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Metal phosphonates containing pyridyl N-oxide groups: Syntheses of $Cd\{(2\text{-}C_5H_4NO)CH(OH)PO_3\}(H_2O)_2$ and $Zn\{(4\text{-}C_5H_4NO)CH(OH)PO_3\}$ with chain and layer structures

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Abstract

This paper reports the syntheses and characterization of two phosphonate compounds $Cd\{(2\text{-}C_5H_4NO)CH(OH)PO_3\}(H_2O)_2$ (**1**) and $Zn\{(4\text{-}C_5H_4NO)CH(OH)PO_3\}$ (**2**) based on hydroxy(2-pyridyl N-oxide)methylphosphonic and hydroxy(4-pyridyl N-oxide)methylphosphonic acids. Compound **1** has a chain structure in which dimers of edge-shared $\{CdO_6\}$ octahedra are linked by $\{CPO_3\}$ tetrahedra through corner-sharing. The pyridyl rings reside on the two sides of the inorganic chain. Compound **2** has a layer structure where the inorganic chains made up of corner-sharing $\{ZnO_4\}$ and $\{CPO_3\}$ tetrahedra are covalently connected by pyridyl N-oxide groups. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 6.834(1)$ Å, $b = 7.539(1)$ Å, $c = 10.595(2)$ Å, $\alpha = 84.628(3)^\circ$, $\beta = 74.975(4)^\circ$, $\gamma = 69.953(4)^\circ$. For **2**: triclinic, space group $P\bar{1}$, $a = 5.219(1)$ Å, $b = 8.808(2)$ Å, $c = 9.270(2)$ Å, $\alpha = 105.618(5)^\circ$, $\beta = 95.179(4)^\circ$, $\gamma = 94.699(4)^\circ$.

Keywords: Zinc; Cadmium; Phosphonate; Hydroxy(2-pyridyl N-oxide)methylphosphonate; Hydroxy(4-pyridyl N-oxide)methylphosphonate; Chain structure; Layer structure

1. Introduction

Metal phosphonate chemistry has gained increasing attention because of its potential applications in the areas of sorption, ion exchange, catalysis and sensors [1–4]. Many efforts have been devoted to the exploration of metal phosphonate materials with new structure types, especially the open-framework structures [4]. Among these, a promising approach is to modify the organic moieties of the phosphonate ligand RPO_3^{2-} by other functional groups [5–11]. Compared with those containing carboxylate groups, metal phosphonate materials containing pyridyl groups are rather limited in number. Based on 4/3-pyridylphosphonate [12,13], hydroxy(4/3/2-pyridyl)methylphosphonate [14,15] and 3-pyridyl-$CH_2N(CH_2PO_3H_2)_2$ [16], a series of compounds with three-dimensional (3D), two-dimensional (2D) and one-dimensional (1D) structures have been obtained. In this paper, two pyridyl N-oxide functionalized phosphonic acids, e.g. hydroxy(2-pyridyl N-oxide) methylphosphonic acid (2-hpompH$_2$) and hydroxy(4-pyridyl N-oxide) methylphosphonic acid (4-hpompH$_2$) (Scheme 1) have been used to react with zinc or cadmium sulfates under hydrothermal conditions. Compounds $Cd\{(2\text{-}C_5H_4NO)CH(OH)PO_3\}(H_2O)_2$ (**1**) and $Zn\{(4\text{-}C_5H_4NO)CH(OH)PO_3\}$ (**2**) with chain and layered structures, respectively, were formed. To the best of our knowledge, the only examples of metal phosphonates that contain pyridyl N-oxide functional groups are two mononuclear compounds $Er\{(2\text{-}C_5H_4NO)CH_2PO_3H\}\{(2\text{-}C_5H_4NO)CH_2PO_3H_2\}\cdot 8H_2O$ and $Er\{(2\text{-}C_5H_4NO)\text{-}CH(OH)PO_3H\}\{(2\text{-}C_5H_4NO)CH(OH)PO_3H_2\}\cdot 8H_2O$ [17].

