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Layered metal phosphonates containing pyridyl groups: Syntheses and characterization of $Mn_2(2\text{-}C_5H_4NPO_3)_2(H_2O)$ and $Zn(6\text{-Me-}2\text{-}C_5H_4NPO_3)$

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Abstract

This paper reports the syntheses and characterization of two phosphonate compounds with layered structures, namely, $Mn_2(2\text{-}C_5H_4NPO_3)_2(H_2O)$ (**1**) and $Zn(6\text{-Me-}2\text{-}C_5H_4NPO_3)$ (**2**). In compound **1**, double chains are found in which the $\{Mn_2O_2\}$ dimers are linked by both aqua and O-P-O bridges. These double chains are connected through corner-sharing of $\{MnO_5N\}$ octahedra and $\{CPO_3\}$ tetrahedra, forming an inorganic layer. The pyridyl groups fill the inter-layer spaces. In compound **2**, each $\{ZnO_3N\}$ tetrahedron is vertex-shared with three $\{CPO_3\}$ 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 $C2/c$, $a = 29.611(7)$ Å, $b = 5.307(1)$ Å, $c = 9.844(2)$ Å, $\beta = 107.3(1)^\circ$. For **2**: orthorhombic, space group $Pbca$, $a = 10.305(2)$ Å, $b = 9.493(2)$ Å, $c = 15.603(3)$ 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 phosphonate 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 $Zn(4\text{-}C_5H_4NHPO_3)(Br)$ with a ladder-like chain structure, $Co(4\text{-}C_5H_4NPO_3)(H_2O)_3$, $Cu_2(4\text{-}C_5H_4NPO_3)_2 \cdot 2H_2O$, $Cd(3\text{-}C_5H_4NPO_3H)_2 \cdot DMSO$, $Cd(4\text{-}C_5H_4NPO_3H)_2$ and $Cd(4\text{-}C_5H_4NPO_3Et)_2$ 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 $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4 \cdot 4H_2O$ with a drum-like cluster structure [8], $Gd\{(4\text{-}C_5H_4N)CH(OH)P(OH)O_2\}_3 \cdot 6H_2O$ with a chain structure, $M\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$ ($M =$ Mn, Fe, Co, Cd) with a layer structure containing inorganic double chains, $Ni\{(4\text{-}C_5H_4N)CH(OH)PO_3\}$

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(H_2O) and Zn{(3-C_5H_4N)CH(OH)PO_3} with a pillared layered structure, and $Cu^I_2Cu^{II}$ {(3-C_5H_4N)CH(OH)PO_3}$_2$ with a framework structure [9–11]. When the pyridyl N-oxide functional group is involved, mononuclear compounds Er{(2-C_5H_4NO)CH_2PO_3H}$_3${(2-C_5H_4NO)$CH_2PO_3H_2$} · $8H_2O$ and Er{(2-C_5H_4NO)CH(OH)PO_3H}$_3${(2-C_5H_4NO)CH(OH) PO_3H_2} · $8H_2O$ [12], chain compound Cd{(2-C_5H_4NO)CH (OH)PO_3}(H_2O)$_2$ and layer compound Zn{(4-C_5H_4NO) CH(OH)PO_3} containing inorganic chains are isolated [13]. Mononuclear compounds are also formed when 6-phosphonopyridine-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-$C_5H_4NPO_3H_2$) and 6-Me-2-pyridylphosphonic acids (6-Me-2-$C_5H_4NPO_3H_2$) 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 Mn_2 (2-$C_5H_4NPO_3$)$_2$(H_2O) (**1**) and Zn(6-Me-2-$C_5H_4NPO_3$) (**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 Zn^{2+}, Cd^{2+}, Ni^{2+} 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 Mn_2(2-$C_5H_4NPO_3$)$_2$(H_2O) (1)

Hydrothermal treatment of a mixture of $MnSO_4 \cdot H_2O$ (0.1 mmol, 0.0169 g), 2-$C_5H_4NPO_3H_2 \cdot H_2O$ (0.1 mmol, 0.0177 g), NaN_3 (0.2 mmol, 0.013 g) and H_2O (8 cm^3) (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-$C_5H_4NPO_3$) (2)

Hydrothermal treatment of a mixture of $ZnSO_4 \cdot 7H_2O$ (0.1 mmol, 0.0282 g), 6-Me-2-$C_5H_4NPO_3H_2 \cdot H_2O$ (0.1 mmol, 0.0191 g), NaN_3 (0.2 mmol, 0.013 g) and H_2O (8 cm^3) (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 $0.28 \times 0.26 \times 0.10\,mm^3$ for **1** and $0.32 \times 0.28 \times 0.24\,mm^3$ for **2** were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ 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 F^2 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 H_2O 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.

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