoKα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data was collected in the θ range 2.90–26.00° for **1** and 2.60–26.00° for **2** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5s/frame. Numbers of observed and unique reflections are 3522 and 1442 (R_{int} = 0.056) for **1** and 7615 and 1499 (R_{int} = 0.078) for **2**, respectively. The data were integrated using the Siemens SAINT program [19], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Absorption corrections were applied. The structures were solved by direct methods and refined on F² by full matrix least squares using SHELXTL [20]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. The H atoms of the pyridyl group were placed in calculated positions (C–H = 0.93 Å) and the H atoms of the methyl group were placed in calculated positions (C–H = 0.96 Å) and allowed to ride on their respective parent atoms. The H atoms in H₂O were found from the Fourier difference maps and refined isotropically. Crystallographic and refinement details of **1** and **2** are listed in Table 1. Selected bond lengths and angles are given in Tables 2–3 for **1** and **2**, respectively.

3. Results and discussion

3.1. Syntheses

Compound **1** is synthesized through hydrothermal reactions of MnSO_4 , $2\text{-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ and NaN_3 at

Table 1
Crystallographic data

Compound	1	2
Formula	$\text{C}_{10}\text{H}_{10}\text{Mn}_2\text{N}_2\text{O}_7\text{P}_2$	$\text{C}_6\text{H}_6\text{ZnNO}_3\text{P}$
<i>M</i>	442.02	236.46
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pbca</i>
<i>a</i> /Å	29.611(7)	10.305(2)
<i>b</i> /Å	5.307(1)	9.493(2)
<i>c</i> /Å	9.844(2)	15.603(3)
β /°	107.3(1)	
<i>V</i> /Å ³	1477.2(6)	1526.4(5)
<i>Z</i>	4	8
<i>D_c</i> /g cm ⁻³	1.987	2.058
<i>F</i> (000)	880	944
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	19.63	33.86
Goodness-of-fit on <i>F</i> ²	0.94	1.06
<i>R</i> 1, <i>wR</i> 2 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0398, 0.0674	0.0483, 0.0987
(all data)	0.0597, 0.0634	0.0687, 0.0911
(Δρ) _{max} , (Δρ) _{min} /e Å ⁻³	0.56, -0.40	0.55, -0.53

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

140 °C for 48 h. When MnSO_4 is replaced by $\text{Mn}(\text{OAc})_2$ or MnCl_2 and molar ratios of the starting materials Mn: $2\text{-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ are 1:1, 1:2 and 2:1, same product results. The presence of NaN_3 is essential in producing the final product of compound **1**. Without it, only clear solutions are obtained under similar condition. In order to investigate whether NaN_3 serves simply as a base, reactions are conducted by using NaOH to adjust the pH of the reaction mixtures. It is found that when the metal source is $\text{Mn}(\text{OAc})_2$ and the pH is 4.3–6.7, compound **1** is obtained as a pure crystalline phase. If the metal source is MnSO_4 or MnCl_2 , colloids or a small amount of precipitates appear in the same pH range.

Compound **2** can be obtained by hydrothermal reactions of ZnSO_4 , $6\text{-Me-2-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ and NaN_3 at 140 °C for 48 h. If NaOH instead of NaN_3 is used to adjust the pH of the reaction mixture (pH = 3.6–7.2), compound **2** can be obtained as a pure phase. When ZnSO_4 is replaced by $\text{Zn}(\text{OAc})_2$, only clear solutions result in the presence of either NaN_3 or NaOH.

