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Two new layered lead(II) diphosphonates with 1,3,5-benzenetricarboxylate ligands as an intercalated species or a multidentate metal linker

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Abstract

Hydrothermal reactions of lead(II) carbonate with 1,3,5-benzenetricarboxylic acid (H₃BTC) and butylimino-bis(methylenephosphonic acid) (CH₃CH₂CH₂CH₂CH₂N(CH₂PO₃H₂)₂, H₄L¹) or lead(II) acetate with H₃BTC and isobutylimino-bis(methylenephosphonic acid) (Me₂CHCH₂N(CH₂PO₃H₂)₂, H₄L²) afforded two novel lead(II) carboxylate phosphonate hybrids, namely, Pb₅(HL¹)₂(L¹)·H₃BTC **1** and Pb₄(BTC)(L²)(CH₃CO₂)(H₂O)₂·1.5H₂O **2**. The structure of compound **1** contains a <002> lead(II) diphosphonate hybrid layer formed by Pb(II) ions interconnected by HL¹ and L¹ anions. In compound **2**, the interconnection of Pb(II) ions through bridging diphosphonate L² anions lead to the formation of the <200> lead(II) diphosphonate 2D layer. In compound **1**, the 1,3,5-benzenetricarboxylic acid acts as an intercalated species whereas in compound **2**, the 1,3,5-benzenetricarboxylate anion adopts a hexadentate chelating and bridging coordination mode.

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Keywords: Hydrothermal synthesis; Layered compounds; Intercalation; Crystal structure

1. Introduction

Open-framework and microporous materials are a class of very important compounds due to their traditional applications in catalysis, separations, sorbents, and ion-exchange as well as their expected future use as hybrid composite materials in electro-optical and sensing applications [1,2]. Studies of metal phosphonates have shown that the use of bisfunctional or multifunctional anionic units, such as diphosphonates, aminophosphonates or phosphonocarboxylates can lead to a number of new materials with microporous or open-framework structures [3–17]. Recently we have also isolated a microporous Cd(II) compound with N,N'-bis(phosphonomethyl)-1,10-diaza-18-crown ether [18]. Several porous Zr(IV) compounds with aza-crown ether functionalised

phosphonic acids have been synthesized by using phosphoric acid as the spacer [19,20]. Direct use of two types of ligands in the preparation, such as the phosphonic acid with the carboxylic acid [21-23], the sulfonic acids [21], the oxalate ion [24,25], the 2,2'-bipy [26], 4,4'-bipy [27], or 1,10-phenanththroline [28], etc. has been found to be another useful method to build hybrid open-frameworks. A 3D openframework of tin(II) phosphonopropionate oxalate and a layered tin(II) methylphosphonate oxalate have been reported by the Cheetham group [24,25], and a microporous zinc(II) compound with phosphonopropionic acid and 1,3,5-benzenetricarboxylic acid (H₃BTC) was isolated, in which the tricarboxylate moiety remains non-coordinated and is also severely disordered [2]. Several Pb(II) compounds of phosphonopropionic acid with 1,3,5-benzenetricarboxylic acid (H₃BTC) or 3-HO₃S-C₆H₄-CO₂H were isolated by our group [21–23]. We have initiated a research program to study the intercalation chemistry of the layered metal diphosphonates with carboxylic acids and sulfonic acids; such hybrids may have good proton conductivity as well as ionexchange properties due to the presence of protons with stronger acidity. As an expansion of our work, we have

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synthesized two new aminodiphosphonic acids, namely butylimino-bis(methylene-phosphonic acid) (CH₃CH₂CH₂ CH₂N(CH₂PO₃H₂)₂, H₄L¹) and isobutylimino-bis(methylene-phosphonic acid) (Me₂CHCH₂N(CH₂PO₃H₂)₂, H₄L²). Hydrothermal reactions of lead(II) salts with 1,3,5-benzenetricarboxylic acid (H₃BTC) and the above two diphosphonate ligands afforded two new layered lead(II) carboxylate phosphonates, namely Pb₅(HL¹)₂(L¹)·H₃BTC and Pb₄(BTC)(L²)(CH₃CO₂)(H₂O)₂·1.5H₂O. Herein we report their syntheses, characterizations and crystal structures.

