Novel Layered Lead(II) Aminodiphosphonates with Carboxylate-Sulfonate and 1,3,5-Benzenetricarboxylate Ligands as Pendant Groups or Intercalated Species

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The hydrothermal reaction of lead(II) carbonate with 3-sulfobenzoic acid, $3\text{-HO}_3\text{S–C}_6\text{H}_4\text{–CO}_2\text{H}$, and isopropylimino-bis(methylenephosphonic acid), $(\text{CH}_3)_2\text{CHN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ (H_4L^1), gave a new layered lead(II) carboxylate-phosphonate, $\text{Pb}_7(3\text{-O}_3\text{S–C}_6\text{H}_4\text{–CO}_2)(\text{L}^1)_3(\text{H}_2\text{O})_2\cdot 2\text{H}_2\text{O}$ (**1**), whereas the hydrothermal reaction of lead(II) carbonate with **1**, 3,5-benzenetricarboxylic acid (H_3BTC) and *N*-cyclohexylimino-bis(methylenephosphonic acid), $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ (H_4L^2), afforded a layered complex, $\text{Pb}_3(\text{HL}^2)(\text{H}_2\text{L}^2)(\text{H}_2\text{BTC})(\text{H}_2\text{O})\cdot\text{H}_3\text{BTC}\cdot\text{H}_2\text{O}$ (**2**). The structure of complex **1** contains <010> lead(II) carboxylate-phosphonate hybrid layers, with the sulfonate group of the carboxylate-sulfonate ligand as the pendant group. In complex **2**, the lead(II) ions are interconnected through bridging diphosphonate ligands, and results in the formation of a lead(II) diphosphonate slab, which are further interlinked via hydrogen bonds between non-coordinated phosphonate oxygen atoms to form a <001> layer. The doubly protonated H_2BTC anion is bidentately chelated to a lead(II) ion through a carboxylate group, whereas the neutral H_3BTC ligand is intercalated between two layers, forming hydrogen bonds with the non-coordinated carboxylate groups of the H_2BTC anion.

Introduction

Materials with open-framework and microporous structures are a class of very important compounds due to their traditional applications in catalysis, separations, sorbents, and ion exchange. Further, it is expected that these compounds could be used as hybrid composite materials in electro-optical and sensing applications.[1,2] Studies of metal phosphonates have shown that the use of bifunctional or multifunctional anionic units, such as diphosphonates, aminophosphonates or phosphonocarboxylates can lead to new materials with microporous or open-framework structures.[3−6] Recently, we have isolated a microporous Cd^{II} complex with the *N*,*N′*-bis(phosphonomethyl)-1,10-diaza-18-crown ether.[7] Several porous Zr^{IV} complexes with aza-crown ether functionalized phosphonic acids have been synthesized using phosphoric acid as the spacer.[8] The direct use of two types of ligands in the preparation, such as a phosphonic acid and a carboxylic acid, has been found to be another effective method for the exploration of hybrid open-frameworks; however, such reports are still rare.[2,9,10] A 3-D open-framework tin(II) phosphonopropionate oxalate and a layered tin(II) methylphosphonate oxalate have previously been reported by Cheetham and co-workers,[9] and a microporous zinc(II) complex of phosphonopropionic acid and 1,3,5-benzene-tricarboxylic acid (H_3BTC) has been isolated, in which the tricarboxylate moiety remains non-coordinated and is also severely disordered.[2] Recently, we reported two novel porous lead(II) carboxylate-phosphonates in which both types of ligands act as multidentate metal linkers.[10] We have initiated a research program in order to study the intercalation chemistry of the layered lead(II) diphosphonates with various types carboxylic acids and sulfonic acids. Such hybrids may have good proton conductivities, as well as ion-exchange properties, due to the presence of protons with greater acidity. The hydrothermal reaction of lead(II) carbonate with 3-sulfobenzoic acid, $3\text{-HO}_3\text{S}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$, and isopropylimino-bis(methylenephosphonic acid), $(\text{CH}_3)_2\text{CHN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ (H_4L^1), gave a new layered lead(II) carboxylate-phosphonate, $\text{Pb}_7(3\text{-O}_3\text{S}-\text{C}_6\text{H}_4-\text{CO}_2)(\text{L}^1)_3(\text{H}_2\text{O})_2\cdot 2\text{H}_2\text{O}$ (**1**), whereas the hydrothermal reaction of lead(II) carbonate with **1**, 3,5-benzenetricarboxylic acid (H_3BTC) and *N*-cyclohexylimino-bis(methylenephosphonic acid), $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ (H_4L^2), afforded a layered complex, $\text{Pb}_3(\text{HL}^2)(\text{H}_2\text{L}^2)(\text{H}_2\text{BTC})(\text{H}_2\text{O})\cdot\text{H}_3\text{BTC}\cdot\text{H}_2\text{O}$ (**2**). Herein, we report on the syntheses, characterizations and crystal structures of these compounds.

