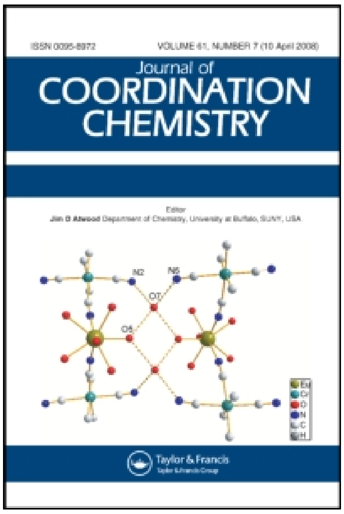

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis and crystal structures of Mn(II) and Cd(II) aminophosphonates with a layered structure

Lei Meng[a]; Jing Li[a]; Zhengang Sun[a]; Xuefang Zheng[b]; Hui Chen[a]; Dapeng Dong[a]; Yanyu Zhu[a]; Yan Zhao[a]; Jing Zhang[a]
[a] Faculty of Chemistry and Chemical Engineering, Institute of Chemistry for Functionalized Materials, Dalian 116029, P.R. China [b] Liaoning Key Laboratory of Bio-Organic Chemistry, Dalian University, Dalian 116622, P.R. China

To cite this Article Meng, Lei , Li, Jing , Sun, Zhengang , Zheng, Xuefang , Chen, Hui , Dong, Dapeng , Zhu, Yanyu , Zhao, Yan and Zhang, Jing(2008) 'Hydrothermal synthesis and crystal structures of Mn(II) and Cd(II) aminophosphonates with a layered structure', Journal of Coordination Chemistry, 61: 15, 2478 — 2487

To link to this Article: DOI: 10.1080/00958970801930021

URL: http://dx.doi.org/10.1080/00958970801930021

Journal of Coordination Chemistry
Vol. 61, No. 15, 10 August 2008, 2478–2487

Taylor & Francis
Taylor & Francis Group

Hydrothermal synthesis and crystal structures of Mn(II) and Cd(II) aminophosphonates with a layered structure

LEI MENG†, JING LI†, ZHENGANG SUN*†, XUEFANG ZHENG‡,
HUI CHEN†, DAPENG DONG†, YANYU ZHU†,
YAN ZHAO† and JING ZHANG†

†Faculty of Chemistry and Chemical Engineering, Institute of Chemistry for Functionalized Materials, Liaoning Normal University, Dalian 116029, P.R. China
‡Liaoning Key Laboratory of Bio-Organic Chemistry, Dalian University, Dalian 116622, P.R. China

(*Received 24 May 2007; in final form 17 July 2007*)

Two new divalent metal aminodiphosphonates with a layered structure, $Mn_2[(HL)(H_2O)F]\cdot H_2O$ (**1**) and $Cd_{3.5}[(HL)L]$ (**2**) ($H_4L = CH_3CH_2CH_2N(CH_2PO_3H_2)_2$), have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction as well as with infrared spectroscopy, elemental analysis and thermogravimetric analysis. In **1**, two MnO_4F_2 and two MnO_5F polyhedra are interconnected *via* edge-sharing into a tetramer, and such tetramers are bridged by the diphosphonate ligands into a Mn(II) phosphonate layer in the *ab*-plane. The structure of **2** also features a 2D layered structure, in which the CdO_5N and CdO_6 polyhedra are interconnected into a 1D chain. The chains are then cross-linked *via* phosphonate oxygen atoms to form Cd(II) phosphonate layers in the *ab*-plane.

Keywords: Metal phosphonates; Crystal structure; Hydrothermal synthesis; Manganese(II); Cadmium(II)

1. Introduction

The chemistry of metal phosphonates has been an active research area due to applications in catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1–5]. Among the metal phosphonate compounds, those containing bifunctional or multifunctional anionic units such as diphosphonates, aminophosphonates or phosphonocarboxylates are of interest because introduction of additional functional groups into the phosphonate ligand will provide layered or porous structures [6–8].

