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Hydrothermal syntheses, characterizations and crystal structures of three new cadmium (II) amino-diphosphonates: effects of substitute groups on the structures of metal phosphonates

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Abstract

Hydrothermal reactions of cadmium(II) chloride with three amino-diphosphonic acids, $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L^1), $C_6H_5CH_2CH_2N(CH_2PO_3H_2)_2$ (H_4L^2) and $4-CH_3-C_6H_4CH_2N(CH_2PO_3H_2)_2$ (H_4L^3) resulted in three new metal amino-diphosphonates, namely, $Cd(H_3L^1)_2$, **1** $Cd(H_3L^2)_2 \cdot 2H_2O$ **2** and $Cd(H_3L^3)_2$ **3**. In all three complexes, the Cd(II) ion is octahedrally coordinated by six phosphonate oxygen atoms from six ligands. Complexes **1** and **3** have a similar structure in which the CdO_6 octahedra are cross-linked by bridging ligands into a double chain along the *c*-axis, such double chains are further interlinked via hydrogen bonds between non-coordinated phosphonate oxygen atoms to form $\langle 100 \rangle$ and $\langle 200 \rangle$ layers with the phenyl groups of the ligands orientated toward the interlayer space. The structure of complex **2** features a $\langle 100 \rangle$ cadmium(II) diphosphonate layer. The effects of the substitute groups attached to the amine groups on the structures of the metal phosphonates are also discussed. © 2003 Elsevier Inc. All rights reserved.

Keywords: Cadmium diphosphonate; Crystal structure; Hydrothermal synthesis; Layered compounds

1. Introduction

Metal phosphonates have attracted a lot of research attention in recent years due to their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1]. Besides the layered species, metal phosphonates also exhibit other structural types such as 1D chains and 3D open frameworks. Materials with open frameworks and microporous structures are expected to find their use as hybrid composite materials in electro-optical and sensing applications in the future [2]. Metal complexes with a diphosphonic acid in which the two phosphonate groups are connected by an alkyl or an aryl group have been extensively investigated [1,3]. Studies from our group and others have shown that diphosphonic acids in which the two phosphonate

groups are attached to the diamine groups ($HO_3PCH_2HNRNHCH_2PO_3H$), can form metal phosphonates with a variety of structures, such as mono-nuclear chelating complexes [4], 1D chains or 3D networks based on dimeric units [5], and layered compounds [6,7]. Only a few structural studies have been reported on metal complexes of aminodiphosphonic acids, $RN(CH_2PO_3H_2)_2$ [8,9]. The crystal structure of a copper complex with ethylaminebis(methylphosphonate), was reported by Makaranets et al. [8a], a cobalt(II) and a lead(II) complexes with $NH(CH_2PO_3H_2)_2$ have been recently reported [8b,8c]. Recently a series of divalent metal complexes with *N*-methyliminodi(methylenephosphonate) were reported in our laboratory [9a,9b,9c]. Several layered zirconium fluoride alkylamino-*N,N*-bis(methylenephosphonate) have been isolated by Vivani et al. [9d]. In order to understand the influence of the *R* group on the structures of the metal phosphonates formed, we have synthesized three derivatives of $HN(CH_2PO_3H_2)_2$,

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namely, $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L^1), $C_6H_5CH_2CH_2N(CH_2PO_3H_2)_2$ (H_4L^2) and $4-CH_3-C_6H_4CH_2N(CH_2PO_3H_2)_2$ (H_4L^3), hydrothermal reactions of the above three diphosphonic acids with cadmium(II) chloride resulted in three new Cd(II) compounds, $Cd(H_3L^1)_2$ **1**, $Cd(H_3L^2)_2 \cdot 2H_2O$ **2** and $Cd(H_3L^3)_2$ **3**. Complexes **1** and **3** are isostructural and feature a hydrogen bonded 2D layer built from 1D double chains of the cadmium diphosphonates, whereas the structure of complex **2** contains a 2D metal diphosphonate layer. Herein we report their syntheses, characterizations and crystal structures.

2. Experimental

Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1} . Solution NMR was recorded on a Varian Unity 500 NMR, using D_2O as solvent. H_3PO_4 was used as ^{31}P standard reference. Thermogravimetric analyses were carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C/min under a nitrogen atmosphere.