Results and Discussion

The hydrothermal reaction of lead(II) carbonate with 3-sulfobenzoic acid, $3\text{-HO}_3\text{S}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$, and isopro-

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pylimino-bis(methylenephosphonic acid), $(CH_3)_2CHN(CH_2PO_3H_2)_2$ (H_4L^1), gave a new layered lead(II) carboxylatephosphonate, $Pb_7(3\text{-}O_3S-C_6H_4-CO_2)(L^1)_3(H_2O)_2\cdot 2H_2O$ (**1**), whereas the hydrothermal reaction of lead(II) carbonate with **1**, 1,3,5-benzenetricarboxylic acid (H_3BTC) and *N*-cyclohexylimino-bis(methylenephosphonic acid), $C_6H_{11}N(CH_2PO_3H_2)_2$ (H_4L^2), afforded a layered complex, $Pb_3(HL^2)(H_2L^2)(H_2BTC)(H_2O)\cdot H_3BTC\cdot H_2O$ (**2**). We believe that many more new inorganic-organic hybrid materials will be developed using the synthetic technique of mixing two different types of ligands.

$Pb_7(3\text{-}O_3S-C_6H_4-CO_2)(L^1)_3(H_2O)_2\cdot 2H_2O$ (**1**) is the first structurally characterized metal phosphonate-sulfonate hybrid. It is composed of seven lead(II) ions, three fully deprotonated L^1 ligands, one $3\text{-}O_3S-C_6H_4-CO_2$ dianion, two aqua ligands and two lattice water molecules. As shown in Figure 1, Pb1 is six-coordinate and is bonded to a tridentate chelating L^1 anion (N3, O52 and O62), two phosphonate oxygen atoms from two other L^1 anions (O13 and O12), as well as to a carboxylate oxygen atom from a carboxylate-sulfonate ligand. Pb1 exhibits a distorted octahedral coordination geometry. Pb2 is four-coordinate and is bonded to three phosphonate oxygen atoms from three L^1 anions and one carboxylate oxygen atom from a sulfonate ligand. The coordination geometry around Pb2 can be described as a ψ-PbO_4 trigonal bipyramid, with the fifth coordination site occupied by the lone pair of electrons from the Pb^{II} ion. Pb3 is five-coordinate and is bonded to a tridentate chelating L^1 anion (N2, O32, O42) and two phosphonate oxygen atoms from two other L^1 anions; it exhibits a ψ-PbO_5 octahedral geometry, with the sixth coordination site occupied by the lone pair of electrons from the Pb^{II} ion. Pb4, Pb5 and Pb6 have a coordination geometry similar to that exhibited by Pb3; they are all five-coordinate and are bonded to a bidentate chelating L^1 ligand (O51 and O52 for Pb4; O31 and O43 for Pb5; O52 and O63 for Pb6) and three phosphonate oxygen atoms from three other L^1 anions. Pb7 is four-coordinate and is bonded to two phosphonate oxygen atoms from two L^1 anions and two aqua ligands, and exhibits a ψ-PbO_4 trigonal bipyramidal geometry with the fifth coordination site occupied by the lone pair of electrons