A series of metal phosphonates, using phosphonic acids with amine, hydroxyl, and carboxylate groups as ligands, have been isolated in our laboratory [9]. For construction of inorganic–organic hybrid compounds, substituted aminodiphosphonic acids, $RN(CH_2PO_3H_2)_2$ are very useful ligands [10–13]. For instance, $Cd(H_3L)_2$ ($H_4L = C_6H_5CH_2N(CH_2PO_3H_2)_2$) features double chains that are further

---

*Corresponding author. Email: szg188@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801930021

interlinked by hydrogen bonds [10]. Manganese(II) and zinc(II) complexes with $CH_3N(CH_2PO_3H_2)_2(H_4L)$ have been reported by Clearfield *et al.* [12]. $Mn(H_3L)_2 \cdot 2H_2O$ has a 2D layered structure, and $Zn_3(HL)_2$ has a 3D network structure built from $[ZnO_4]$ tetrahedra linked by bridging phosphonate groups. To the best of our knowledge, reports on metal phosphonates based on alkyl-substituted aminodiphosphonates are still rare. As part of a program of investigating metal diphosphonates, we are interested in exploring new metal phosphonate compounds based on alkyl-substituted aminodiphosphonic acids, $CH_3CH_2CH_2N(CH_2PO_3H_2)_2$. In this paper, we report the synthesis, crystal structure, and thermal stability of two new divalent metal aminodiphosphonates $Mn_2[(HL)(H_2O)F] \cdot H_2O$ (**1**) and $Cd_{3.5}[(HL)L]$ (**2**) containing $CH_3CH_2CH_2N(CH_2PO_3H_2)_2(H_4L)$ as ligand with a layered structure.

2. Experimental

2.1. *Materials and methods*

The aminodiphosphonic acids, $CH_3CH_2CH_2N(CH_2PO_3H_2)_2$, were prepared by a Mannich type reaction according to procedures previously described [14]. All other chemicals were used as obtained without further purification. The syntheses were carried out in 20 mL poly(tetrafluoroethylene) lined stainless steel containers under autogenous pressure. C, H and N were determined using a PE–2400 elemental analyzer. Mn, Cd and P were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer. IR spectra were recorded on a Bruker AXS TENSOR–27 FT–IR spectrometer with KBr pellets in the range 4000–400cm^{-1}. TG and DTA analyses were performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system in static air, with a heating rate of 10 K min^{-1} from 50°C to 900°C.

2.2. *Synthesis of $Mn_2[(HL)(H_2O)F] \cdot H_2O$ (1)*

A mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.12 g, 0.5 mmol), H_4L (0.25 g, 1 mmol), NaF (0.08 g, 2 mmol) and 10 mL of water was sealed into a 20 mL Teflon-lined stainless steel autoclave and heated at 180°C for 5 days under autogenous pressure. The initial and final pH values of solution were 4.0 and 5.0, respectively. After the mixture cooled slowly to room temperature, colorless plate crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 0.08 g, 68.5% based on Mn). Anal. Calcd for **1**, $C_5H_{16}NO_8FP_2Mn_2$ (%): C, 14.68; H, 3.94; N, 3.42; P, 15.15; Mn, 26.86. Found: C, 14.56; H, 3.82; N, 3.35; P, 15.28; Mn, 26.78. Selected IR bands (4000–400 cm^{-1} region): 3564, 3416, 3167, 3068, 2960, 1676, 1153, 1107, 1016, 972, 866, 754, 577.

2.3. *Synthesis of $Cd_{3.5}[(HL)L]$ (2)*

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.34 g, 1.1 mmol), H_4L (0.25 g, 1 mmol), NaF (0.17 g, 4 mmol) and 10 ml of water was sealed into a 20 ml Teflon-lined stainless steel autoclave and heated at 180°C for 5 days. The initial and final pH values of solution were 4.0 and 5.0, respectively. After the mixture cooled slowly to room temperature, colorless plate crystals were filtered off, washed with distilled water, and dried at room temperature (Yield: 0.11 g, 39.7% based on Cd). Anal. Calcd for **2**, $C_{10}H_{23}N_2O_{12}P_4Cd_{3.5}$ (%): C, 13.64; H, 2.63; N, 3.18; P, 14.07; Cd, 44.68. Found: C, 13.68; H, 2.68; N, 3.10; P, 14.15; Cd, 44.59. Selected IR bands (4000–400 cm^{-1} region): 3439, 2960, 2872, 2762, 1632, 1263, 1180, 1119, 1057, 960, 914, 584, 565, 509.

2.4. *Crystal structure determinations of compounds 1 and 2*

Suitable single crystals for **1** and **2** were glued to a thin glass fiber and mounted on a Bruker Smart APEX II X–diffractometer equipped with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.071073$ Å) at 295 ± 2 K. The cell constants were indexed from reflections obtained from 60 frames with an exposure time of 10 s/frame. A hemisphere of intensity data was collected with ω-scans, in the range of $1.77 \leq \theta \leq 26.49°$ for **1** and $1.73 \leq \theta \leq 26.50°$ for **2**. An empirical absorption correction was applied using the SADABS program. The structure were solved by direct methods and refined by full-matrix least squares fitting on F^2 by SHELXTL-97 [15−16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. A summary of crystal data and structure refinements for the two compounds are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

The asymmetric unit of **1** contains two crystallographically independent Mn(II) ions, one partially deprotonated HL^{3-} anion, one fluoride and two water molecules (figure 1).