2. Experimental

2.1. Materials and methods

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out with a NETZSCH/STA 449C unit at a heating rate of 15 °C/min under an oxygen atmosphere. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer using KBr pellets in the 4000–400 cm⁻¹. ¹H and ³¹P NMR spectra were recorded on a Varian Unity 500 NMR in D₂O. H₃PO₄ was used as ³¹P standard reference. XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated Cu Ka radiation in the angular range $2\theta = 5-70^{\circ}$ with a step size of 0.02° and a counting time of 3 s per step. Since the bulk reaction products contain some impurities based on XRD powder studies, single crystals for compounds 1 and 2 are selected manually and used for EA, IR and TGA analyses.

2.2. Syntheses of H_4L^1 and H_4L^2

 H_4L^1 and H_4L^2 were prepared by a Mannich type reaction according to the procedures previously described [29].

Butylamine (100 mmol, about 10 ml) was mixed with 36% hydrochloric acid (16.0 cm³), deionized water (20 ml) and phosphorous acid (400 mmol, 32.8 g). The mixture was allowed to reflux at 120 °C for 1 h, then paraformaldehyde (300 mmol, 9 g) was added in small portions over a period of 1 h, and the mixture was then refluxed for an additional hour. Removal of solvents afforded 18.1 g of a white powder of H₄L¹ (yield 72% based on butylamine). Its purity was confirmed by NMR measurements and elemental analysis. ³¹P NMR shows a single peak at 8.5 ppm. ¹H NMR: 0.94 ppm (CH₃-, t, 3H), 1.39 ppm (Me-CH₂-, q, 2H), 1.75 ppm (Et-CH₂-, t, 2H), 3.51 ppm (R-CH₂-N, t, 2H), 3.56 ppm (N-CH₂-PO₃, d, 4H, J_{H-P} =9.5 Hz). Elemental analysis for H₄L¹, C₆H₁₇NP₂O₆ (M_r =261.12): C, 27.38; H, 6.75; N, 5.20%. Calcd: C, 27.57; H, 6.51; N, 5.36%.

 H_4L^2 was prepared by a method similar to that for $H_4L^{1.31}P$ NMR shows a single peak at 9.0 ppm. ¹H NMR: 1.02 ppm (CH₃-, d, 6H, J_{H-H} =6.5 Hz), 2.19 ppm (Me₂CH-, t, 1H),

3.38 ppm (R-CH₂–N, d, 2H, $J_{H-H}=7$ Hz), 3.57 ppm (N–CH₂–PO₃, d, 4H, $J_{H-P}=12.0$ Hz). Elemental analysis for H₄L², C₆H₁₇NP₂O₆ ($M_r=261$): C, 27.37; H, 6.10; N, 5.14%. Calcd: C, 27.57; H, 6.51; N, 5.36%.

2.3. Syntheses of $Pb_5(HL^1)_2(L^1) \cdot H_3BTC \mathbf{1}$

A mixture of 0.271 g of PbCO₃ (1.0 mmol), 0.130 g of H_4L^1 (0.5 mmol), 0.106 g of 1,3,5-benzenetricarboxylic acid (0.5 mmol) and 15 ml of deionized water were sealed into a bomb equipped with a Teflon liner (20 ml), and then heated at 180 °C for 5 days. The initial and final pH values of solution were 4.0 and 5.0, respectively. Colorless plate crystals of compound **1** were recovered in ca. 59% yield based on Pb. Elemental analysis for **1**, C₂₇H₄₇N₃O₂₄P₆Pb₅ (M_r =2019.45): C, 16.20; H, 2.03; N, 2.02%. Calcd: C, 16.04; H, 2.32; N, 2.08%. IR data (KBr, cm⁻¹): 2959(s), 2873(s), 1735(s), 1710(s), 1610(s), 1521(s), 1435(s), 1350(s), 1263(s), 1207(s), 1015(vs), 731(s), 661(m), 591(s), 547(s), 507(s), 491(m).