2.1. Syntheses of H_4L^1 , H_4L^2 and H_4L^3

All three aminodiphosphonic acids were prepared by a Mannich type reaction according to the procedures previously described [10]. Their purities were confirmed by NMR measurements and elemental analyses. For H_4L^1 , ^{31}P NMR: 8.025 ppm (s). 1H NMR: 3.493 ppm (N–CH₂–PO₃, d, 4H, J_{H-P} = 12.0 Hz), 4.738 ppm (Ph–CH₂–N, s, 2H), 7.554 and 7.590 ppm (C_6H_5 , s, 5H). Elemental analysis for $C_9H_{15}NO_6P_2$: C, 36.41; H, 4.94; N, 4.58. Calcd: C, 36.62; H, 5.11; N, 4.75%. IR data (KBr, cm^{-1}): 2987(m), 2939(m), 2752(m), 2551(m), 2297(m), 1458(s), 1292(m), 1230(s), 1171(vs), 941(vs), 752(s), 700(s), 579(m), 490(m). For H_4L^2 , ^{31}P NMR: 7.753 ppm (s), 1H NMR: 3.157 ppm (C–CH₂–N, t, 2H) and 3.625 ppm (N–CH₂–P, d, 4H), 3.773 ppm (Ph–CH₂–, t, 2H), 7.739 ppm (C_6H_5 , m, 5H). Elemental analysis for $C_{10}H_{17}NO_6P_2$: C, 38.70; H, 5.35; N, 4.38; Calcd: C, 38.85; H, 5.54; N, 4.53%. IR (KBr, cm^{-1}): 3030(m), 2991(m), 2954(m), 2740(m), 2290(m), 1460(m), 1335(w), 1163(vs), 945(vs), 856(m), 810(w), 752(m), 702(m), 579(s), 499(m), 436(m). For H_4L^3 , ^{31}P NMR: 8.023 ppm (s). 1H NMR: 2.376 ppm (CH₃–Ph, s, 3H), 3.482 ppm (NCH₂PO₃, d, 4H), 4.687 ppm (PhCH₂, s, 2H), 7.469 ppm (C_6H_4 , q, 4H). Elemental analysis for $C_{10}H_{17}NO_6P_2$: C, 38.46; H, 5.32; N, 4.35; Calcd: C, 38.85; H, 5.54; N, 4.53%. IR (KBr, cm^{-1}) data: 2991(m), 2943(m), 2748(m), 2550(m), 2287(m), 1456(w), 1228(m), 1169(s), 1014(m), 937(m), 795(m), 719(w), 706(w), 582(m), 457(w).

2.2. Syntheses of $Cd(H_3L^1)_2$ **1**, $Cd(H_3L^2)_2 \cdot 2H_2O$ **2** and $Cd(H_3L^3)_2$ **3**

All complexes were synthesized by hydrothermal reactions by a similar method. A mixture of 0.25 mmol $CdCl_2 \cdot 2H_2O$, 0.5 mmol H_4L^1 (H_4L^2 or H_4L^3), and 10 mL deionized water in a 20 mL Teflon-lined autoclave wash heated and crystallized at 180 °C for 4 days. For all three reactions, the initial and final pH values are about 4.0 and 2.0, respectively. Colorless crystals for complexes **1**, **2** and **3** were obtained in 68.5%, 72.3% and 56.4% yields (based on the cadmium atom), respectively. Elemental analysis for **1**, $C_{18}H_{28}CdN_2O_{12}P_4$: C, 30.74; H, 3.88; N, 3.91. Calcd: C, 30.85; H, 4.02; N, 4.00%. IR (KBr, cm^{-1}) for complex **1**: 3450(br), 3005(m), 2947(m), 2816(m), 2742(m), 2692(w), 2596(s), 2295(w), 1456(s), 1250(vs), 1153(vs), 1080(vs), 1028(s), 924(vs), 762(m), 741(s), 708(m), 552(s), 482(s). Elemental analysis for **2**, $C_{20}H_{36}CdN_2O_{14}P_4$: C, 31.34; H, 4.50; N, 3.56. Calcd: C, 31.41; H, 4.74; N, 3.66%. IR (KBr, cm^{-1}) for complex **2**: 3500(br), 3032(s), 2953(m), 2839(m), 2750(w), 2285(s), 1626(m), 1455(w), 1434(m), 1373(w), 1289(m), 1216(vs), 1160(vs), 1058(vs), 945(vs), 748(s), 710(s), 574(s), 447(s). Elemental analysis for **3**, $C_{20}H_{32}CdN_2O_{12}P_4$: C, 32.86; H, 4.24; N, 3.73. Calcd: C, 32.99; H, 4.43; N, 3.85%. IR (KBr, cm^{-1}) for complex **3**: 3350(br), 2995(m), 2953(m), 2746(m), 2580(m), 2290(m), 1452(m), 1184(vs), 1163(vs), 1086(s), 920(vs), 779(m), 758(m), 521(s), 478(m).