Mn1 is octahedrally coordinated by four oxygen atoms from four different L^{4-} anions (O3, O4A, O6B and O2C) and two fluorides (F1 and F1A). Mn2 is also octahedrally coordinated by four phosphonate oxygen atoms from three ligands (O3, O4, O1C and O5D), one water molecule (O7) and one fluoride (F1). The Mn–O distances range from 2.271(3) to 2.081(2) Å, which are comparable to those reported for other Mn(II) aminodiphosphonates [12–13]. The Mn–F distances range from 2.2603(19) to 2.2100(19) Å; reports about Mn–F distances are rare. Each ligand is octadentate chelating with Mn2 bidentately (O3 and O4), bridging with Mn1 (O3) and also bridging five other Mn(II) ions. Two phosphonate oxygen atoms are bidentate (O3 and O4). All six phosphonate oxygen atoms are involved in metal coordination. The nitrogen of the amine group is protonated based on charge balance.

Two $Mn(1)O_4F_2$ and two $Mn(2)O_5F$ polyhedra, shown in figure 2, are interconnected into a tetramer *via* edge-sharing. The tetramers are bridged by the diphosphonate ligands into a Mn(II) phosphonate layer in the *ab*-plane. The interlayer distance is *ca.* 11.59 Å. The propyl groups of the ligands are orientated toward the interlayer space (figure 3).

Table 1. Crystal data and structure refinements for compound **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_5H_{16}NO_8FP_2Mn_2$	$C_{10}H_{23}N_2O_{12}P_4Cd_{3.5}$
Formula weight	409.01	880.58
Crystal size (mm^3)	$0.16 \times 0.14 \times 0.07$	$0.14 \times 0.10 \times 0.02$
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.471(3)	6.6574(13)
b (Å)	7.565(3)	11.825(2)
c (Å)	11.590(5)	14.241(3)
α (°)	86.166(7)	92.977(3)
β (°)	82.259(7)	93.939(3)
γ (°)	75.061(6)	92.317(3)
V (Å^3)	626.8(4)	1115.8(4)
Z	2	2
D_c ($g\,cm^{-3}$)	2.167	2.621
Absorption coefficient (mm^{-1})	2.316	3.644
F (000)	412	842
θ range for data collection	1.77–26.49	1.73–26.50
Limiting indices	$-8 \le h \le 9$, $-9 \le k \le 9$ $-9 \le l \le 14$	$-8 \le h \le 10$, $-14 \le k \le 13$, $-17 \le l \le 15$
Reflections collected	3698	6495
Independent reflections	2526 ($R_{int} = 0.0160$)	4503 ($R_{int} = 0.0291$)
Completeness to $\theta = 26.50$	97.1%	97.2%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.8565 and 0.7125	0.9176 and 0.6276
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.036	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0323$, $wR_2 = 0.0741$	$R_1 = 0.0518$, $wR_2 = 0.1191$
R indices (all data)	$R_1 = 0.0417$, $wR_2 = 0.0806$	$R_1 = 0.0743$, $wR_2 = 0.1319$

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

The crystal structure of **2** contains four crystallographically independent Cd(II) ions (the occupancy of Cd3 is 0.5), one fully deprotonated L^{4-} ligand and one single-protonated HL^{3-} ligand in an asymmetric unit (figure 4).

All Cd−atoms have distorted octahedral environments. Cd1 is six-coordinate by a tridentate chelating HL^{3-} ligand (O3, O4 and N1) and three phosphonate oxygen atoms from a HL^{3-} ligand and two separate L^{4-} ligands. Cd2 is surrounded by three phosphonate oxygen atoms from three different ligands and three other atoms (O7, O10, N2) belonging to one L^{4-}. The Cd3 sites are six phosphonate oxygen atoms from six separate ligands, and Cd4 is coordinated by six oxygen atoms from five separate ligands. The Cd–O distances are in the range 2.511(7) to 2.161(6) Å and the Cd–N distances range from 2.407(8) to 2.482(7) Å, comparable with those reported in other cadmium phosphonates [10, 17]. The HL^{3-} ligand chelates with a Cd1 tridentately and also bridges with six other Cd(II) ions (1Cd1, 1Cd2, 2Cd3 and 2Cd4). Three phosphonate oxygen atoms (O1, O3 and O4) are bidentate metal linkers. O5 remains non-coordinated. The L^{4-} chelates with a Cd2 tridentately and a Cd4 bidentately. It also bridges with seven other Cd(II) ions (2Cd1, 2Cd2, Cd3 and 2Cd4). One phosphonate oxygen (O10) is a tridentate metal linker and three atoms (O7, O9 and O12) are bidentate metal linkers. Based on P–O distances and the requirements of charge balance, the O5 atom is protonated.