Efforts have also been made to react manganese sources with $6\text{-Me-2-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ or zinc sources with $2\text{-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ under similar conditions. In the former case, however, white precipitates are obtained in the pH range of 3.7–5.6. In the latter case, very thin colorless plate-like crystals are isolated. Powder XRD measurements show that the structure of $\text{Mn}/6\text{-Me-2-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ precipitate should be similar to that of compound **1**, while

Table 2
Selected bond lengths (Å) and angles (deg) for **1**^a

Mn(1)–O(1)	2.205(2)	Mn(1)–O(2B)	2.132(3)
Mn(1)–O(1W)	2.321(2)	Mn(1)–O(1C)	2.185(3)
Mn(1)–N(1)	2.315(3)	Mn(1)–O(3A)	2.067(3)
P(1)–O(1)	1.523(3)	P(1)–O(2)	1.510(2)
P(1)–O(3)	1.509(3)		
O(1)–Mn(1)–O(1W)	83.4(1)	O(1C)–Mn(1)–O(1W)	77.0(1)
O(1)–Mn(1)–N(1)	76.0(1)	O(1W)–Mn(1)–O(3A)	90.0(1)
O(1)–Mn(1)–O(2B)	92.1(1)	O(2B)–Mn(1)–N(1)	90.5(1)
O(1)–Mn(1)–O(1C)	82.2(1)	O(1C)–Mn(1)–N(1)	157.1(1)
O(1)–Mn(1)–O(3A)	159.5(1)	O(3A)–Mn(1)–N(1)	87.4(1)
O(1W)–Mn(1)–N(1)	106.7(1)	O(1C)–Mn(1)–O(2B)	83.6(1)
O(1W)–Mn(1)–O(2B)	160.5(1)	O(2B)–Mn(1)–O(3A)	100.2(1)
Mn(1)–O(1)–Mn(1C)	97.8(1)	Mn(1)–O(1C)–Mn(1C)	97.8(1)
Mn(1)–O(1W)–Mn(1D)	118.7(1)		

^aSymmetry transformations used to generate equivalent atoms: A: *x*, $-y$, $-1/2+z$; B: *x*, $-1+y$, *z*; C: $1-x$, $-y$, $-z$; D: $1-x$, *y*, $-1/2-z$.

Table 3
Selected bond lengths (Å) and angles (deg) for **2**^a

Zn(1)–O(1)	1.976(3)	Zn(1)–O(2A)	1.893(4)
Zn(1)–N(1)	2.046(3)	Zn(1)–O(3B)	1.908(3)
P(1)–O(1)	1.507(3)	P(1)–O(2)	1.507(4)
P(1)–O(3)	1.499(3)		
O(1)–Zn(1)–N(1)	88.9(2)	O(2A)–Zn(1)–N(1)	118.6(2)
O(1)–Zn(1)–O(2A)	113.5(2)	O(3B)–Zn(1)–N(1)	117.9(2)
O(1)–Zn(1)–O(3B)	109.8(2)	O(2A)–Zn(1)–O(3B)	107.1(2)

^aSymmetry transformations used to generate equivalent atoms: A: $1-x$, $-1/2+y$, $1/2-z$; B: $-1/2+x$, *y*, $1/2-z$.

the structure of thin plate-like $\text{Zn}/2\text{-C}_5\text{H}_4\text{NPO}_3\text{H}_2$ compound could be different from that of **2** (see supporting information).

3.2. Description of structure **1**

Compound **1** crystallizes in monoclinic lattice with $C2/c$ space group. The asymmetric unit consists of one Mn atom, one $2\text{-C}_5\text{H}_4\text{NPO}_3^{2-}$ ligand and $0.5\text{H}_2\text{O}$ (Fig. 1). The Mn(1) atom has a distorted octahedral coordination environment. The six positions are occupied by one pyridyl nitrogen atom N(1), four phosphonate oxygen atoms [O(1), O(1C), O3(A), O(2B)] from four equivalent $2\text{-C}_5\text{H}_4\text{NPO}_3^{2-}$ ligands and O(1W) from aqua ligand. The Mn–O bond distances are in the range 2.067(3)–2.321(2) Å, while the Mn(1)–N(1) distance is 2.315(3) Å. The axial bond angles are in the range 157.1(1)–160.5(1)°.