2.3. X-ray crystallography

Single crystals of complexes **1**, **2** and **3** were mounted on a Siemens Smart CCD using $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), and a graphite monochromator. Intensity data were collected in the narrow frame method at 293 K. The data sets were corrected for Lorentz polarization as well as for absorption by the SADABS program [11]. The structures of **1** and **2** were solved by direct methods whereas that of **3** was solved by the heavy atom method. All three structures were refined by full-matrix least-square fitting on F^2 by SHELX-97 [12]. All non-hydrogen atoms in all three complexes were refined with anisotropic thermal parameters. Hydrogen atoms except those of lattice water molecule in complex **2** were located at geometrically calculated positions. The hydrogen atoms of the lattice water molecule were not refined. Crystallographic data and refinements are summarized in Table 1. Important bond distances and angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the three structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 208751, 208752 and 208753. Copies of the data can be obtained free of charge on application to CCDC, 12 Union

Table 1
Crystal data and structure refinement for complexes **1**, **2** and **3**

Complex	1	2	3
Empirical formula	C ₁₈ H ₂₈ N ₂ O ₁₂ P ₄ Cd	C ₂₀ H ₃₆ N ₂ O ₁₄ P ₄ Cd	C ₂₀ H ₃₂ N ₂ O ₁₂ P ₄ Cd
<i>M</i>	700.70	764.79	728.76
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i> (No.15)	<i>P2₁/c</i> (No. 14)	<i>C2/c</i> (No.15)
<i>a</i> (Å)	24.4085(8)	16.3010(19)	28.0172(18)
<i>b</i> (Å)	12.9198(6)	8.7567(10)	12.8603(6)
<i>c</i> (Å)	7.8169(4)	10.3038(12)	7.7102(5)
β (deg)	95.396(2)	94.037(2)	92.850(2)
<i>V</i> (Å ³)	2454.16(19)	1467.1(3)	2774.6(3)
<i>Z</i>	4	2	4
<i>D_c</i> (g cm ⁻³)	1.896	1.722	1.745
μ (MoK α) (mm ⁻¹)	1.218	1.031	1.081
<i>F</i> (000)	1416	772	1480
Reflections collected	3659	4327	3964
Independent reflections	2134 (<i>R</i> _{int} = 0.0366)	2564 (<i>R</i> _{int} = 0.0463)	2414 (<i>R</i> _{int} = 0.0594)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1702	1895	1570
Goodness-of-fit on <i>F</i> ²	1.144	1.108	1.081
<i>R1</i> , <i>wR2</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0487, 0.0960	0.0569, 0.1095	0.0646, 0.1160
<i>R1</i> , <i>wR2</i> (all data)	0.0712, 0.1073	0.0923, 0.1290	0.1225, 0.1416

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \frac{\sum w[(F_o)^2 - (F_c)^2]^2}{\sum w[(F_o)^2]^{1/2}}.$$

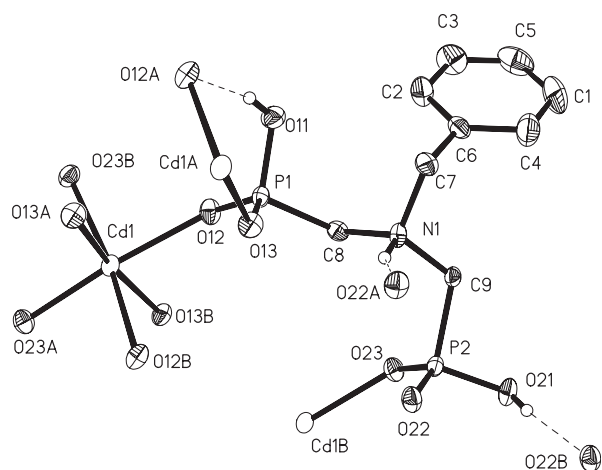


Fig. 1. ORTEP representation of the asymmetry unit of complex **1**. Thermal ellipsoids are drawn at 50% probability. The dotted lines represent hydrogen bonds.