Table 2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Compound **1**			
Mn(1)–O(3)	2.231(2)	Mn(2)–O(3)	2.232(2)
Mn(1)–F(1)	2.2346(19)	Mn(2)–O(4)	2.257(2)
Mn(1)–O(2)#2	2.138(2)	Mn(2)–O(7)	2.271(3)
Mn(1)–O(4)#3	2.143(2)	Mn(2)–F(1)	2.2603(19)
Mn(1)–O(6)#1	2.133(2)	Mn(2)–O(1)#2	2.166(2)
Mn(1)–F(1)#3	2.2100(19)	Mn(2)–O(5)#4	2.081(2)
O(6)#1–Mn(1)–O(2)#2	98.60(9)	O(5)#4–Mn(2)–O(1)#2	88.94(9)
O(6)#1–Mn(1)–O(4)#3	87.43(8)	O(5)#4–Mn(2)–O(3)	117.48(9)
O(2)#2–Mn(1)–O(4)#3	104.54(9)	O(1)#2–Mn(2)–O(3)	88.02(8)
O(6)#1–Mn(1)–F(1)#3	92.72(8)	O(5)#4–Mn(2)–O(4)	110.57(9)
O(2)#2–Mn(1)–F(1)#3	168.30(7)	O(1)#2–Mn(2)–O(4)	160.39(8)
O(4)#3–Mn(1)–F(1)#3	78.78(8)	O(3)–Mn(2)–O(4)	81.27(8)
O(6)#1–Mn(1)–O(3)	99.78(8)	O(5)#4–Mn(2)–F(1)	160.61(8)
O(2)#2–Mn(1)–O(3)	88.85(8)	O(1)#2–Mn(2)–F(1)	86.81(8)
O(4)#3–Mn(1)–O(3)	163.77(8)	O(3)–Mn(2)–F(1)	81.28(7)
F(1)#3–Mn(1)–O(3)	86.32(8)	O(4)–Mn(2)–F(1)	75.41(7)
O(6)#1–Mn(1)–F(1)	167.98(8)	O(5)#4–Mn(2)–O(7)	79.40(9)
O(2)#2–Mn(1)–F(1)	93.32(8)	O(1)#2–Mn(2)–O(7)	104.17(9)
O(4)#3–Mn(1)–F(1)	88.12(8)	O(3)–Mn(2)–O(7)	159.77(9)
F(1)#3–Mn(1)–F(1)	75.46(8)	O(4)–Mn(2)–O(7)	82.21(9)
O(3)–Mn(1)–F(1)	81.88(8)	F(1)–Mn(2)–O(7)	83.32(8)
Compound **2**			
Cd(1)–O(1)#2	2.511(7)	Cd(3)–O(2)#2	2.276(8)
Cd(1)–O(3)	2.344(6)	Cd(3)–O(2)#5	2.276(8)
Cd(1)–O(4)	2.300(6)	Cd(3)–O(4)	2.425(6)
Cd(1)–O(8)#1	2.229(6)	Cd(3)–O(4)#4	2.425(6)
Cd(1)–O(12)	2.304(6)	Cd(3)–O(11)	2.161(6)
Cd(1)–N(1)	2.482(7)	Cd(3)–O(11)#4	2.161(6)
Cd(2)–O(1)#1	2.298(6)	Cd(4)–O(3)#1	2.275(6)
Cd(2)–O(7)	2.392(6)	Cd(4)–O(6)#6	2.232(7)
Cd(2)–O(9)#2	2.324(6)	Cd(4)–O(7)	2.324(6)
Cd(2)–O(10)	2.353(5)	Cd(4)–O(9)#1	2.282(6)
Cd(2)–O(10)#3	2.333(6)	Cd(4)–O(10)#3	2.340(6)
Cd(2)–N(2)	2.407(8)	Cd(4)–O(12)#1	2.260(6)
O(8)#1–Cd(1)–O(4)	164.4(2)	O(11)–Cd(3)–O(11)#4	180.0(3)
O(8)#1–Cd(1)–O(12)	88.3(2)	O(11)–Cd(3)–O(2)#5	90.3(3)
O(4)–Cd(1)–O(12)	103.8(2)	O(11)#4–Cd(3)–O(2)#5	89.7(3)
O(8)#1–Cd(1)–O(3)	83.6(2)	O(11)–Cd(3)–O(2)#2	89.7(3)
O(4)–Cd(1)–O(3)	89.4(2)	O(11)#4–Cd(3)–O(2)#2	90.3(3)
O(12)–Cd(1)–O(3)	77.1(2)	O(2)#5–Cd(3)–O(2)#2	180.000(1)
O(8)#1–Cd(1)–N(1)	85.1(2)	O(11)–Cd(3)–O(4)	96.2(2)
O(4)–Cd(1)–N(1)	79.7(2)	O(11)#4–Cd(3)–O(4)	83.8(2)
O(12)–Cd(1)–N(1)	153.8(2)	O(2)#5–Cd(3)–O(4)	108.9(2)
O(3)–Cd(1)–N(1)	77.0(2)	O(2)#2–Cd(3)–O(4)	71.1(2)
O(8)#1–Cd(1)–O(1)#2	78.4(2)	O(11)–Cd(3)–O(4)#4	83.8(2)
O(4)–Cd(1)–O(1)#2	111.8(2)	O(11)#4–Cd(3)–O(4)#4	96.2(2)
O(12)–Cd(1)–O(1)#2	86.2(2)	O(2)#5–Cd(3)–O(4)#4	71.1(2)
O(3)–Cd(1)–O(1)#2	155.80(19)	O(2)#2–Cd(3)–O(4)#4	108.9(2)
N(1)–Cd(1)–O(1)#2	117.0(2)	O(4)–Cd(3)–O(4)#4	180.0(3)
O(1)#1–Cd(2)–O(9)#2	110.6(2)	O(6)#6–Cd(4)–O(12)#1	90.1(2)
O(1)#1–Cd(2)–O(10)#3	85.5(2)	O(6)#6–Cd(4)–O(3)#1	101.2(2)
O(9)#2–Cd(2)–O(10)#3	105.6(2)	O(12)#1–Cd(4)–O(3)#1	79.4(2)
O(1)#1–Cd(2)–O(10)	163.0(2)	O(6)#6–Cd(4)–O(9)#1	90.1(2)
O(9)#2–Cd(2)–O(10)	75.8(2)	O(12)#1–Cd(4)–O(9)#1	104.7(2)
O(10)#3–Cd(2)–O(10)	77.6(2)	O(3)#1–Cd(4)–O(9)#1	168.1(2)
O(1)#1–Cd(2)–O(7)	91.7(2)	O(6)#6–Cd(4)–O(7)	174.2(2)
O(9)#2–Cd(2)–O(7)	157.61(19)	O(12)#1–Cd(4)–O(7)	84.4(2)
O(10)#3–Cd(2)–O(7)	76.9(2)	O(3)#1–Cd(4)–O(7)	79.5(2)