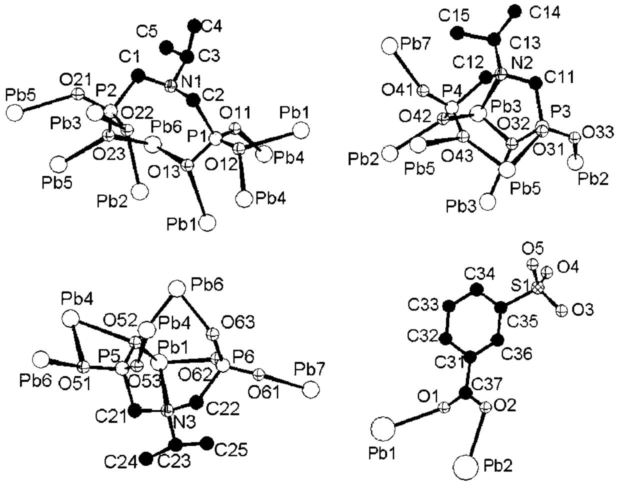

Figure 2. The coordination modes of L^2 and sulfo-carboxylate ligands in complex **1**

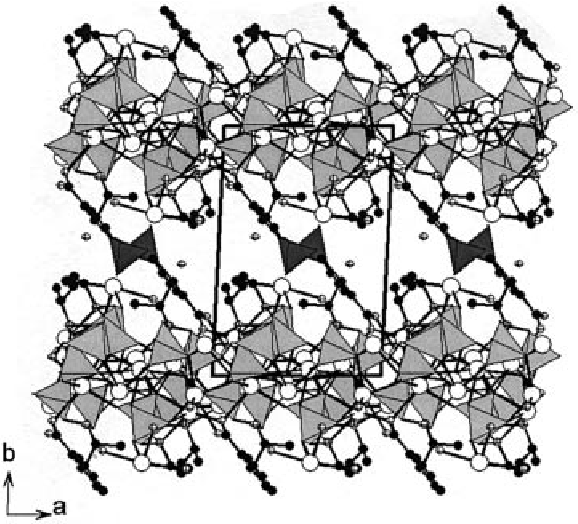

Figure 3. View of the structure of complex **1** down the c-axis. The $C-PO_3$ and $C-SO_3$ tetrahedra are shaded in light and dark gray, respectively. Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively.

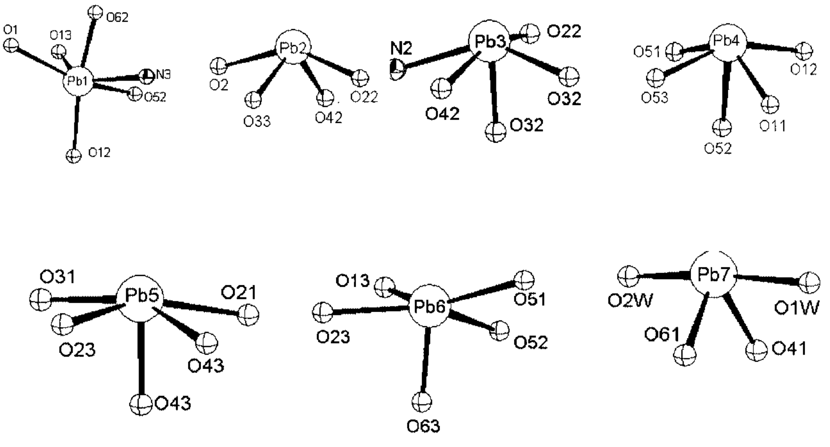

Figure 1. The coordination geometries around the lead(II) ions in complex **1**

Table 1. Bond lengths [Å] and angles [°] for complex **1** (symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+2, -z$; #2 $-x+2, -y+2, -z+1$; #3 $-x+1, -y+2, -z$; #4 $x-1, y, z$; #5 $-x+1, -y+2, -z+1$; #6 $x, 1+y, z$)