2. Experimental

2.1. Materials and methods

The hydroxy(2-pyridyl N-oxide)methylphosphonic acid (2-hpompH$_2$) was synthesized according to literature procedure [17]. All other starting materials were reagent

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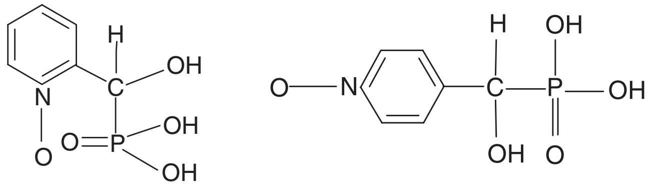

2-hpompH$_2$ 4-hpompH$_2$

Scheme 1.

grade and used as purchased. The elemental analyses were performed with a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer in pressed KBr pellets. Thermal analyses were performed in nitrogen in the temperature range 20–800 °C with a heating rate of 10 °C/min on a TGA-DTA V1.1B TA Inst 2100. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer.

2.2. Synthesis of hydroxy(4-pyridyl N-oxide)methylphosphonic acid (4-hpompH$_2$)

To a mixture of 4-pyridinecarboxyaldehyde (37 mmol, 4.0 g) and NEt$_3$ (37 mmol, 3.7 g) in benzene (80 mL) was added HOP(OEt)$_2$ (5.6 g). The solution was kept at room temperature for 24 h with stirring. After removing benzene by rotary evaporation, a light yellow sticky solution resulted, which was dissolved in acetic acid (20 mL) and then 30% H_2O_2 (5 mL) was added. The solution was heated at 75 °C for 17 h, additional 30% H_2O_2 (5 mL) was added and heating continued (1 h). The acetic acid and water were removed, and the resulting light yellow sticky solution was dissolved in 12 M HCl (30 mL) and H_2O (20 mL). The mixture was refluxed for 16 h. After completely removing water, ethanol was added until lots of white precipitate was obtained. The mixture was kept in the refrigerator for 4 h. White solids were collected and washed with cold ethanol. Yield: 4.2 g (55%). IR (KBr, cm^{-1}): 3289(w), 3114(w), 3038(w), 2930(w), 2876(w), 2852(w), 2829(w), 2671(w), 2360(w), 2346(w), 1654(w), 1631(m), 1578(w), 1534(w), 1491(m), 1447(m), 1384(m), 1242(m), 1217(m), 1204(m), 1183(m), 1150(m), 1128(m), 1056(s), 1031(s), 930(s), 856(m), 797(w), 761(w), 699(w), 662(w), 602(w), 560(s), 520(w), 460(w).

2.3. Synthesis of Cd{(2-C_5H_4NO)CH(OH)PO_3}$(H_2O)_2$ (**1**)

A mixture of $CdSO_4 \cdot 8/3H_2O$ (0.25 mmol, 0.0633 g), 2-hpompH$_2$ (0.25 mmol, 0.0512 g) in 8 mL H_2O, adjusted to pH = 2.3 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, colorless needle-like crystals were collected as a monophasic material, based on the powder X-ray diffraction pattern. Yield: 34 mg (39%). Anal. found (calcd) for $C_6H_{10}CdNO_7P$: C, 20.45 (20.50); H, 2.84 (2.87); N, 4.02 (3.98)%. IR (KBr, cm^{-1}): 3463(m,br), 3094(m,br), 1571(w), 1495(m), 1441(m), 1385(w), 1315(w), 1270(w), 1211(m), 1180(m), 1163(w), 1099(s), 1060(s), 968(s), 851(w), 821(m), 790(m), 767(m), 707(w), 642(m), 576(m), 562(m), 525(w), 481(m), 473(m). Thermal analysis showed that compound **1** experienced the first step of decomposition below 210 °C. The observed weight loss (10.3%) corresponds to the removal of two coordinated water molecules (calculated 10.2%). The XRD measurements showed that the structure of **1** collapsed after the dehydration process with the formation of an amorphous phase. The decomposition above 210 °C is due to the release of the organic group.

2.4. Synthesis of Zn{(4-C_5H_4NO)CH(OH)PO_3} (**2**)

A mixture of $ZnSO_4 \cdot 7H_2O$ (0.25 mmol, 0.0718 g), 4-hpompH$_2$ (0.25 mmol, 0.0512 g) in 8 mL H_2O, adjusted to pH = 2.9 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, colorless needle-like crystals were obtained as a monophasic material based on the powder X-ray diffraction pattern. Yield: 45 mg (67%). Anal. found (calcd.) for $C_6H_6NO_5PZn$: C, 26.77 (26.84); H, 2.24 (2.26); N, 5.15 (5.22)%. IR (KBr, cm^{-1}): 3318(m,br), 3112(m), 3052(m), 1501(m), 1457(m), 1420(w), 1331(w), 1226(s), 1189(s), 1164(s), 1130 (m), 1074(s), 999(s), 866(m), 814(m), 709(w), 670(w), 633(m), 580(s), 541(m), 524(m), 443(w). Thermal analysis revealed that compound **2** was stable up to ca. 300 °C, above which the compound decomposes and the structure collapses.