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3. Results and discussion

The structures of complexes **1** and **3** are iso-structural and feature a double chain of cadmium(II) diphosphonate along the *c*-axis, thus only the structure of complex **1** will be discussed in detail. As shown in Fig. 1, the cadmium(II) ion in complex **1** lies on a position of two-fold symmetry, it is octahedrally coordinated by six phosphonate oxygen atoms from six ligands. The Cd–O distances range from 2.259(4) to 2.314(4) Å for complex

1, and from 2.247(5) to 2.327(5) Å for complex **3**, respectively, which are slightly longer than those in Cd(II) complex with MeN(CH₂PO₃H₂)₂ [9b]. The diphosphonate ligand acts as a tridentate metal linker, and bridges with three Cd(II) ions, the phosphonate group containing P(1) atom is bidentate (O12, O13), whereas the one containing P(2) atom is unidentate (O23) (Fig. 1). The MeN(CH₂PO₃H₂)₂ in its Mn(II) and Cd(II) complexes is also tridentate, however, it chelates with a metal(II) bidentately and bridges with another metal ion [9a,9b]. Similar to that in the cadmium(II) complex with MeN(CH₂PO₃H₂)₂, the nitrogen atom and both phosphonate groups of L¹ are 1H-protonated, hence each ligand carries one negative charge, and two ligands are needed to balance the two positive charges of a Cd(II) ion. Based on the P–O distances (Table 2), O(11) and O(21) atoms of L¹ are most likely to be protonated, so too with O(13) and O(23) atoms of L³ in complex **3**. The protonated nitrogen atom forms a hydrogen bond with non-coordinated phosphonate oxygen atoms. The N(1)–H(11B)⋯O(22) bond length and angle are 2.698 Å and 152.2°, respectively for **1** (N(1)–H(11a)⋯O(21), 2.696 Å and 151.6°, respectively for **3**) (Table 2).

The cross-linkage of CdO₆ octahedra by bridging diphosphonate ligands resulted in a double chain along the *c*-axis (Fig. 2). Each CdO₆ octahedron connects with two neighboring CdO₆ octahedra via four bidentate bridging phosphonate tetrahedra. These double chains are further interlinked via hydrogen bonds between non-coordinated phosphonate oxygen atoms, resulting in <100> and <200> layers with the phenyl rings of the ligands orientated toward the interlayer space (Figs. 3