Pb(1)−O(62)	2.39(2)	Pb(1)−O(52)	2.450(15)
Pb(1)−O(13)	2.495(15)	Pb(1)−O(12)#1	2.619(15)
Pb(1)−N(3)	2.643(19)	Pb(1)−O(1)	2.712(15)
Pb(2)−O(33)	2.372(16)	Pb(2)−O(22)	2.512(16)
Pb(2)−O(42)#2	2.556(16)	Pb(2)−O(2)	2.647(16)
Pb(3)−O(32)	2.339(15)	Pb(3)−O(42)	2.369(15)
Pb(3)−O(32)#2	2.577(15)	Pb(3)−N(2)	2.618(17)
Pb(3)−O(22)	2.651(14)	Pb(4)−O(53)#3	2.409(17)
Pb(4)−O(11)	2.427(16)	Pb(4)−O(12)#1	2.530(15)
Pb(4)−O(51)	2.574(18)	Pb(4)−O(52)	2.747(18)
Pb(5)−O(43)#4	2.391(16)	Pb(5)−O(23)	2.471(15)
Pb(5)−O(31)#4	2.537(15)	Pb(5)−O(21)#5	2.567(14)
Pb(5)−O(43)#2	2.664(15)	Pb(6)−O(63)	2.30(2)
Pb(6)−O(23)	2.621(16)	Pb(6)−O(13)	2.669(14)
Pb(6)−O(51)#3	2.680(17)	Pb(6)−O(52)	2.710(16)
Pb(7)−O(61)#2	2.287(18)	Pb(7)−O(41)	2.335(16)
Pb(7)−O(1 W)	2.56(2)	Pb(7)−O(2 W)	2.65(3)
Hydrogen bonds			
O(3 W)···O(1 W)	2.80(3)	O(4 W)···O(1 W)	2.85(5)
O(4 W)···O(4)#6	2.80(3)		
O(62)−Pb(1)−O(52)	92.5(7)	O(62)−Pb(1)−O(13)	76.1(7)
O(52)−Pb(1)−O(13)	74.0(5)	O(62)−Pb(1)−O(12)#1	165.2(7)
O(52)−Pb(1)−O(12)#1	73.0(5)	O(13)−Pb(1)−O(12)#1	96.2(5)
O(62)−Pb(1)−N(3)	72.4(6)	O(52)−Pb(1)−N(3)	70.8(6)
O(13)−Pb(1)−N(3)	130.8(5)	O(12)#1−Pb(1)−N(3)	104.9(6)
O(62)−Pb(1)−O(1)	74.8(6)	O(52)−Pb(1)−O(1)	157.2(5)
O(13)−Pb(1)−O(1)	84.4(5)	O(12)#1−Pb(1)−O(1)	117.5(5)
N(3)−Pb(1)−O(1)	121.1(5)	O(33)−Pb(2)−O(22)	80.1(5)
O(33)−Pb(2)−O(42)#2	103.8(5)	O(22)−Pb(2)−O(42)#2	84.7(5)
O(33)−Pb(2)−O(2)	78.9(6)	O(22)−Pb(2)−O(2)	146.9(5)
O(42)#2−Pb(2)−O(2)	75.9(6)	O(32)−Pb(3)−O(42)	79.1(6)
O(32)−Pb(3)−O(32)#2	80.4(5)	O(42)−Pb(3)−O(32)#2	77.9(5)
O(32)−Pb(3)−N(2)	71.2(5)	O(42)−Pb(3)−N(2)	72.9(5)
O(32)#2−Pb(3)−N(2)	142.3(5)	O(32)−Pb(3)−O(22)	74.3(5)
O(42)−Pb(3)−O(22)	151.6(5)	O(32)#2−Pb(3)−O(22)	106.9(4)
N(2)−Pb(3)−O(22)	89.0(5)	O(53)#3−Pb(4)−O(11)	81.8(7)
O(53)#3−Pb(4)−O(12)#1	150.8(6)	O(11)−Pb(4)−O(12)#1	83.5(6)
O(53)#3−Pb(4)−O(51)	83.0(6)	O(11)−Pb(4)−O(51)	130.5(6)
O(12)#1−Pb(4)−O(51)	87.6(6)	O(53)#3−Pb(4)−O(52)	82.4(6)
O(11)−Pb(4)−O(52)	76.1(5)	O(12)#1−Pb(4)−O(52)	69.7(5)
O(51)−Pb(4)−O(52)	55.2(5)	O(43)#4−Pb(5)−O(23)	87.2(5)
O(43)#4−Pb(5)−O(31)#4	82.9(5)	O(23)−Pb(5)−O(31)#4	76.5(5)
O(43)#4−Pb(5)−O(21)#5	76.8(5)	O(23)−Pb(5)−O(21)#5	148.7(5)
O(31)#4−Pb(5)−O(21)#5	126.7(5)	O(43)#4−Pb(5)−O(43)#2	79.9(5)
O(23)−Pb(5)−O(43)#2	76.7(5)	O(31)#4−Pb(5)−O(43)#2	148.7(4)
O(21)#5−Pb(5)−O(43)#2	74.2(5)	O(63)−Pb(6)−O(23)	82.7(7)
O(63)−Pb(6)−O(13)	95.0(7)	O(23)−Pb(6)−O(13)	77.3(5)
O(63)−Pb(6)−O(51)#3	109.3(8)	O(23)−Pb(6)−O(51)#3	139.4(6)
O(13)−Pb(6)−O(51)#3	136.6(5)	O(63)−Pb(6)−O(52)	78.1(7)
O(23)−Pb(6)−O(52)	137.5(5)	O(13)−Pb(6)−O(52)	67.1(5)
O(51)#3−Pb(6)−O(52)	83.0(5)	O(61)#2−Pb(7)−O(41)	80.2(6)
O(61)#2−Pb(7)−O(1 W)	83.1(7)	O(41)−Pb(7)−O(1 W)	84.5(7)
O(61)#2−Pb(7)−O(2 W)	99.4(10)	O(41)−Pb(7)−O(2 W)	83.8(9)
O(1 W)−Pb(7)−O(2 W)	167.4(10)		