The $2\text{-C}_5\text{H}_4\text{NPO}_3^{2-}$ acts as a tetra-dentate ligand. One of its three phosphonate oxygen atoms [O(1)] serves as a $\mu_3\text{-O}$ and links the two equivalent Mn atoms into a $\{\text{Mn}_2\text{O}_2\}$ dimer. The Mn(1)...Mn(1C) distance over the $\mu_3\text{-O(1)}$ bridge is 3.309(3) Å. The Mn(1)–O(1)–Mn(1) bond angle is 97.8(1)°. The dimers are bridged by one aqua ligand and two O(1)–P–O(3) units, forming a chain along the c -axis (Fig. 2). The Mn(1)...Mn(1D) distance across the O(1w) bridge is 3.994(10) Å. The Mn(1)–O(1w)–Mn(1D) bond angle is 118.7(1)°. These chains are connected by the phosphonate oxygen atoms [O(2)], forming a two dimensional inorganic layer (Fig. 3). Hydrogen bond interactions are found within the layer [O(1W)...O(2): 2.720(3) Å]. The adjacent layers are connected by van der Waals contacts between the pyridyl rings (Fig. 4).

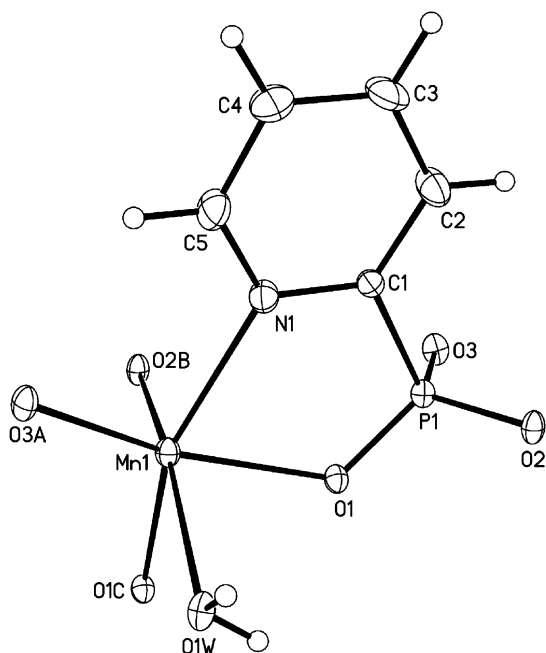


Fig. 1. Building unit of **1** with the atomic labeling scheme (30% probability).

The layer structure of compound **1** is remarkably different from those of $\text{Mn}(\text{RPO}_3) \cdot \text{H}_2\text{O}$ ($R = \text{alkyl, phenyl}$) [21] and $\text{Mn}(\text{O}_3\text{PCH}_2\text{CH}_2\text{COOH}) \cdot \text{H}_2\text{O}$ [22] which consist of approximately square planar sheets of Mn(II) ions, coordinated in a strongly distorted octahedron by

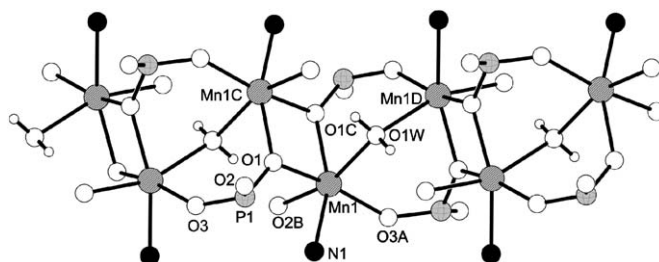


Fig. 2. A fragment of the inorganic chain in compound **1**.