(*Continued*)

Table 2. Continued.

O(10)–Cd(2)–O(7)	83.21(19)	O(9)#1–Cd(4)–O(7)	89.7(2)
O(1)#1–Cd(2)–N(2)	113.6(3)	O(6)#6–Cd(4)–O(10)#3	107.5(2)
O(9)#2–Cd(2)–N(2)	96.2(2)	O(12)#1–Cd(4)–O(10)#3	162.4(2)
O(10)#3–Cd(2)–N(2)	143.8(2)	O(3)#1–Cd(4)–O(10)#3	95.80(19)
O(10)–Cd(2)–N(2)	80.3(2)	O(9)#1–Cd(4)–O(10)#3	76.8(2)
O(7)–Cd(2)–N(2)	72.4(2)	O(7)–Cd(4)–O(10)#3	78.1(2)

Symmetry transformations used to generate equivalent atoms:
For **1**: #1 $x, y+1, z$; #2 $-x+2, -y+2, -z+1$; #3 $-x+1, -y+2, -z+1$; #4 $-x+2, -y+1, -z+1$.
For **2**: #1 $-x+1, -y+2, -z$; #2 $x-1, y, z$; #3 $-x, -y+2, -z$; #4 $-x, -y+1, -z$; #5 $-x+1, -y+1, -z$; #6 $x, y+1, z$.

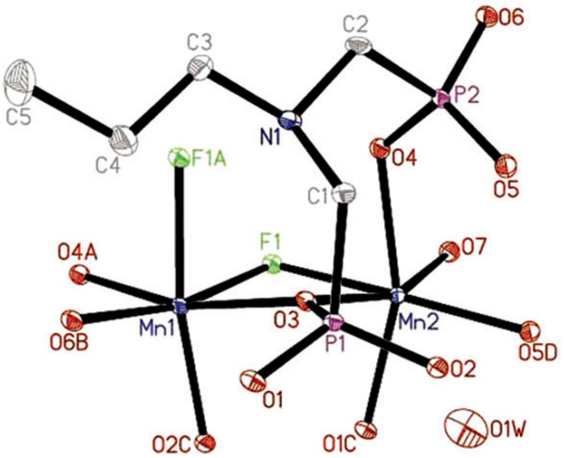

Figure 1. ORTEP representation of the selected unit in compound **1**. Thermal ellipsoids are drawn at 30% probability. Symmetry codes for the generated atoms: (a) $-x+1, -y+2, -z+1$; (b) $x, y+1, z$; (c) $-x+2, -y+2, -z+1$; (d) $-x+2, -y+1, -z+1$.