from the Pb^{II} ion. The Pb−O distances are in the range 2.287(18) to 2.747(18) Å, and the Pb−N distances range from 2.618(17) to 2.643(19) Å; these distances are similar to those reported for other Pb^{II} aminodiphosphonates.[10−12] The three L^1 anions in complex **1** adopt three different types of coordination modes (see Figure 2). The L^1 anion that contains P1 and P2 chelates Pb6 in a bidentate fashion, and also forms bridges with eight other Pb^{II} ions. Its amine group remains non-coordinated and four phosphonate oxygen atoms act as μ_2 metal linkers. The diphosphonate anion that contains P3 and P4 chelates Pb3 in a tridentate manner (N2, O32 and O42), chelates Pb5 in a bidentate fashion (O31, O43), and forms bridges with five other lead(II) ions. The three phosphonate oxygen atoms are bidentate. The third L^1 anion is bonded to Pb1 in a tridentate fashion, chelates Pb4 and Pb6 bidentately and also forms bridges with three other lead(II) ions. O52 acts as a μ_3 metal linker, and only O51 is a μ_2 bridging group. This kind of coordination mode has not been reported before. The carboxylate-sulfonate anion is bidentate, forming bridges with two Pb^{II} ions through the carboxylate group. The sulfonate group remains non-coordinated. Based on the requirements of charge balance, both types of ligands have been completely deprotonated.

The interconnection of the above Pb^{II} polyhedra through the diphosphonate L^1 anions, as well as through the carboxylate-sulfonate ligands, results in a <010> hybrid layer. The interlayer distance is approximately 14.9 Å. The sulfonate group acts as a pendant group, hanging between two layers (Figure 3). The lattice water molecules are also located in the middle of the interlayer space, forming hydrogen bonds with the non-coordinated sulfonate groups, as well as with the aqua ligands (Table 1). The O(4 W)···O(4) (symmetry code: x, $1 + y$, z) contact distance is only 2.60(4) Å, indicating that the hydrogen bond between the lattice water molecule and the sulfonate group is very strong.

$Pb_3(HL^2)(H_2L^2)(H_2BTC)(H_2O)\cdot H_3BTC\cdot H_2O$ (**2**) also has a layered structure and contains 1,3,5-benzene-tricarboxylate ligands that behave both as a pendant group and as an intercalated species. As shown in Figure 4, Pb1 is four-coordinate and is bonded to four phosphonate oxygen atoms from three diphosphonate ligands (1 H_2L^2 and 2 HL^2). Its coordination geometry can be described as a ψ-PbO_4 square pyramid with the fifth coordination site occupied by the lone pair of electrons. Pb2 is five-coordinate and is bonded to a bidentate carboxylate group of the H_2BTC anion and three phosphonate oxygen atoms from three diphosphonate ligands (1 H_2L^2 and 2 HL^2). Its coordination geometry can be described as a ψ-PbO_5 octahedron with the sixth site occupied by the lone pair of electrons. The Pb(2)−O(6) bond of 2.766(10) Å is significantly longer than the Pb(2)−O(5) bond [2.584(13) Å]. Pb3 is five-coordinate and is bonded to four phosphonate oxygen atoms from three diphosphonate ligands (1 H_2L^2 and 2 HL^2) and an aqua ligand. It has a ψ-PbO_5 octahedral geometry that is similar to that of Pb2. The Pb−O distances range from 2.407(12) to 2.767(13) Å; these distances are similar to those in complex **1** and those observed in other lead(II) phosphonates,[10−12] as well as to those reported for the lead(II) complex with H_3BTC.[13]