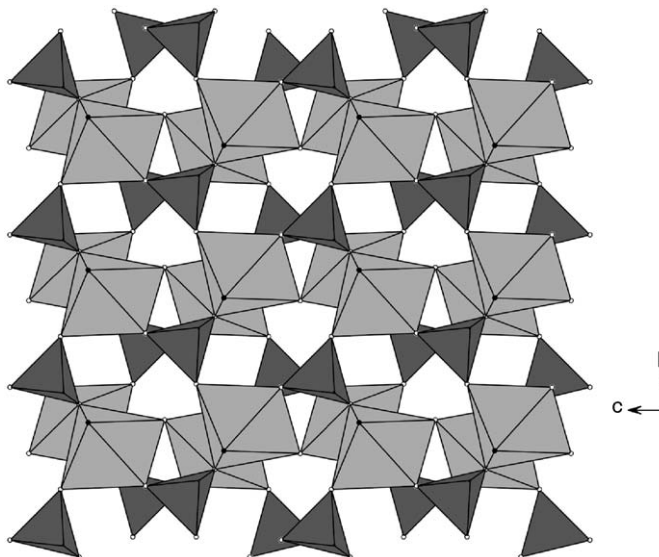


Fig. 3. One inorganic layer of structure **1** viewed approximately along the a -axis. The $\{\text{MnO}_5\text{N}\}$ octahedra and $\{\text{CPO}_3\}$ tetrahedra are shaded with light and dark gray, respectively.

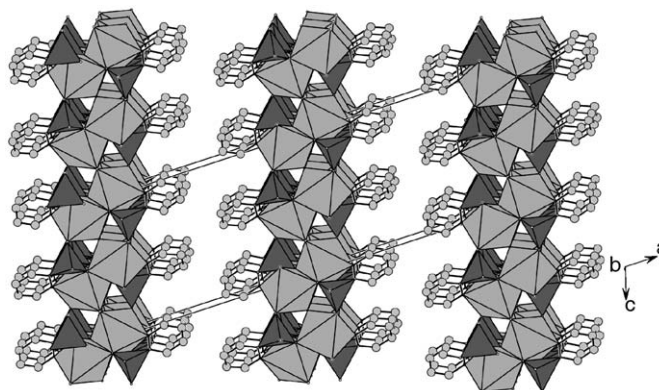


Fig. 4. Structure **1** projected along the b -axis. All H atoms are omitted for clarity.

phosphonate and water oxygens. In these compounds each $\{\text{CPO}_3\}$ tetrahedron is connected to four $\{\text{MO}_6\}$ octahedra through corner- or edge-sharing and vice versa. The inorganic layer in **1** may be compared with that of a diphosphonate compound $\text{Mn}_2(\text{H}_2\text{L}^2)_2(\text{H}_2\text{O})$ [$\text{L}^2 = 4\text{-CH}_3\text{-C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$] [23] which also contains zigzag chains composed of phosphonate oxygen bridged Mn_2O_2 dimers interconnected through both aqua ligands and $\{\text{CPO}_3\}$ groups. It has to be noted, however, that in $\text{Mn}_2(\text{H}_2\text{L}^2)_2(\text{H}_2\text{O})$, neighboring chains are linked by the $\{\text{CPO}_3\}$ groups using two of their three phosphonate oxygen atoms. While in compound **1**, each $\{\text{CPO}_3\}$ tetrahedron is corner-shared with three $\{\text{MnO}_5\text{N}\}$ octahedra from one chain and one $\{\text{MnO}_5\text{N}\}$ octahedron from the adjacent chain using its three phosphonate oxygen atoms, thus forming a new type of manganese phosphonate layer structure.