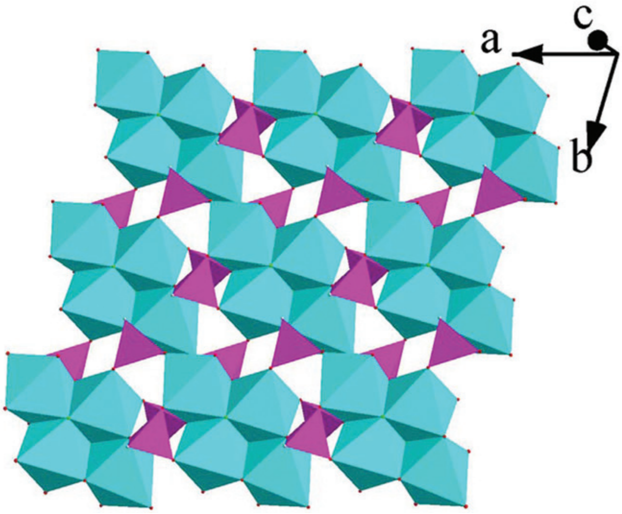

Figure 2. Polyhedral representation of a Mn(II) phosphonate layer for **1** in the *ab*-plane. MnO_4F_2 and MnO_5F polyhedra are shaded in cyan and CPO_3 tetrahedra are shaded in purple. The propyl groups of the ligands have been omitted for clarity.

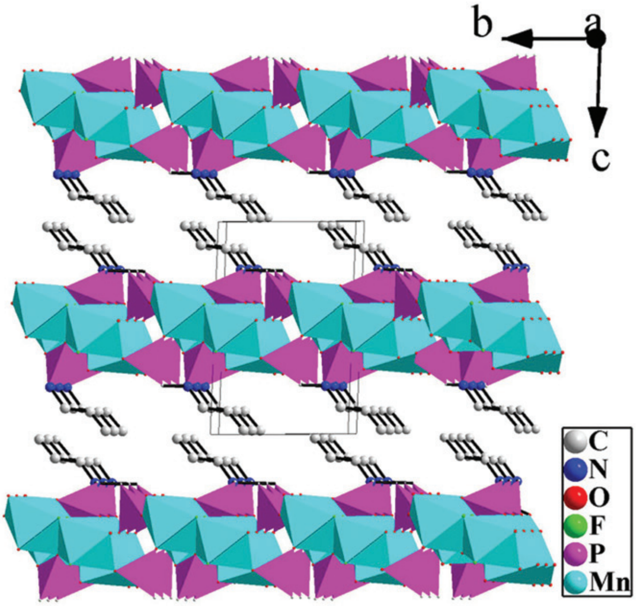

Figure 3. View of the structure of **1** along the *a*–axis. MnO_4F_2 and MnO_5F polyhedra are shaded in cyan, and CPO_3 tetrahedra are shaded in purple. The propyl groups of the ligands are orientated toward the interlayer space. The water molecules are omitted for clarity.

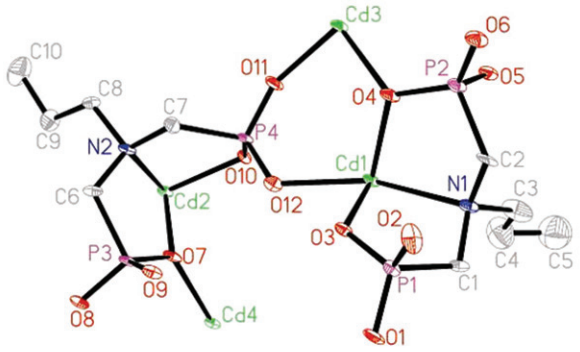

Figure 4. ORTEP representation of the asymmetric unit of **2**. Thermal ellipsoids are drawn at 30% probability.

The overall structure of **2** can be described as the stacking of 2D layers along the *c*-axis (figure 5). The interconnection of Cd(1)O_5N, Cd(3)O_6 and Cd(1)O_5N polyhedra *via* corner-sharing forms a trimer (figure 6a). Two Cd(2)O_5N and two Cd(4)O_6 polyhedra are interconnected into a tetramer *via* edge-sharing. The so-built trimer and tetramer are interconnected alternately *via* edge-sharing into a 1D chain. The 1D cadmium oxide chains are then cross-linked *via* phosphonate oxygen atoms to form Cd(II) phosphonate layers in the *ab*-plane (figure 6b). The propyl groups occupy the interlayer space as in **1**, The interlayer distance is ca 11.79 Å.