The HL^2 anion that contains P2 and P3 is heptadentate; it chelates Pb1 in a bidentate manner (O21 and O32) and forms bridges with five other lead(II) ions. The O23 and O32 atoms are bidentate metal linkers. Both phosphonate groups are fully deprotonated, but the amine group remains protonated. The H_2L^2 anion containing P4 and P5 is tetradentate; it chelates Pb3 in a bidentate fashion (O41 and O53) and also connects with two other Pb^{II} ions. The O42 atom is a bidentate metal linker. The P4 and P5 phosphonate groups are tridentate and unidentate, respectively. Based on the P−O distance and the charge balance, the P5 phosphonate group should be 1H-protonated, so does the amine group, hence the doubly protonated diphosphonate anion carries two negative charges. The H_2BTC anion in complex **2** is bidentately chelated to Pb2 (O5 and O6) and the other two carboxylate groups remain non-coordinated, while all three carboxylate groups of the neutral H_3BTC ligand in complex **2** are non-coordinated (Figure 4). This is unlike the situation in porous lead(II) phosphonate-carboxylates in which all three carboxylate groups are involved in metal coordination.[10]

The interconnecting lead(II) ions, via bridging amino diphosphonate ligands, leads to the formation of a slab along the a-axis. Such slabs are further interlinked via strong hydrogen bonds between the non-coordinated phosphonate oxygen atoms to form a <001> layer (Figure 5). The O(33)···O(52) distance (symmetry code: $-x$, $y - 1$, $-z$) is 2.509(17) Å (Table 2). The non-coordinated dicarboxylate moiety of H_2BTC is orientated towards the interlayer space, and is able to form hydrogen bonds with the carboxylate groups of the neutral H_3BTC ligand (Table 2, Figure 6).

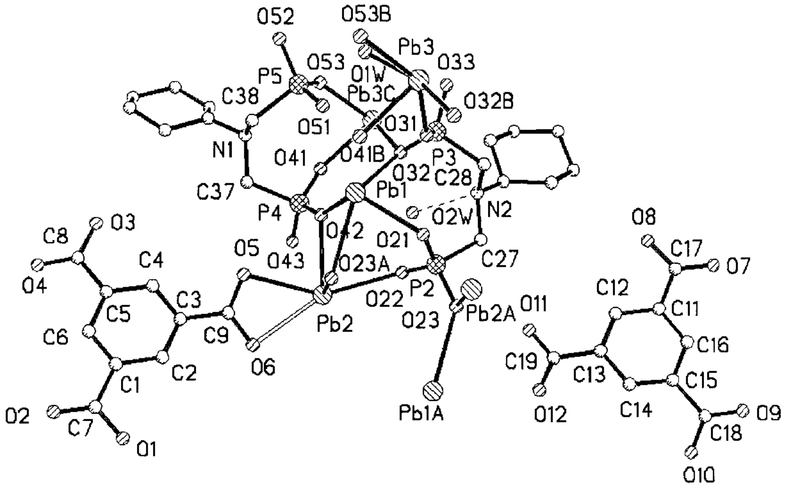

Figure 4. The asymmetric unit of complex **2**. The elongated Pb-O bond is represented by an open line; hydrogen bond is drawn as a dotted line; symmetry codes for the generated atoms: a) $-x$, $-y$, $-z$; b) $x + 1$, y, z; c) $-1 + x$, y, z

Such hydrogen bonding creates a six-membered ring that consists of two carboxylate groups, one from H_3BTC and one from H_2BTC (Figure 6). The aqua ligands are located at the cavities within the 2-D layer, and form hydrogen bonds with the non-coordinated phosphonate oxygen atoms, as well as with the amine groups (Table 2). The interlayer space of about 21.4 Å is much larger than that of complex **1**, mainly due to the intercalation of the H_3BTC molecules.