Table 2
Bond lengths (Å) and angles (deg) for complexes **1**, **2** and **3**

Cd(H₃L¹)₂ 1			
Cd(1)–O(23)#1	2.259(4)	Cd(1)–O(13)#3	2.289(4)
Cd(1)–O(12)	2.314(4)		
O(23)#1–Cd(1)–O(23)#2	89.5(2)	O(23)#1–Cd(1)–O(13)#3	105.23(14)
O(23)#2–Cd(1)–O(13)#3	83.68(14)	O(13)#3–Cd(1)–O(13)#4	167.7(2)
O(23)#1–Cd(1)–O(12)#5	89.03(14)	O(23)#2–Cd(1)–O(12)#5	165.75(13)
O(13)#3–Cd(1)–O(12)#5	83.04(14)	O(13)#4–Cd(1)–O(12)#5	88.69(13)
O(23)#1–Cd(1)–O(12)	165.75(13)	O(12)#5–Cd(1)–O(12)	95.8(2)
Hydrogen bonding			
N(1)⋯O(22)#6	2.698(6)	N(1)–H(11B)⋯O(22)#6	152.2
O(11)⋯O(12)#7	2.598(5)	O(11)–H(11A)⋯O(12)#7	166.0
O(11)⋯O(22)#8	2.650(6)	O(21)–H(21A)⋯O(22)#8	165.9
Cd(H₃L²)₂ · 2H₂O 2			
Cd(1)–O(11)	2.222(4)	Cd(1)–O(12)#1	2.296(4)
Cd(1)–O(21)#2	2.304(5)		
Hydrogen bonding			
O(1w)⋯O(22)#3	2.783(8)	O(1w)⋯H(23A)–O(23)	164.6
O(1w)⋯O(23)	2.644(8)	O(13)–H(13A)⋯O(22)#4	163.4
O(13)⋯O(22)#4	2.563(7)	N(1)–H(11A)⋯O(12)#5	144.3
N(1)⋯O(12)#5	2.818(7)	O(11)–Cd(1)–O(21)#4	87.25(16)
O(11)–Cd(1)–O(12)#2	93.42(15)	O(12)#3–Cd(1)–O(21)#4	83.72(17)
O(12)#2–Cd(1)–O(21)#4	96.28(17)		
Cd(H₃L³)₂ 3			
Cd(1)–O(22)	2.247(5)	Cd(1)–O(11)#2	2.274(5)
Cd(1)–O(12)#4	2.327(5)		
Hydrogen bonding			
N(1)⋯O(21)#2	2.696(8)	N(1)–H(11A)⋯O(21)#2	151.6
O(13)⋯O(12)#6	2.580(7)	O(13)–H(13A)⋯O(12)#6	164.9
O(23)⋯O(21)#7	2.641(8)	O(23)–H(23A)⋯O(21)#7	166.5
O(22)#1–Cd(1)–O(22)	88.8(3)	O(22)#1–Cd(1)–O(11)#2	103.51(18)
O(22)–Cd(1)–O(11)#2	84.78(18)	O(11)#2–Cd(1)–O(11)#3	168.5(3)
O(22)#1–Cd(1)–O(12)#4	166.09(17)	O(22)–Cd(1)–O(12)#4	88.55(18)
O(11)#2–Cd(1)–O(12)#4	89.84(18)	O(11)#3–Cd(1)–O(12)#4	82.57(18)
O(12)#4–Cd(1)–O(12)#5	97.1(3)		

Symmetry transformations used to generate equivalent atoms: For complex **1**: #1: $-x, -y - 1, -z$; #2: $x, -y - 1, z - 1/2$; #3: $-x, -y - 1, -z - 1$; #4: $x, -y - 1, z + 1/2$; #5: $-x, y, -z - 1/2$; #6: $1 - x, y, 3/2 - z$; #7: $x, -y, 1/2 + z$; #8: $1 - x, 1 - y, 1 - z$.

For complex **2**: #1: $x, -y - 1/2, z + 1/2$; #2: $x, -y + 1/2, z + 1/2$; #3: $x, 1/2 - y, -1/2 + z$; #4: $x, -1 + y, z$; #5: $-x, 1/2 + y, 1/2 - z$.

For complex **3**: #1: $-x, y, -z + 3/2$; #2: $-x, y, -z + 1/2$; #3: $x, y, z + 1$; #4: $x, -y + 1, z + 1/2$; #5: $-x, -y + 1, -z + 1$; #6: $x, 1 - y, -1/2 + z$; #7: $-x, -y, 1 - z$.

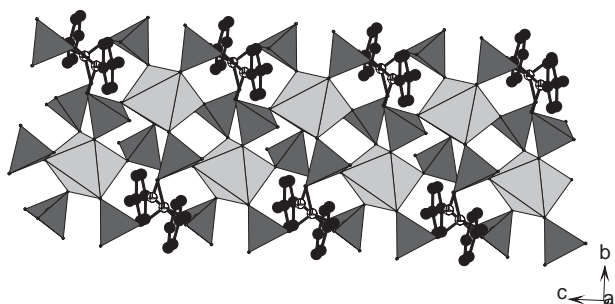


Fig. 2. A cadmium diphosphonate double chain along the *c*-axis in **1**. CdO₆ octahedra and C–PO₃ tetrahedra are shaded in light and dark gray, respectively. N and C atoms are shown as white and black circles, respectively.

and **4**). The above two types of layers are related to each other by the “C” lattice symmetry. O(11)–H(11a)⋯O(12) and O(21)–H(21a)⋯O(22) hydrogen-bond lengths are 2.598 and 2.650 Å, respectively, and the corresponding bond angles are 166.0° and 165.9°, respectively (Fig. 1, Table 2). These O⋯O contacts and angles are comparable to those for the complex **3** (Table 2). The interlayer distance of 12.2 Å of **1** is much smaller than that of **3** (14.0 Å), which can be attributed to the additional methyl group on the phenyl ring in L³. These interlayer distances are larger than that of cadmium complex with MeN(CH₂PO₃H₂)₂ (about 10.6 Å).