The structures of the two compounds were compared with those of metal complexes of the related ligands [10–13]. The organic substituent on the amine plays a subtle role

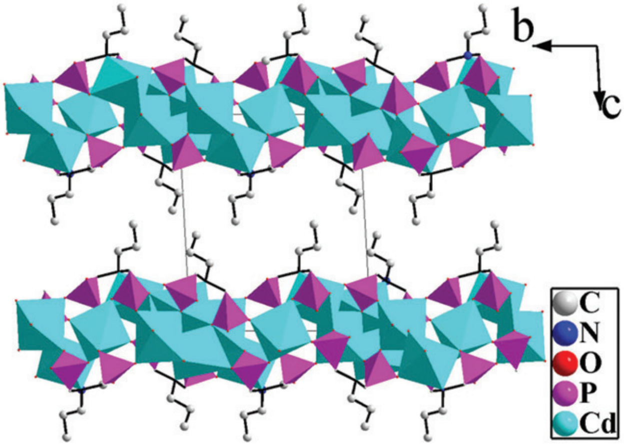

Figure 5. View of the structure of **2** down the *a*-axis. CdO_5N and CdO_5 polydredra are shaded in cyan, and CPO_3 tetrahedra are shaded in purple. The propyl groups of the ligands are orientated toward the interlayer space.

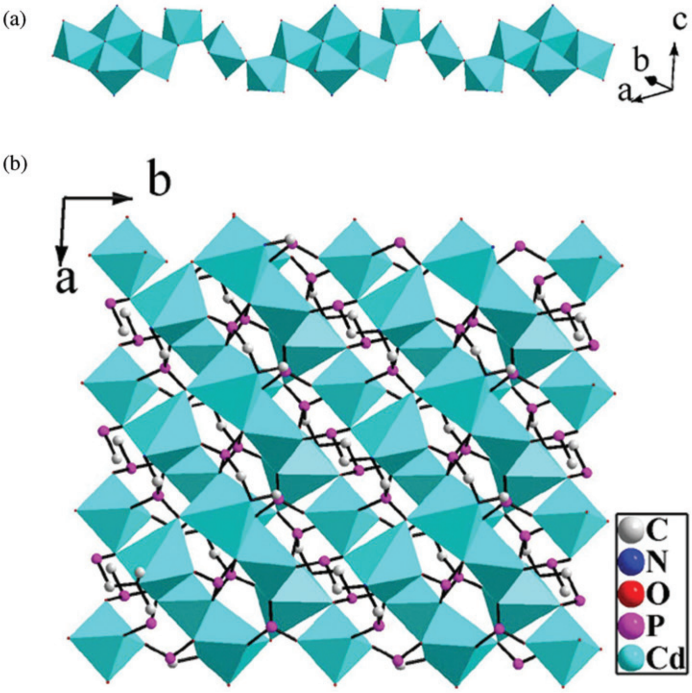

Figure 6. (a) A cadmium(II) oxide chain in the *ab*-plane; (b) a cadmium(II) phosphonate layer in **2**. CdO_5N and CdO_5 polydredra are shaded in cyan, and CPO_3 tetrahedra are shaded in purple. The propyl groups of the ligands have been omitted for clarity.

on the structures of the metal phosphonates. The different groups not only change the coordination modes of the diphosphonate ligands and the structural types of the metal phosphonates formed, but also have a strong effect on the d-spacing. However more studies are needed to further understand the subtle role which the substituents play.

3.2. *IR spectra*

IR spectra for the two compounds were recorded between 4000 and 400 cm^{-1}. The bands centered at 3564 cm^{-1} and 3416 cm^{-1} for **1** correspond to the O–H stretching vibration of the lattice water and the hydrogen bonds. The weak band at 2762 cm^{-1} for **2** is likely due to ν(P–OH), which is characteristic of hydrogen phosphonate [10]. The bands around 3000 cm^{-1} for both compounds originate from the CH_2 stretching vibrations. The O–H bending vibration is located at 1676 cm^{-1} for **1** and 1632 cm^{-1} for **2**. The set of bands between 1200 cm^{-1} and 900 cm^{-1} are due to stretching vibrations of the tetrahedral O_3PC groups [18–19]. Additional medium and sharp bands at low energy (between 800 and 400 cm^{-1}) are found, probably due to bending vibrations of the tetrahedral O_3PC groups and M–O (M=Mn and Cd) stretching vibrations.