2.4. Syntheses of $Pb_4(BTC)(L^2)(CH_3CO_2)(H_2O)_2 \cdot 1.5H_2O$ 2

A mixture of 0.570 g mmol of Pb(CH₃COO)₂·3H₂O (1.5 mmol), 0.133 g of H₄L² (0.5 mmol), 0.102 g of 1,3,5benzenetricarboxylic acid (0.5 mmol) and 15 ml of deionized water were sealed into a bomb equipped with a Teflon liner (20 ml), and then heated at 180 °C for 5 days. The initial and final pH values of the solution were 5.0 and 6.0, respectively. Prismatic colorless crystals of compound **2** were recovered in ca. 70% yield based on Pb. Elemental analysis for **2**, $C_{17}H_{26}NO_{17.5}P_2Pb_4$ (M_r =1415.09): C, 14.50; H, 1.83; N, 1.00%. Calcd: C, 14.43; H, 1.85; N, 0.99%. IR data (KBr, cm⁻¹): 3371(m), 3189(m), 2959(m), 1680(m), 1611(s), 1544(s), 1432(s), 1364(vs), 1107(s), 1071(s), 1011(s), 980(s), 959(s), 769(m), 723(s), 601(m), 571(m), 537(m), 517(m), 477(m).

2.5. X-ray crystallography

Single crystal of compounds 1 (size: $0.26 \times 0.24 \times$ 0.06 mm) and 2 (size: $0.62 \times 0.12 \times 0.10$ mm) were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$ respectively. Intensity data were collected by the narrow frame method at 293 K. Both data sets were corrected for Lorentz and Polarization factors as well as for absorption by ψ scan technique. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX-97 [30]. Phosphonate oxygen atoms (O(11), O(12), O(13), O(32) and O(33)) of compound **1** and C(5), C(6) and O(2W) of compound 2 were disordered and were split into two orientations each with 50% occupancy. These atoms as well as C(5), O(31), O(52) and O(53) of compound 1 as well as O(1) of compound 2 were refined with isotropic thermal parameters. O(4w) atom with a short Selected bond lengths (Å) for compound 1

Table 1

Compound

Empirical formula

Formula weight

Crystal system

Crystal size (mm)

Space group

b (Å)

c (Å)

α (°)

 β (°)

 γ (°)

Ζ

 $V(Å^3)$

F(000)

 $D_{\rm c} \,({\rm g}\,{\rm cm}^{-3})$

 μ (Mo K α) (mm⁻¹⁾

Reflections collected

Goodness-of-fit on F²

*R*1, *wR*2 [$I > 2\sigma(I)$]

R1, wR2 (all data)

Unique reflections

Observed data

 $[I > 2\sigma(I)]$

Table 2

Crystal data and structural refinements for compounds 1 and 2

2019.45

Triclinic

P - 1 (No. 2)

12.6374(3)

19.6463(6)

76.4100(10)

81.6600(10)

76.4730(10)

2354.65(13)

2

2.848

18.104

10,983

7597 ($R_{int} = 0.0459$)

0.0613, 0.1317

0.0751, 0.1440

 $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|, wR2 = \left\{ \sum w[(F_0)^2 - (F_c)^2]^2 / \sum w[(F_0)^2]^2 \right\}^{1/2}$