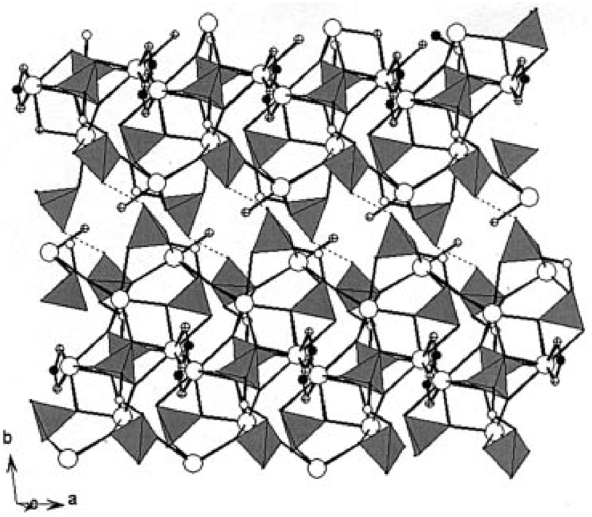

Figure 5. A <001> layer formed by the interconnection of lead(II) ion by bridging diphosphonate ligands in complex **2**; the pendant H_2BTC anions have been omitted for clarity; the $C-PO_3$ tetrahedra are shaded in gray, and Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively

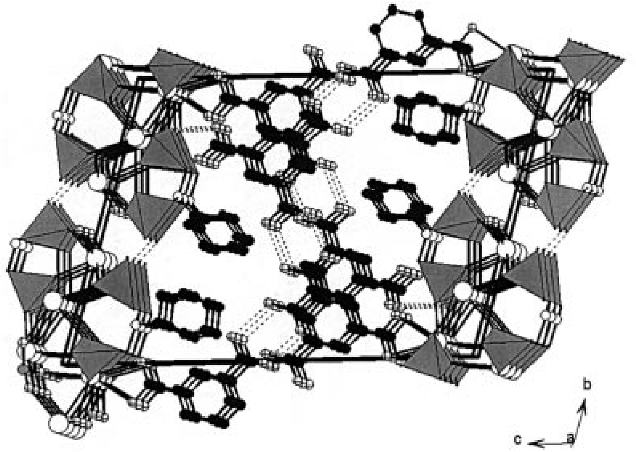

Figure 6. View of the structure of complex **2** down the *a*-axis; the $C-PO_3$ tetrahedra are shaded in gray, and Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively; hydrogen bonds are drawn as dotted lines.

The XRD powder patterns for complexes **1** and **2** were collected on a Philips X′Pert-MPD diffractometer using graphite-monochromated Cu-K_α radiation in the angular range $2\theta = 5-70°$. The powder patterns of **1** and **2** match those calculated from their single-crystal structure data, thus both compounds exist as a single phase.

The IR spectra of complexes **1** and **2** show the asymmetric and symmetric vibrations of the carboxyl group at 1531

Table 2. Bond lengths [Å] and angles [°] for complex **2** (symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $x + 1, y, z$; #3 $x - 1, -1 - y, -z$; #4 $x - 1, y, z$; #5 $x, y, z - 1$; #6 $x - 1, y - 1, z - 1$; #7 $-x - 1, -y, -z$)