3.3. *Thermogravimetric analysis*

The TGA diagram of **1** reveals three weight losses. The first corresponds to the loss of a lattice water. The weight loss begins at 60°C and is completed at 142°C with weight loss of 4.1% close to the calculated value (4.4%). The second step occurs in the range of 142–320°C, attributed to the loss of the crystal water and hydrogen fluoride. The third weight loss corresponds to combustion of organic groups. The total weight loss of 30.3% is close to the calculated value (30.6%) if the final product is assumed to be $Mn(PO_3)_2$ and MnO in the molar ratio of 1 : 1. The TGA of **2** shows that it is stable up to 300°C. Above this temperature, it gradually loses weight until 873°C. The total weight loss (15.8%) corresponds to burning of the organic ligands in good agreement with the calculated value (16.7%). The final product is assumed to be mixture of $Cd(PO_3)_2$ and CdO in a molar ratio of 4 : 3.

Supplementary material

Crystallographic data for the structure of **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data center, CCDC Number 611976 for **1** and 627400 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

This work was supported by grants from the Natural Science Foundation of Liaoning Province of China (20062140) and the Education Department of Liaoning Province of China (05L214).

References

[1] K. Maeda. *Micropor. Mesopor. Mater.*, **73**, 47 (2004), and references herein.
[2] A. Clearfield. *Chem. Mater.*, **10**, 2801 (1998).

[3] A. Clearfield. Metal phosphonate chemistry. In: *Progress in Inorganic Chemistry*, K.D. Karlin (Ed.), Vol. 47, p. 371, Wiley, New York (1998), and references therein.

[4] A.K. Cheetham, G. Férey, T. Loiseau. *Angew. Chem. Int. Ed.*, **38**, 3268 (1999).

[5] G. Alberti, U. Costantino. In: *Comprehensive Supramolecular Chemistry*, J.M. Lehn (Ed.), p. 1 and 151, Pergamon-Elsevier Science Ltd, London (1996).

[6] J.G. Mao, Z.K. Wang, A. Clearfield. *J. Chem. Soc., Dalton Trans.*, 4541 (2002).

[7] J.L. Song, J.G. Mao. *J. Solid State Chem.*, **178**, 3514 (2005).

[8] J.G. Mao, Z.K. Wang, A. Clearfield. *Inorg. Chem.*, **41**, 6106 (2002).

[9] (a) Z.G. Sun, H. Chen, Z.M. Liu, L.Y. Cui, Y.Y. Zhu, Y. Zhao, J. Zhang, W.S. You, Z.M. Zhu. *Inorg. Chem. Commun.*, **10**, 283 (2007); (b) Z.G. Sun, L.Y. Cui, Z.M. Liu, L. Meng, H. Chen, D.P. Dong, L.C. Zhang, Z.M. Zhu, W.S. You. *Inorg. Chem. Commun.*, **9**, 999 (2006); (c) Z.G. Sun, L.Y. Cui, Z.M. Liu, D.P. Dong, L. Meng, H. Chen, L.C. Zhang, Z.M. Zhu, W.S. You. *Inorg. Chem. Commun.*, **9**, 1121 (2006); (d) L.Y. Cui, Z.G. Sun, Z.M. Liu, W.S. You, Z.M. Zhu, L. Meng, H. Chen, D.P. Dong. *Inorg. Chem. Commun.*, **9**, 1232 (2006).

[10] Z.M. Sun, B.P. Yang, Y.Q. Sun, J.G. Mao, A. Clearfield. *J. Solid State Chem.*, **176**, 62 (2003).

[11] J.G. Mao, Z.K. Wang, A. Clearfield. *J. Chem. Soc., Dalton Trans.*, 4457 (2002).

[12] J.G. Mao, Z.K. Wang, A. Clearfield. *Inorg. Chem.*, **41**, 2334 (2002).

[13] Z.M. Sun, J.G. Mao, Z.C. Dong. *Polyhedron*, **24**, 571 (2005).

[14] K. Moedritzer, R.R. Irani. *J. Org. Chem.*, **31**, 1603 (1966).

[15] G.M. Sheldrick. *SHELXTL–97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).

[16] G.M. Sheldrick. *SHELXTL–97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[17] J.G. Mao, Z.K. Wang, A. Clearfield. *Inorg. Chem.*, **41**, 3713 (2002).

[18] Z.M. Sun, J.G. Mao, B.P. Yang, S.M. Ying. *Solid State Sci.*, **6**, 295 (2004).

[19] A. Cabeza, X.Q. Yang, C.V.K. Sharma, M.A.G. Aranda, S. Bruque, A. Clearfield. *Inorg. Chem.*, **41**, 2325 (2002).