1844

6677

1.207

C27H47N3O24P6Pb5

 $0.26 \times 0.24 \times 0.06$

1

| Pb(1)-O(13) | 2.397(18) | Pb(1)-O(51) | 2.515(15) |
|----------------|-----------|---------------|-----------|
| Pb(1)–O(22) | 2.536(16) | Pb(1)-O(42)#1 | 2.645(13) |
| Pb(1)–N(1) | 2.732(17) | Pb(1)-O(53)#1 | 2.758(13) |
| Pb(2)-O(32)#2 | 2.19(2) | Pb(2)-O(12)#3 | 2.313(16) |
| Pb(2)-O(42)#2 | 2.601(14) | Pb(2)–O(31) | 2.65(2) |
| Pb(3)-O(33)#6 | 2.460(18) | Pb(3)–O(13) | 2.592(19) |
| Pb(3)–O(51) | 2.631(16) | Pb(3)–O(22) | 2.705(14) |
| Pb(3)-O(11)#5 | 2.75(2) | Pb(4)-O(23) | 2.281(13) |
| Pb(4)-O(52)#7 | 2.436(11) | Pb(4)-O(21)#3 | 2.479(12) |
| Pb(4)-O(31)#6 | 2.71(2) | Pb(4)–O(61) | 2.750(14) |
| Pb(5)–O(53) | 2.422(12) | Pb(5)–O(61) | 2.516(14) |
| Pb(5)–O(43) | 2.569(14) | Pb(5)–O(22) | 2.712(15) |
| Pb(5)-O(21)#3 | 2.751(14) | P(1)–O(11) | 1.563(15) |
| P(1)-O(12) | 1.418(15) | P(1)–O(13) | 1.512(14) |
| P(1)-C(5) | 1.82(2) | P(2)–C(6) | 1.814(19) |
| P(2)–O(21) | 1.501(12) | P(2)–O(22) | 1.525(13) |
| P(2)-O(23) | 1.537(14) | P(3)–O(32) | 1.430(15) |
| P(3)–O(31) | 1.476(14) | P(3)–O(33) | 1.542(16) |
| P(3)-C(11) | 1.80(2) | P(4)-C(12) | 1.79(2) |
| P(4)–O(41) | 1.497(14) | P(4)–O(43) | 1.538(14) |
| P(4)-O(42) | 1.566(15) | P(5)-O(52) | 1.521(13) |
| P(5)–O(51) | 1.524(15) | P(5)–O(53) | 1.532(13) |
| P(5)-C(17) | 1.845(19) | P(6)–C(18) | 1.787(19) |
| P(6)-O(63) | 1.498(14) | P(6)–O(61) | 1.505(16) |
| P(6)-O(62) | 1.552(14) | C(27)–O(1) | 1.17(4) |
| C(27)–O(2) | 1.30(4) | C(28)–O(3) | 1.26(4) |
| C(28)–O(4) | 1.22(4) | C(29)–O(5) | 1.33(4) |
| C(29)–O(6) | 1.24(4) | | |
| Hydrogen bonds | | | |
| O(2)···O(41)#7 | 2.49(2) | O(63)····O(3) | 2.63(3) |

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

Table 3 Selected bond lengths (Å) for compound **2**

| Pb(1)-O(22) | 2.340(11) | Pb(1)-O(23)#1 | 2.349(12) |
|----------------------|-----------|-----------------------|-----------|
| Pb(1)-O(13) | 2.474(11) | Pb(1)–N | 2.655(16) |
| Pb(2)-O(1W) | 2.51(2) | Pb(2)-O(2W) | 2.58(4) |
| Pb(2)–O(3) | 2.619(14) | Pb(2)-O(1)#2 | 2.70(3) |
| Pb(3)-O(5)#3 | 2.534(12) | Pb(3)–O(13) | 2.543(11) |
| Pb(3)–O(2) | 2.577(15) | Pb(3)-O(6)#3 | 2.626(12) |
| Pb(3)-O(11)#4 | 2.674(12) | Pb(3)-O(4)#5 | 2.727(13) |
| Pb(3)-O(21)#1 | 2.730(12) | Pb(4)–O(12) | 2.362(15) |
| Pb(4)-O(21)#2 | 2.375(12) | Pb(4)-O(11)#4 | 2.378(14) |
| Pb(4)–O(8) | 2.68(2) | P(1)–O(11) | 1.547(13) |
| P(1)-O(12) | 1.533(15) | P(1)–O(13) | 1.519(12) |
| P(1)–C(1) | 1.840(17) | P(2)–C(2) | 1.806(17) |
| P(2)-O(21) | 1.532(11) | P(2)–O(22) | 1.514(12) |
| P(2)-O(23) | 1.510(13) | C(13)–O(1) | 1.22(3) |
| C(13)–O(2) | 1.24(2) | C(14)–O(3) | 1.25(2) |
| C(14)–O(4) | 1.24(2) | C(15)–O(5) | 1.24(2) |
| C(15)–O(6) | 1.29(2) | C(17)–O(8) | 1.226(18) |
| C(17)–O(7) | 1.27(3) | | |
| Hydrogen bonds | | | |
| $O(1w) \cdots O(4w)$ | 2.42(4) | $O(2w') \cdots O(4w)$ | 2.40(5) |
| O(2w)…O(1)#2 | 2.81(5) | O(2w)…O(3)#6 | 2.77(5) |
| O(4w)…O(8)#7 | 2.81(4) | | |
| | | | |