The structure of complex **2** features a $\langle 100 \rangle$ cadmium(II) diphosphonate layer. As shown in Fig. 5,

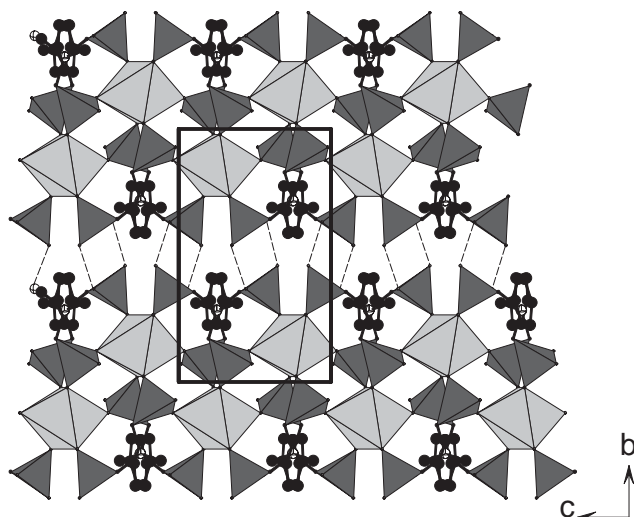


Fig. 3. A $\langle 200 \rangle$ hydrogen bonded layer built from cadmium diphosphonate double chains in **1**. CdO_6 octahedra and C-PO_3 tetrahedra are shaded in light and dark gray, respectively. N and C atoms are shown as octand and black circles, respectively. Hydrogen bonds are represented by dotted lines.

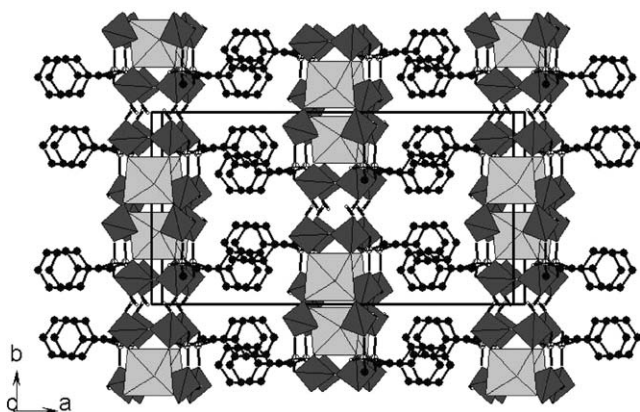


Fig. 4. View of structure of **1** along the c -axis. CdO_6 octahedra and C-PO_3 tetrahedra are shaded in light and dark gray, respectively. N and C atoms are shown as octand and black circles, respectively.

the cadmium atom lies on a position of -1 symmetry, and is octahedrally coordinated by six phosphonate oxygen atoms of six ligands. The Cd–O distances are in the range of 2.222(4)–2.304(5) Å, which are comparable to those of complexes **1** and **3** as well as other cadmium phosphonates [9b]. Similar to L^1 and L^3 , the L^2 ligand also adopts the tridentate bridging coordination mode, the phosphonate group containing P(1) atom is bidentate (O11 and O12), whereas the one containing P(2) atom is unidentate (O21) (Fig. 4). The lattice water molecules (O1w) is not coordinated to the Cd(II) ions, but forms hydrogen bonds with phosphonate oxygen atoms (O(1w)⋯O(21) 2.790 and O(1w)⋯O(22) 2.658) (Table 2). O(13), O(23) and N(1) atoms are protonated. Similar to that in complexes **1** and **3**, hydrogen bonds are also formed between the non-coordinated phosphonate oxygen atoms (Table 2).