2.5. Crystallographic studies

Single crystals of dimensions 0.10 × 0.04 × 0.04 mm for **1** and 0.04 × 0.04 × 0.04 mm for **2** were selected for indexing and intensity data collection at 298 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation. A hemisphere of data was collected in the θ range 1.99–25.00° for **1**, 2.30–25.00° for **2** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s per frame. Numbers of measured and observed reflections [$I > 2\sigma(I)$] are 2457 and 1416 ($R_{\text{int}} = 0.0302$) for **1**, and 1994 and 1126 ($R_{\text{int}} = 0.0260$) for **2**, respectively. The data were integrated using the Siemens SAINT program [18], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multi-scan absorption corrections were applied. The structures were solved by direct methods, and were refined on F^2 by full matrix least squares using SHELXTL [19]. All the non-hydrogen atoms were refined anisotropically. All H atoms were refined isotropically. The O4 atom in **2** is disordered over two sites. The H atom attached to C6 in **2** was not located. Crystallographic and refinement details are listed

Table 1
Crystallographic Data for **1**–**2**

Compound	**1**	**2**
Empirical formula	$C_6H_{10}NO_7PCd$	$C_6H_6NO_5PZn$
Fw	351.52	268.46
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.8344(13)	5.2190(13)
b (Å)	7.5389(14)	8.808(2)
c (Å)	10.595(2)	9.270(2)
α (°)	84.628(3)	105.618(5)
β (°)	74.975(4)	95.179(4)
γ (°)	69.953(4)	94.699(4)
V (Å^3)	495.31(16)	406.23(2)
Z	2	2
d_{calcd} (g cm^{-3})	2.357	2.195
F (000)	344	268
Goodness-of-fit on F^2	0.959	1.070
R_1, wR_2 [$I > 2\sigma(I)$]^a	0.0438, 0.0826	0.0466, 0.0980
R_1, wR_2 (All data)^a	0.0543, 0.0855	0.0569, 0.1007
$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$(e Å^{-3})	0.998, −0.626	0.591, −0.489

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$, w$R_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

Cd(1)–O(1)	2.261(4)	Cd(1)–O(1B)	2.339(4)
Cd(1)–O(2A)	2.202(6)	Cd(1)–O(5A)	2.244(5)
Cd(1)–O(1W)	2.315(5)	Cd(1)–O(2W)	2.304(5)
P(1)–O(1)	1.532(5)	P(1)–O(2)	1.519(4)
P(1)–O(3)	1.510(5)		
O(5A)–Cd(1)–O(2A)	91.99(17)	O(5A)–Cd(1)–O(1)	89.79(18)
O(2A)–Cd(1)–O(1)	98.45(16)	O(5A)–Cd(1)–O(2W)	177.4(2)
O(2A)–Cd(1)–O(2W)	90.4(2)	O(1)–Cd(1)–O(2W)	88.75(18)
O(5A)–Cd(1)–O(1W)	91.8(2)	O(2A)–Cd(1)–O(1W)	91.34(18)
O(1)–Cd(1)–O(1W)	170.02(17)	O(2W)–Cd(1)–O(1W)	89.3(2)
O(5A)–Cd(1)–O(1B)	86.87(17)	O(2A)–Cd(1)–O(1B)	177.98(16)
O(1)–Cd(1)–O(1B)	79.87(16)	O(2W)–Cd(1)–O(1B)	90.7(2)
O(1W)–Cd(1)–O(1B)	90.37(17)	P(1)–O(1)–Cd(1)	129.8(3)
P(1)–O(1)–Cd(1B)	129.6(3)	Cd(1)–O(1)–Cd(1B)	100.13(16)
P(1)–O(2)–Cd(1A)	137.4(3)	N(1)–O(5)–Cd(1A)	119.0(4)

^{a}Symmetry codes: A: $-x+1$, $-y+2$, $-z$; B: $-x$, $-y+2$, $-z$.