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

 $O(4w)\cdots O(4w)$ separation of 2.2 Å (symmetry code: 3-x, -2-y, -z) and a high thermal parameter were also considered to be disordered and refined with 50% occupancy. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The final difference Fourier maps showed featureless residual peaks of 2.770 e Å⁻³ (for compound **1**, 0.917 Å from Pb(2) atom) or 3.92 e Å⁻³(for compound **2**, 0.716 Å from Pb(4) atom), respectively. All hydrogen atoms were located at geometrically calculated positions. The hydrogen atoms of the water molecules were not included in the refinements. Crystallographic data and structural refinements are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively, for compounds 1 and 2. More details about the crystallographic data have been deposited as supplementary materials.

CCDC-232745 and -232746 contain the supplementary crystallographic data for this paper. These data can be



Fig. 1. The coordination geometries around the lead(II) ions in compound 1.

C17H26NO17.5P2Pb4

1415.09

Triclinic

P - 1 (No. 2)

10.1260(7)

16.0737(10)

99.4650(10) 98.7020(10)

105.8750(10)

1512.43(17)

5289 ($R_{int} = 0.0793$)

2

3.107

22.377

1276

7918

4611

1.055

0.0611, 0.1540

0.0715, 0.1661

 $0.62 \times 0.12 \times 0.10$



Fig. 2. The coordination modes of aminodiphosphonate anions in compound 1.

obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; E-mail: deposit@ccdc. cam.ac.uk].

3. Results and discussion

Compound 1 contains five lead(II) ions, one full deprotonated L¹ anions, two single-protonated anions, and one neutral 1,3,5-benzenetricarboxylic acid in its asymmetric unit. As shown in Fig. 1, Pb(1) is six-coordinated by a tridentate chelating L^1 anion (N(1), O(13) and O(22)) and three phosphonate oxygen atoms from three HL¹ anions in an irregular PbO₅N polyhedron. Pb(2) is four-coordinated by four phosphonate oxygen atoms from two HL¹ and one L^1 anions. The coordination geometry around Pb(2) can be described as a severely distorted ψ -PbO₄ square pyramid with one square site occupied by the lone pair of the Pb(II) ion. Pb(3) is five-coordinated by a bidentate chelating L^{1} anion (O(13), O(22)) and three phosphonate oxygen atoms from two HL^1 and one L^1 anions. The coordination geometry around Pb(3) can be described as a ψ -PbO₅ octahedron with one apex occupied by the lone pair of the Pb(II) ion. Pb(4) is five-coordinated by five phosphonate oxygen atoms from two HL^1 and three L^1 anions. Pb(5) is five-coordinated by a bidentate chelating HL^1 anion (O(53) and O(61)) and three phosphonate oxygen atoms from one HL^{1} and two L^{1} anions. Pb(4) and Pb(5) have coordination geometry similar to that of Pb(3). The Pb-O distances range from 2.19(2) to 2.758(13) Å and Pb(1)-N(1) distance is 2.732(17) Å (Table 2), which are comparable to those reported for other Pb(II) aminodiphosphonates [21-23].

The diphosphonate anions in compound **1** adopt three different types of coordinated modes (Fig. 2). The diphosphonate anion containing P(1) and P(2) is undecadentate, it chelates with Pb(1) tridentately (N(1), O(13) and O(22)), and chelates with Pb(3) bidentately (O(13) and O(22)) and also bridges with six other Pb(II) ions. All six phosphonate oxygen atoms are involved in metal coordination, hence this diphosphonate ligand has been deprotonated completely. Two phosphonate oxygen atoms (O(13) and O(21)) are bidentate metal linkers and O(22) acts as a tridentate metal

linker. The diphosphonate anion containing P(3) and P(4) is heptadentate. It chelates with Pb(2) bidentately (O(32) and O(42)) and bridges with five other Pb(II) ions. One phosphonate oxygen (O(41)) remains non-coordinated. Two phosphonate oxygen atoms (O(31) and O(42)) are bidentate metal linkers. Its amine group is singly protonated and remains non-coordinated. The diphosphonate anion containing P(5) and P(6) is also heptadentate, it chelates with Pb(5) bidentately (O(53) and O(61)) and bridges with five other Pb(II) ions. Two phosphonate oxygen atoms (O(62) and O(63)) remain non-coordinated and O(62) is considered to be singly protonated based on its longer P-O distance (1.552(14) Å compared with 1.505(16) and 1.498(14) Å for two other P–O bonds). Three phosphonate oxygens (O(51), O(53) and O(61)) are bidentate metal linkers. The amine group is non-coordinated.