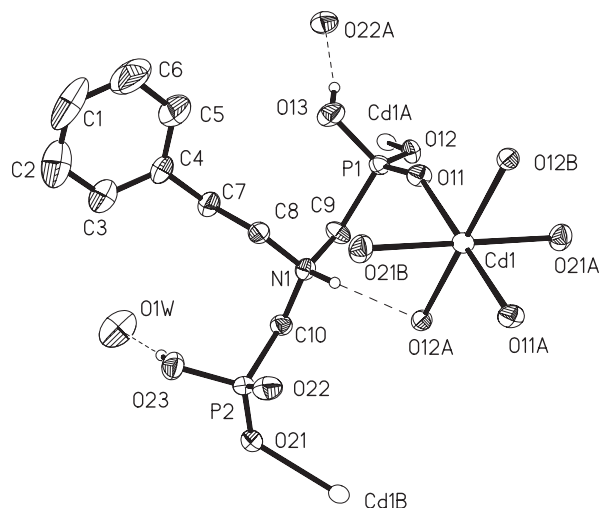


Fig. 5. ORTEP representation of the asymmetry unit of **2**. Thermal ellipsoids are drawn at 50% probability. The dotted lines represent hydrogen bonds.

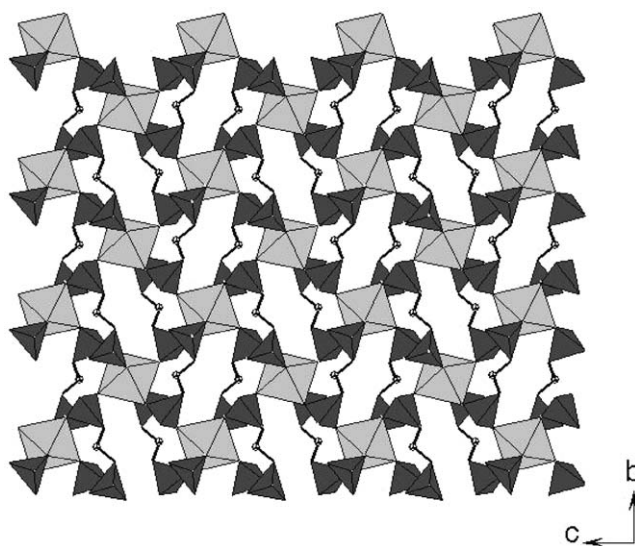


Fig. 6. A $\langle 100 \rangle$ cadmium diphosphonate layer in **2**. CdO_6 octahedra and C-PO_3 tetrahedra are shaded in light and dark gray, respectively. N and C atoms are shown as octand and black circles, respectively.

Unlike those in complexes **1** and **3**, the CdO_6 octahedra in complex **2** are interconnected via bridging ligands into a $\langle 100 \rangle$ layer (Fig. 6). Each pair of CdO_6 octahedra are bridged by two diphosphonate ligands, forming a 16-membered ring ($\text{Cd}-(\text{O}-\text{P}-\text{C}-\text{N}-\text{C}-\text{P}-\text{O})_2-\text{Cd}$). Similar to that in the cadmium complex with $\text{MeN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$, each CdO_6 octahedron bridges with four neighboring octahedra via four bidentate bridging phosphonate groups. As in complexes **1** and **3**, the phenyl groups act as pendant groups between two layers (Fig. 7). The lattice water molecules are also located at the interlayer space, forming hydrogen bonds with non-coordinated phosphonate oxygen atoms. The d -spacing

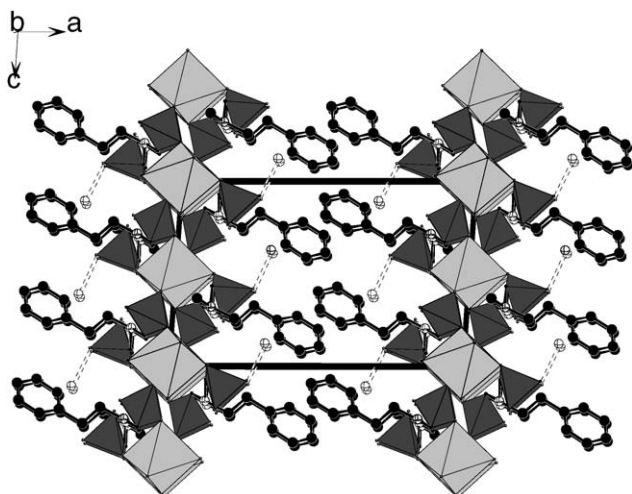


Fig. 7. View of structure of **2** along the *b*-axis. CdO_6 octahedra and C-PO_3 tetrahedra are shaded in light and dark gray, respectively. N, O and C atoms are shown as octahed, crossed and black circles, respectively. Hydrogen bonds are represented by dotted lines.

is about 16.3 \AA , which is much larger than those in complexes **1** and **3**.