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

Zn1–O1	1.914(3)	P1–O1	1.511(4)
Zn1–O2B	1.941(4)	P1–O2	1.516(4)
Zn1–O3A	1.914(4)	P1–O3	1.497(4)
Zn1–O5C	1.963(4)	N1–O5	1.341(5)
O1–Zn1–O2B	108.38(16)	O3A–Zn1–O5C	106.65(17)
O1–Zn1–O3A	113.72(19)	P1–O1–Zn1	136.7(2)
O1–Zn1–O5C	103.60(16)	P1–O2–Zn1D	123.7(2)
O2B–Zn1–O5C	109.9(2)	P1–O3–Zn1A	140.1(3)
O3A–Zn1–O2B	114.08(19)	N1–O5–Zn1E	126.9(3)

^{a}Symmetry codes: A: $-x+1$, $-y$, $-z+2$; B: $x+1$, y, z; C: $x+1$, $y-1$, z; D: $x-1$, y, z; E: $x-1$, $y+1$, z.

in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

CCDC-260462 (**1**) and 260463 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

3. Results and discussion

3.1. Synthesis

Compounds **1–2** were prepared under similar experimental conditions when the molar ratio of M:ligand is 1:1 and the initial pH value is 2–3. The same compound can be obtained when the initial pH values of the reaction mixtures were adjusted in the range of 2–4.5 by 1 M NaOH. Therefore, the structural differences of compounds **1** and **2** are mainly caused by the different coordination modes of the metal ions as well as the phosphonate ligands 2-hpomp^{2-} and 4-hpomp^{2-}.

In order to study the effects of the metal ions on the structures of the final products, the hydrothermal reactions between $ZnSO_4$ and 2-hpompH$_2$ or between $CdSO_4$ and 4-hpompH$_2$ were also explored under similar experimental conditions. However, only tiny polycrystalline materials were obtained for the $ZnSO_4$/2-hpompH$_2$ system. The XRD measurement revealed a different pattern from that of compound **1**, indicating that a new phase was obtained (see Supporting Information). For the $CdSO_4$/4-hpompH$_2$ system, similar reactions produced only clear solutions when the initial pH value was adjusted to 2–4.5.

3.2. Description of the structures

Compound **1** crystallizes in triclinic space group $P\bar{1}$. It has a one-dimensional chain structure. The asymmetric unit consists of one Cd atom, one 2-hpomp^{2-} ligand and two coordinated water molecules (Fig. 1). The Cd atom has a distorted octahedral environment. Three of the six coordination sites are filled with phosphonate oxygen atoms (O1, O1B, O2A) from three equivalent 2-hpomp^{2-} ligands. The remaining sites are occupied by the O5A atom from the pyridyl N-oxide group and O1W and O2W from two water molecules. The Cd-O bond lengths fall in the range 2.202(6)–2.339(4) Å, in agreement with those in compounds $Cd_2(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ [2.241(8)–2.493(4) Å] [20] and $Cd(O_3PC_2H_4NH_2)$ [2.189(8)–2.516(9) Å] [5]. It is noted that the Cd1–O1B distance [2.339(4) Å] is much longer than the others, attributed to the presence of a μ_3-O(P) bridge. A long Cd–O(P) distance is also observed in $Cd_2(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ [2.493(4) Å] and $Cd(O_3PC_2H_4NH_2)$ [2.516(9) Å].

The 2-hpomp^{2-} serves as a tri-dentate ligand. It chelates the Cd atom through O2 and O5 atoms, forming

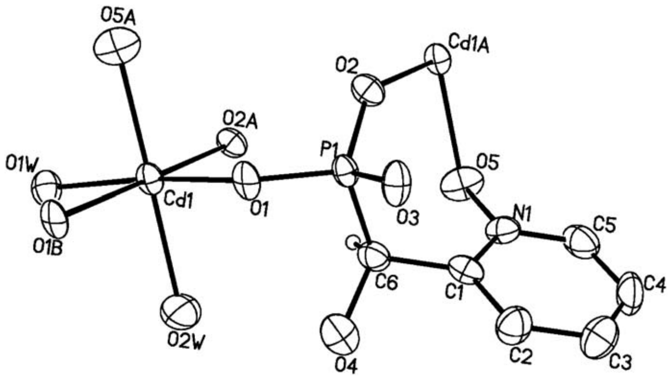

Fig. 1. Building unit of **1** with the atomic labeling scheme (50% probability). All H atoms except H6 were omitted for clarity.