3.3. Description of structure 2

Compound **2** crystallizes in orthorhombic space group *Pbca*. It also adopts a layer structure but significantly different from that of compound **1**. The asymmetric unit consists of one Zn(II) ion and one 6-Me-2- $\text{C}_5\text{H}_4\text{NPO}_3^{2-}$ ligand (Fig. 5). Each Zn atom has a tetrahedral geometry with four positions filled with N(1), O(1), O(2A) and O(3B) atoms from three equivalent 6-Me-2- $\text{C}_5\text{H}_4\text{NPO}_3^{2-}$ ligands. The Zn(1)-N(1) bond length is 2.046(3) Å. The Zn–O bond distances [1.893(4)–1.976(3) Å] are comparable with those in $\text{Zn}\{(4\text{-C}_5\text{H}_4\text{NO})\text{CH}(\text{OH})\text{PO}_3\}$ [1.914(3)–1.963(4) Å] [13]. The 6-Me-2- $\text{C}_5\text{H}_4\text{NPO}_3^{2-}$ behaves as a tetra-dentate ligand. Each $\{\text{CPO}_3\}$ tetrahedron is vertex-shared with three $\{\text{ZnNO}_3\}$ tetrahedra through three phosphonate oxygens, thus forming a honeycomb layer structure containing 12-member rings (Fig. 6). The layers are packed

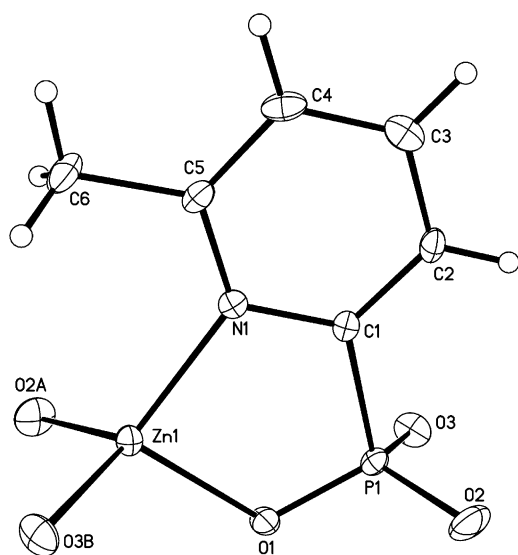


Fig. 5. Building unit of **2** with the atomic labeling scheme (30% probability).

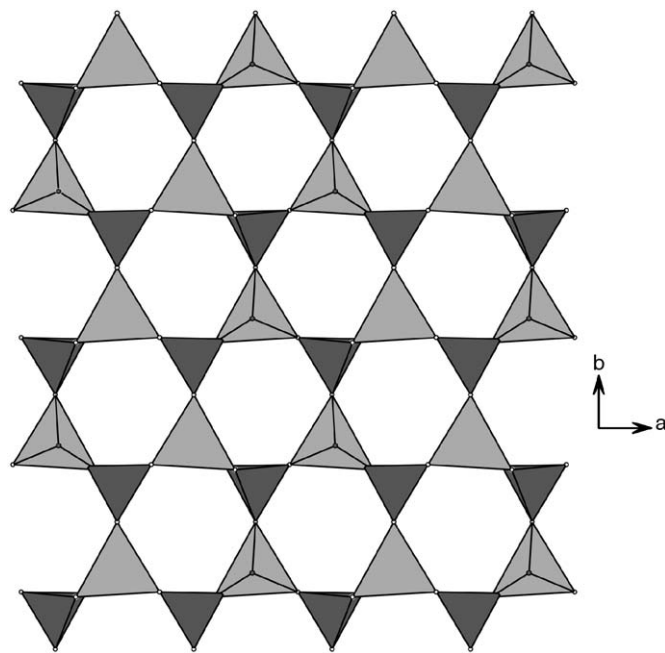


Fig. 6. One inorganic layer of structure **2** viewed along *c*-axis. The $\{\text{ZnO}_4\}$ and $\{\text{CPO}_3\}$ tetrahedra are shaded with light and dark gray, respectively.