The interconnection of the lead(II) ions via diphosphonate ligands lead to a <002> lead(II) diphosphonate layer (Fig. 3). Based on C–O distances as well as the requirement for charge balance, all three carboxylate groups of the 1,3,5-benzenetricarboxylate remain protonated (Table 2). This neutral carboxylate ligand acts as an intercalated species between two metal phosphonate layers (Fig. 4), forming strong hydrogen bonds with the uncoordinated phosphonate



Fig. 3. View of a <002> 2D layer of lead(II) diphosphonate in compound 1 along the *c*-axis. The butyl groups were omitted for clarity. The C–PO₃ tetrahedra are shaded in gray. Pb and N atoms are represented by open and octanded circles.



Fig. 4. View of the structure of compound 1 along the *b*-axis. The C–PO₃ tetrahedra are shaded in gray. Pb, N, O and C atoms are represented by open, octanded, crossed and black circles. Hydrogen bonds are drawn as dotted lines.

oxygen atoms (O(41) and O(63)) of the L¹ ligands. The O···O contacts are 2.49(2) and 2.63(3) Å, respectively (Table 2). There is no $\pi \cdots \pi$ interaction between neighboring H₃BTC molecules since the shortest distance between two parallel benzene rings is 5.435 Å.

Pb₄(BTC)(L²)(CH₃CO₂)(H₂O)₂ \cdot 1.5H₂O **2** has a layered structure in which the 1,3,5-benzenetricarboxylate ligand functioned as a multidentate metal linker. Compound **2** is composed of one full deprotonated L² ligand, one fully deprotonated 1,3,5-benzenetricarboxylate anion, two aqua ligands as well as two lattice water molecules. As shown in Fig. 5, Pb(1) is four-coordinated by three phosphonate oxygen atoms and one N atom from two diphosphonate ligands, its coordination geometry can be viewed as ψ -PbO₄ square pyramid with the pyramidal site occupied by the lone pair of the Pb(II) ion. Pb(2) is four-coordinated by two carboxylate oxygen atoms from two 1,3,5-benzenetricarboxylate anions and two aqua ligands, its coordination geometry can be viewed as ψ -PbO₄ trigonal bipyramid with

one pyramidal site occupied by the lone pair of the Pb(II) ion. Pb(3) is seven-coordinated by three carboxylate groups from three BTC anions, one in a bidenate chelating fashion and the other two in a unidentate fashion, as well as three phosphonate oxygens from three diphosphonate anions in an irregular PbO₇ polyhedron. Pb(4) is four-coordinated by three phosphonate oxygen atoms from three diphosphonate anions and an oxygen atom from an acetate anion (O(8)). The coordination geometry around Pb(4) can be viewed as ψ -PbO₄ trigonal bipyramid with one trigonal site occupied by the lone pair of the Pb(II) ion. The Pb–O distances are in the range from 2.340(11) to 2.730(12) Å, and the Pb(1)–N distance is 2.655(16) Å (Table 3), which are comparable to those reported for other Pb(II) aminodiphosphonates [21-23]. The iso-butyl-substituted aminodiphosphonate ligand adopts a coordination mode which is different from those of the *n*-butyl-substituted aminodiphosphonate ligands in compound 1. The diphosphonate anion is decadentate, it chelates with one Pb tridentately and also



Fig. 5. The coordination geometries around the lead(II) ions and the coordination modes of aminodiphosphonate anions in compound 2.