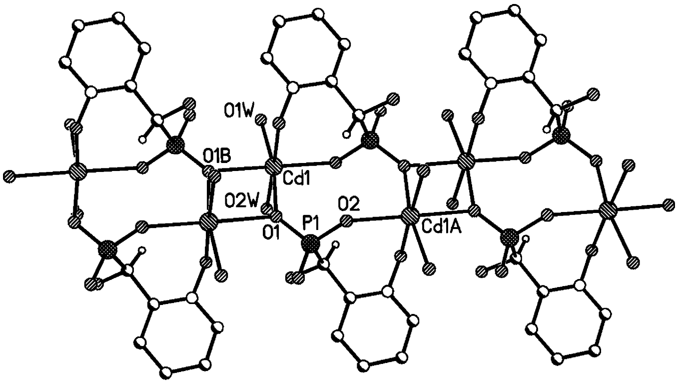

Fig. 2. A fragment of the chain in structure **1**. All H atoms attached to the pyridyl rings are omitted for clarity.

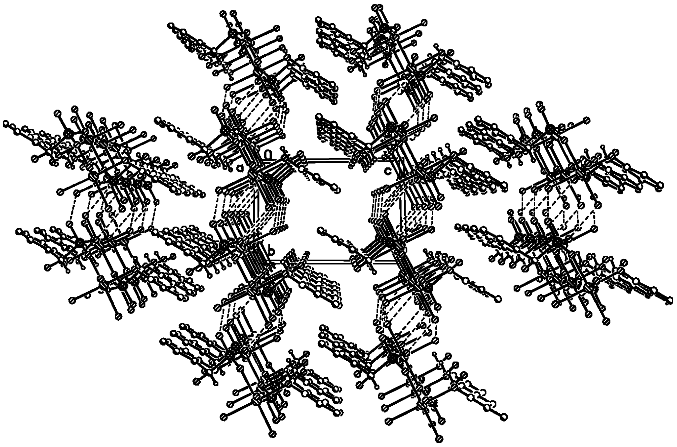

Fig. 3. Structure **1** projected approximately along the *a*-axis. All H atoms attached to the pyridyl rings are omitted for clarity.

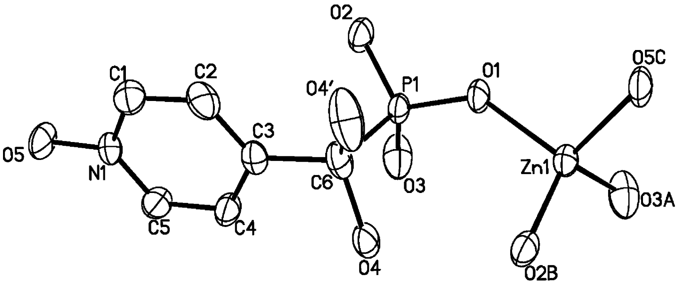

Fig. 4. Building unit of **2** with the atomic labeling scheme (50% probability). All H atoms are omitted for clarity.

a seven-member ring (Fig. 1). Seven-member ring was also observed in the mononuclear compound Er{(2-C_5H_4NO)CH(OH)PO_3H} {(2-C_5H_4NO)CH(OH)PO_3H_2} · $8H_2O$ [17]. One of the phosphonate oxygens (O1) behaves as a μ_3-O and bridges the equivalent Cd atoms, forming a one-dimensional chain parallel to the *a*-axis, which contains four- and eight-membered rings alternatively (Fig. 2). The remaining phosphonate oxygen (O3) is pendant [P1-O3 1.510(5) Å] and is involved in the hydrogen bond network. The chains are stacked in the lattice with extensive inter-chain hydrogen bonds, resulting in a supramolecular layer (Fig. 3). The shortest contacts between the chains are 2.628(7) Å for O1w…O3^{a}, 2.753(8) Å for O1w…O2^{b} and 2.648(7) Å for O2w…O1w^{c} (symmetry codes: *a*: $-x$, $-y+2$, $-z$; *b*: x, $y-1$, z; *c*: $-x+1$, $-y+1$, $-z$).