It is interesting to compare the structures of the cadmium(II) complexes with $\text{RN}(\text{CH}_2\text{PO}_3\text{H}_2)$ ($R = \text{Me}$, $\text{C}_6\text{H}_5\text{-CH}_2\text{-}$, $4\text{-Me-C}_6\text{H}_5\text{-CH}_2\text{-}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{-}$). All four complexes have a metal/ligand ratio of 1:2 in which both phosphonate and the amine group of the ligand are 1H-protonated, due to the acidic media of the reactions. In all four cadmium complexes, the diphosphonic ligands are tridentate. The methyl group is small, so $\text{MeN}(\text{CH}_2\text{PO}_3\text{H}_2)$ can adopt a chelating and bridging coordination mode, the other three substitute groups are much larger in size and hence have greater steric hindrance, thus their diphosphonic acids adopt a tridentate bridging coordination mode. Since $\text{C}_6\text{H}_5\text{-CH}_2\text{-}$ and $4\text{-Me-C}_6\text{H}_5\text{-CH}_2\text{-}$ have a similar symmetry, thus complexes **1** and **3** have a same space group and a similar hydrogen bonded layered structure, the additional methyl group on the phenyl ring only increases the interlayer distance. When the substitute group is $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{-}$, the ligand has a different symmetry from those of H_4L^1 and H_4L^3 , thus complex **2** has a different space group and also a different layered structure with a larger *d*-spacing.

IR spectra for the three diphosphonate ligands and their cadmium(II) complexes were recorded between 4000 and 400 cm^{-1} and these spectra are quite similar. The region between 4000 and 1400 cm^{-1} can be selected to study in detail the hydrate water and the P–O–H groups. The weak band around 2939 to 2950 cm^{-1} can be attribute to the vibration of N–H group. The broad and intense band at 3350 cm^{-1} (for complex **2**) or 3450 cm^{-1} (for complex **3**) is due to the O–H stretching vibration of the hydrate water interacting by hydrogen bonding. The bending H–O–H vibration of the hydra-

tion water is located at around 1614 cm^{-1} (for complex **2**) or 1626 cm^{-1} (complex **3**). The bands in the region from 2742 to 2760 cm^{-1} for the ligands and their Cd(II) complexes are likely due to $\nu(\text{P-OH})$, which are characteristic of the hydrogen phosphonate groups. The set of bands between 1200 and 900 cm^{-1} is due to stretching vibrations of the tetrahedral C– PO_3 groups.

The TGA diagram for complex **2** indicates two main steps of weight losses, whereas those for complexes **1** and **3** show only one main step of weight loss. The first step for complex **2** is the loss of two lattice water molecules, which started at about 50°C and is completed at about 150°C , the observed weight loss of 3.9% is slightly less than the calculated value (4.8%). The second step covering a temperature range from 280°C to 1000°C , is similar to complexes **1** and **3**, during which two overlapping processes are taking place: the release of two water molecules formed by the condensation of hydrogen phosphonate groups and the pyrolysis of the organic group. The total weight losses are 46.2%, 54.3% and 50.6% for **1**, **2** and **3**, respectively, which are much less than the calculated ones of 61.4%, 60.0% and 62.2% respectively, for complexes **1**, **2** and **3**, if the final products are assumed to be $\text{Cd}(\text{PO}_3)_2$. As a result, the decomposing process is not complete at 1000°C because of the non-oxidizing N_2 atmosphere.

4. Conclusions

In conclusion, we have synthesized three new Cd(II) compounds with two different types of layered structures. The different substitute groups on the amine group can not only change the coordination modes that the diphosphonate ligands adopt and the structural types of the metal phosphonates formed, but also have a strong effect on the *d*-spacing. Future efforts will focus on the intercalation chemistry of these layered materials.

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