Fig. 6. A 1D chain of lead(II) diphosphonate (a) and a 1D double chain of lead(II) tricarboxylate (b) in compound **2**. The C–PO₃ tetrahedra are shaded in gray. The Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively.

bridges with seven other Pb atoms (Fig. 5). Several factors that may affect the coordination mode of the diphohphonate ligand include the pH value, the different substituents on the amine group, the nature of the second ligand, the metal/ ligand ratio, and the nature of the metal ion used [18,22]. In current case, we deem that the pH value, the metal/ ligand ratio as well as the substituent are key factors. Unlike non-coordination H₃BTC in compound **1**, the BTC anion in compound **2** is hexadentate, it chelates one Pb atom bidentately and bridges with other four Pb atom (Fig. 5). Based on coordination modes as well as P–O and C–O distances, both 1,3,5-benzenetricarboxylate anion and the L² anion have been fully deprotonated (Table 3). The acetate ligand is unidentate (O(8)) and one carboxylate oxygen atom (O(7)) remains non-coordinated. The interconnection of Pb(II) ions via bridging L² anions lead to a 1D chain along *b*-axis, whereas the cross-linkage of Pb(II) by BTC anions resulted in a 1D chains along *b*-axis (Fig. 6). The interconnection of the above two types of 1D chains lead to the formation of a <002> lead(II) carboxylate-phosphonate layer (Fig. 7). The lattice water molecules are located at the cavities of the lead(II) carboxylate-phosphonate layer and are involved in hydrogen-bonding (Fig. 8, Table 3). These 2D layers are held together via hydrogen bond between O(2w) and O(3) (2.77(5) Å, symmetry code: 2-x, 2-y, -z) (Fig. 8).

IR spectra of compound **1** shows the absorption bands of the non-coordination carboxyl groups (ν_{COO} at 1710 and 1435 cm⁻¹ (see Supporting materials). These bands are shifted to 1611 and 1432 cm⁻¹ in compound **2** due to the coordination of the carboxylate groups with the lead(II) ions. The vibrations of the phosphonate groups are in the region 900–1100 cm⁻¹ [18].

TGA curves of compound **1** exhibit two steps of weight losses (see Supporting materials). Compound **1** is stable up to 292 °C. The first step started at 292 °C and completed at 537 °C corresponding to the release of the intercalated H₃BTC molecules and the partial decomposition of the diphosphonate ligands. The observed weight loss is 19.8%. The second started at 820 °C and continued up to 1000 °C, corresponding to the further burning of the aminodiphosphonate anions. The final product is Pb₂P₂O₇. The total weight loss of 27.9% is close to the calculated value (27.2%). The TGA curves of compound **2** reveal three main steps of weight losses (see Supporting materials). The first step started at about 60 °C and completed at about 151 °C



Fig. 7. A <002> lead carboxylate-phosphonate hybrid layer in compound **2** down the *c*-axis. The C–PO₃ tetrahedra are shaded in gray, and Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively. The water molecules are omitted for clarity.



Fig. 8. View of the structure of compound **2** along the *a*-axis. The C–PO₃ tetrahedra are shaded in gray, and Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively.

corresponding to the release of aqua ligands and lattice water molecules, the observed weight loss of 4.56% is close to the calculated value (4.45%). The second weight loss started at 378 °C and complete at about 509 °C corresponding to the loss of the BTC anion, and the acetate anion. The observed weight loss of 20.4% is slightly large than the calculated value (18.8%). The third step started at 802 °C and continued up to 1000 °C, corresponds to the burning of the diphosphonate ligand. The final product is PbO. The total weight loss (35.4%) is slightly smaller than the calculated value (37.4%).

4. Conclusions

In summary, by hydrothermal reactions of lead(II) carbonate (or lead(II) acetate) with amino-diphosphonic acid and 1,3,5-benzenetricarboxylic acid, two new layered lead(II) carboxylate–phosphonate hybrids were obtained. The 1,3,5-benzenetricarboxylate ligand in compound 1 acts as an intercalated species between the 2D layers, whereas the 1,3,5-benzenetricarboxylate ligands in compound 2 functions as a multidentate metal linker. Under acidic conditions, the 1,3,5-benzenetricarboxylate ligand will remain protonated and act as intercalated species, whereas under higher pH condition it will be deprotonated and function as a multidentate metal linker. It is believed that a wide range of other new open-frameworks and microporous materials can be developed by using this ligand-hybrid technique.

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Appendix. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2005. 03.008

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