Compound **2** also crystallizes in triclinic space group $P\bar{1}$. However, it has a layer structure. Fig. 4 shows clearly that the Zn atom is four-coordinated and has a distorted tetrahedral geometry. The four binding sites are occupied by O1, O2B, O3A and O5C atoms from four equivalent 4-hpomp^{2-} ligands. The Zn–O bond lengths [1.914(3)–1.963(4) Å] in compound **2** are comparable with those in Zn_2[(S)-$O_3PCH_2NHC_4H_7CO_2$]$_2$ [Zn-O: 1.922(4)–1.978(4) Å] [21] and Zn(H_3L) · $2H_2O$ [Zn-O: 1.944–1.948 Å] [22] where tetrahedral environments are found around the zinc atoms, but are obviously shorter than those containing six-coordinating zinc atoms such as Zn[(HO_3PCH_2)$_2$N(H)(CH_2)$_6$N(H)(CH_2PO_3H)$_2$] · H_2O [2.022-2.622 Å] [23]. The 4-hpomp^{2-} ligand is tetra-dentate by using three phosphonate oxygen and one pyridyl N-oxygen atoms. Three phosphonate oxygen atoms are each coordinated to a zinc atom. As a result, each {CPO_3} tetrahedron is corner-shared with three {ZnO_4} tetrahedra and vice versa, thus leading to an inorganic double chain parallel to the *a*-axis which contains eight-membered rings (Fig. 5). Such a double chain is identical to the motif in a zinc macrocyclic leaflet [24]. The adjacent double chains are linked through the coordination of zinc atoms from one chain to the pyridyl N-oxygen from the other, forming a two-dimensional layer (Fig. 6). These layers are further connected by inter-layer hydrogen bonds [O4…O2^{a} 2.831(8) Å] (symmetry code: *a*: $x+1$, y, z), leading to a three-dimensional supramolecular network (Fig. 7).

Transition metal monophosphonates are commonly found to exhibit layered structures, where the inorganic layers made up of {CPO_3} tetrahedra and {MO_6} octahedra are separated by the organic groups. Examples of zinc and cadmium compounds of this kind include Zn(O_3PR)(H_2O) ($R = CH_3, C_2H_5, C_6H_5, C_2H_3$) [25] and Cd($O_3PCH_3$)($H_2O$) [26]. With the introduction of

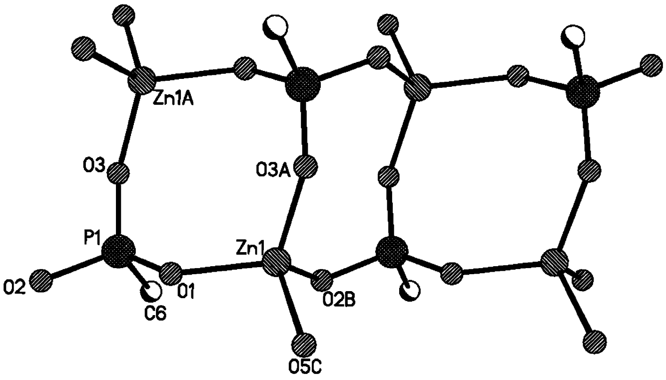

Fig. 5. A fragment of the inorganic chain in compound **2**.

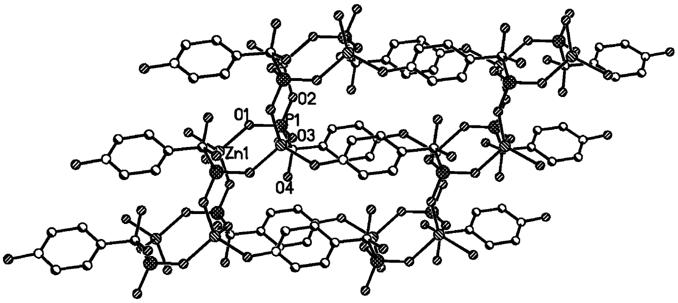

Fig. 6. One layer of structure **2** viewed approximately along the *c*-axis. All H atoms are omitted for clarity.

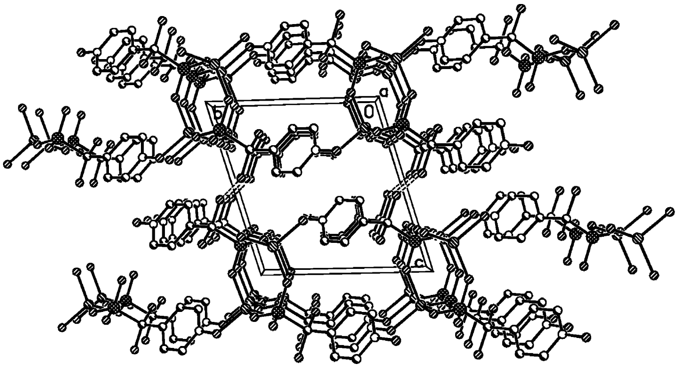

Fig. 7. Structure **2** projected along the *a*-axis. All H atoms are omitted for clarity.