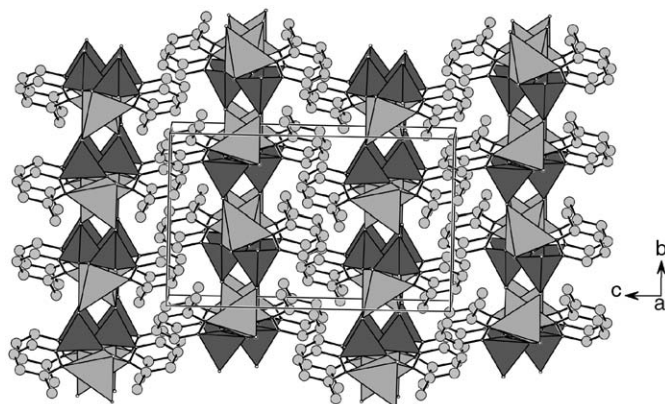


Fig. 7. Structure **2** projected along the *a*-axis. All H atoms are omitted for clarity.

along the *c*-axis with inter-layer π – π stacking interactions found between the pyridyl rings. The centroid-centroid distance between the phenyl rings is 3.482 Å (Fig. 7).

The structure of compound **2** is unique compared with the other zinc monophosphonates containing inorganic layers. Compounds $\text{Zn}(\text{O}_3\text{PR})(\text{H}_2\text{O})$ ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_2\text{H}_3, \text{CH}_2\text{Cl}$) [24–26] display layer structures very similar to $\text{Mn}(\text{RPO}_3) \cdot \text{H}_2\text{O}$. In these compounds, the zinc atoms are all six-coordinated with a distorted octahedral geometry. Each $\{\text{CPO}_3\}$ tetrahedron is connected to four $\{\text{ZnO}_6\}$ octahedra through corner- or edge-sharing, forming a square planar layer. In $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl}) \cdot 3\text{H}_2\text{O}$ [26], zinc atoms are both tetrahedrally and octahedrally coordinated and are bridged by phosphonate groups, forming an inorganic layer containing 4-, 12- and 14-membered rings. In $\text{Zn}(\text{O}_3\text{PCH}_2$

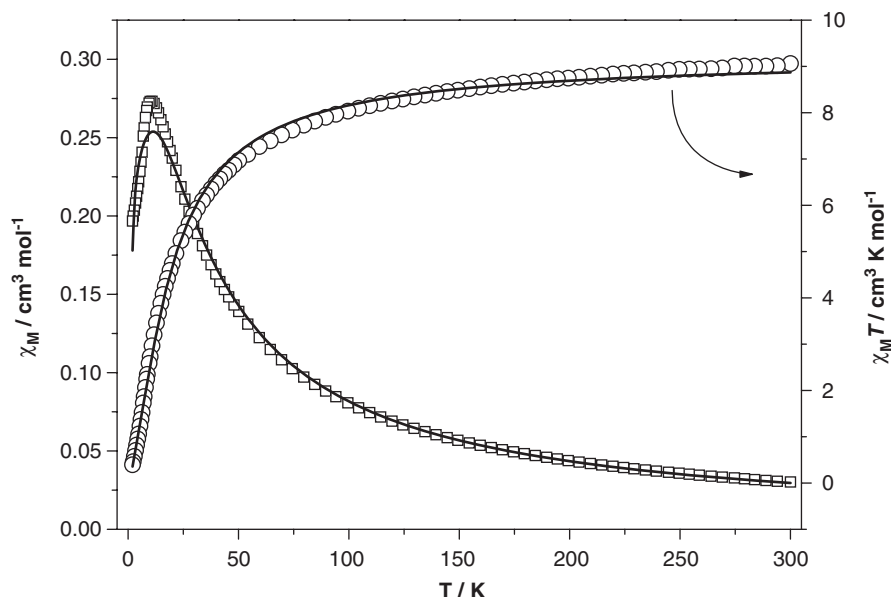


Fig. 8. χ_M and $\chi_M T$ plots for compound **1**.