functional groups, compounds with other structure types and interesting properties can be achieved. For example, the carboxylate group introduced to the phosphonate ligands may either coordinates directly to the metal ions by using its two oxygen atoms, or remain pendant in the resulting structures. Thus, compounds $Zn_3(O_3PCH_2CO_2)_2 \cdot nH_2O$ ($n = 3$, 4) are prepared showing three-dimensional porous structures in stead of a "normal" layered structure [27a]. In $Zn(O_3PCH_2CH(NH_3)COO)$ and $Zn(O_3PCH_2CH_2CH(NH_3)COO)$, three-dimensional framework structures are also observed in which both the amino groups and half of the carboxylate oxygen atoms remain terminal in the voids [27b]. A zinc monophosphonate compound containing ferrocene $Zn(HO_3PFc)_2 \cdot 2H_2O$ was recently reported by Le Bideau et al. which shows a reversible surface oxidation of ferrocene [28]. When the additional functional group is pyridine, compound $ZnBr\{(3\text{-}C_5H_4NH)PO_3\}$, $Cd\{(3\text{-}C_5H_4N)PO_3H\}_2 \cdot DMSO$ and $Cd\{(4\text{-}C_5H_4N)PO_3H\}_2$ with 1D ladder-like and 3D framework structures have been prepared [12]. Compounds $M\{(4\text{-}C_5H_4N)CH(OH)PO_3\}(H_2O)$ ($M = Zn^{2+}, Cd^{2+}$) [15a], where the hydroxy(4-pyridyl)methylphosphonic acid was used, also show layer structures in which corner-sharing $\{MO_4N\}$ trigonal bipyramids and $\{CPO_3\}$ tetrahedra are connected by pyridine groups. Compound $Zn\{(3\text{-}C_5H_4N)CH(OH)PO_3\}$ has a pillared layered structure with the inorganic layer containing 8- and 16-member rings made up of $\{ZnO_3N\}$ and $\{CPO_3\}$ tetrahedral [15b]. When the hydroxy(2-pyridyl)methylphosphonic acid is allowed to react with the zinc sulfate, compound $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4 \cdot 4H_2O$ with a drum-like cage structure was obtained [15c]. In the present cases, the pyridine nitrogen atoms in $(2\text{-}C_5H_4N)CH(OH)PO_3$ and $(4\text{-}C_5H_4N)CH(OH)PO_3$ are oxidized. Subsequently, a chain compound $Cd\{(2\text{-}C_5H_4NO)CH(OH)PO_3\}(H_2O)_2$ (**1**) and a layer compound $Zn\{(4\text{-}C_5H_4NO)CH(OH)PO_3\}$ (**2**) are resulted. Clearly, the oxidation of the pyridyl nitrogen in the hydroxy(4/2-pyridyl)methylphosphonic acids causes different coordination modes with the metal ions, and consequently affects the crystal engineering of the corresponding metal phosphonates.

4. Conclusions

This paper reports the syntheses and crystal structures of a cadmium and a zinc phosphonate compounds incorporating pyridyl N-oxide functional groups, namely $Cd\{(2\text{-}C_5H_4NO)CH(OH)PO_3\}(H_2O)_2$ (**1**) and $Zn\{(4\text{-}C_5H_4NO)\text{-}CH(OH)PO_3\}$ (**2**). The former has a chain structure in which dimers of edge-shared $\{CdO_6\}$ octahedra are linked by $\{CPO_3\}$ tetrahedra through corner-sharing. The latter has a layer structure where the inorganic chains made up of corner-sharing $\{ZnO_4\}$ and $\{CPO_3\}$ tetrahedra are covalently connected by pyridyl N-oxide groups. The result demonstrates that the modification of the organic moieties of the phosphonate ligand RPO_3^{2-} can pose significant influences on the structures of the final products. Since the variations of the organic groups are almost unlimited, phosphonate materials with particular compositions and structures may be finally designed and synthesized, and interesting chemical functionalities may be introduced in the solids. Further work is in progress to study the coordination chemistry of the metal phosphonates containing different functional groups.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2005.11.015.

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