$\text{P(O)(CH}_3\text{)(C}_6\text{H}_5\text{)} \cdot 0.67\text{H}_2\text{O}$ [27], zinc atoms are tetrahedrally coordinated and are bridged by $\{\text{CPO}_3\}$ groups into an inorganic layer containing 8- and 16-membered rings. In compound $\text{Zn}\{(3\text{-C}_5\text{H}_4\text{N})\text{CH(OH)PO}_3\}$ [11], inorganic layers containing 8- and 16-membered rings made up of $\{\text{ZnO}_3\text{N}\}$ and $\{\text{CPO}_3\}$ tetrahedral are also found. Therefore, compound **2** gives the first example of zinc

Considering that the Mn...Mn distances across the $\mu\text{-O(P)}$ and $\mu\text{-OH}_2$ bridges are 3.309(3) Å and 3.994(10) Å, respectively, antiferromagnetic interactions through $\mu\text{-O(P)}$ should be dominant between the equivalent Mn atoms. The susceptibility data were thus analyzed by the following expression based on a Heisenberg Hamiltonian $H = -2JS_1S_2$: [18]

$$\chi'_M = \frac{2Ng^2\beta^2}{kT} \frac{\exp(2J/kT) + 5\exp(6J/kT) + 14\exp(12J/kT) + 30\exp(20J/kT) + 55\exp(30J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT) + 9\exp(20J/kT) + 11\exp(30J/kT)}$$

$$\chi_M = \frac{\chi'_M}{1 - (zj'/Ng^2\beta^2)\chi'_M}$$

phosphonates that shows a honeycomb layer structure containing 12-membered rings.

3.4. Magnetic property

The temperature dependent molar magnetic susceptibility of **1** was measured at 1 kOe in the temperature range 2–300 K. The χ_M and $\chi_M T$ vs. T plots for **1** is shown in Fig. 8. The room temperature magnetic moment per Mn_2 is $8.48 \mu_B$, close to the theoretical value ($8.37 \mu_B$) for spin only value of $S = 5/2$. The appearance of a maximum in the χ_M vs. T plot at ca. 12 K and the continuous decreasing of $\chi_M T$ on cooling indicate that antiferromagnetic couplings are mediated between the Mn(II) ions.

According to the structure of compound **1**, the magnetic exchanges between the Mn(II) ions may be propagated through the $\mu\text{-O(P)}$ and $\mu\text{-OH}_2$ bridges within the chain and through the O–P–O units within or between the chains. Compared with the $\mu\text{-O}$ bridge, the O–P–O pathway plays a negligible role in propagating the magnetic exchanges.

where J is the coupling constant between the Mn atoms across the $\mu\text{-O(P)}$ bridge, N , g , β and k have their usual meanings, zj' accounts for the exchanges between the $\{\text{Mn}_2\text{O}_2\}$ dimers. A good fit, shown as the solid line in Fig. 8, can be obtained resulting in parameters $g = 1.94$, $J = -1.24 \text{ cm}^{-1}$ and $zj' = 0.00091 \text{ cm}^{-1}$.

4. Conclusions

The hydrothermal reaction of manganese sulfate and 2-pyridylphosphonic acid results in compound $\text{Mn}_2(2\text{-C}_5\text{H}_4\text{NPO}_3)_2(\text{H}_2\text{O})$ (**1**) with a new type of layer structure. The inorganic layer in this structure contains chains of aqua-bridged $\{\text{Mn}_2\text{O}_2\}$ dimers, which are connected by $\{\text{CPO}_3\}$ tetrahedra through corner-sharing. The pyridyl groups fill in the inter-layer space. By introducing an additional methyl group, the reaction of 6-methyl-2-pyridylphosphonic acid and zinc sulfate leads to the formation of compound $\text{Zn}(6\text{-Me-2-C}_5\text{H}_4\text{NPO}_3)$ (**2**) with a new type of honeycomb layer structure where each $\{\text{ZnO}_3\text{N}\}$ tetrahedron is corner-shared with three $\{\text{CPO}_3\}$

tetrahedra and vice versa. The results demonstrate that the introduction of functional pyridyl groups, the substitution position of pyridyl group and the presence of additional methyl group could have significant effects on the structures of the corresponding metal phosphonate compounds.

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2006.05.030](https://doi.org/10.1016/j.jssc.2006.05.030).

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