Pb(1)−O(21)	2.429(12)	Pb(1)−O(42)	2.495(13)
Pb(1)−O(32)	2.605(12)	Pb(1)−O(23)#1	2.688(11)
Pb(2)−O(23)#1	2.418(11)	Pb(2)−O(42)	2.517(13)
Pb(2)−O(5)	2.584(13)	Pb(2)−O(22)	2.628(12)
Pb(3)−O(41)#2	2.316(12)	Pb(3)−O(1 W)	2.345(13)
Pb(3)−O(53)#2	2.407(12)	Pb(3)−O(31)	2.687(11)
Pb(3)−O(32)#2	2.744(11)		
Hydrogen bonds			
O(1 W)···O(51)	2.601(22)	O(1 W)···O(33)#3	2.803(19)
O(33)···O(52)#3	2.509(17)	O(2 W)···N(2)	2.858(19)
O(2 W)···O(31)#4	2.735(17)	O(2 W)···O(22)	2.769(16)
O(1)···O(7)#5	2.695(18)	O(2)···O(8)#5	2.625(19)
O(3)···O(9)#6	2.613(18)	O(4)···O(10)#6	2.657(19)
O(11)···O(43)#7	2.613(19)		
O(21)−Pb(1)−O(42)	99.6(5)	O(21)−Pb(1)−O(32)	74.9(4)
O(42)−Pb(1)−O(32)	77.7(4)	O(21)−Pb(1)−O(23)#1	74.7(4)
O(42)−Pb(1)−O(23)#1	70.4(4)	O(32)−Pb(1)−O(23)#1	130.8(3)
O(23)#1−Pb(2)−O(42)	74.6(4)	O(23)#1−Pb(2)−O(5)	82.8(4)
O(42)−Pb(2)−O(5)	74.0(4)	O(23)#1−Pb(2)−O(22)	82.2(4)
O(42)−Pb(2)−O(22)	75.6(4)	O(5)−Pb(2)−O(22)	148.7(4)
O(41)#2−Pb(3)−O(1 W)	77.0(5)	O(41)#2−Pb(3)−O(53)#2	80.5(4)
O(1 W)−Pb(3)−O(53)#2	74.0(5)	O(41)#2−Pb(3)−O(31)	71.4(4)
O(1 W)−Pb(3)−O(31)	76.3(5)	O(53)#2−Pb(3)−O(31)	142.8(4)
O(41)#2−Pb(3)−O(32)#2	89.3(4)	O(1 W)−Pb(3)−O(32)#2	157.5(5)
O(53)#2−Pb(3)−O(32)#2	86.3(4)	O(31)−Pb(3)−O(32)#2	116.5(3)

and 1419 cm^{-1} for complex **1**, and 1576 and 1454 cm^{-1} for complex **2**, respectively. The differences in ν_{as}(COO) and ν_s(COO) are much larger than 95 cm^{-1} in both complexes, indicating the bidentate coordination mode for the carboxylate groups.[14] Complex **2** also exhibits a strong absorption band at 1722 cm^{-1} assigned to the non-coordinating carboxylate groups (COOH). The vibrations of the phosphonic group groups can be seen in the region 900−1100 cm^{-1}.[7] The broad bands at 3406 cm^{-1} (for complex **1**) and 3428 cm^{-1} (for complex **2**) indicate the presence of the water molecules in both compounds. Those frequencies which are characteristic of the fundamental and split ν_{as}(S−O) stretching modes for complex **1** appear in the range 1200−1000 cm^{-1}.

The TGA curves of complex **1** exhibit two steps corresponding to weight losses. The first step indicates the loss of two lattice water molecules and two aqua ligands, which starts at 55 °C and ends at 210 °C. The observed weight loss of 2.8% is in good agreement with the theoretical weight loss (2.94%). The second weight loss step starts at 375 °C and continues up to 800 °C, and indicates the loss of the aminodiphosphonate and carboxylate-sulfonate ligands. The final products are $Pb_2P_2O_7$ and $PbSO_4$ (in a molar ratio of about 3:1), based on the X-ray power pattern. The total weight loss of 14.2% is similar to that calculated (15.65%). The TGA diagram for complex **2** reveals three main steps corresponding to weight losses. The first step involves the loss of the lattice water molecule and the aqua ligand, which starts at about 90 °C and ends at about 282 °C. The observed weight loss of 2.4% is in good agreement with the calculated value (2.2%). The second step, which covers a temperature range from 282 °C to 345 °C, corresponds to the loss of intercalated H_3BTC. The third step starts at 345 °C and ends at 710 °C, and involves two overlapping processes: the loss of one water molecule formed by the condensation of the hydrogen phosphonate groups, and the loss of the diphosphonate ligand and the H_2BTC anion. The final products are $Pb_2P_2O_7$ and $Pb(PO_3)_2$ (in a molar ratio of 1:1), based on the XRD powder pattern. The total weight loss is 41.3% is similar to that calculated (42.1%).

Conclusion

In summary, two novel layered lead(II) carboxylate-phosphonate hybrids were obtained by the hydrothermal reactions of lead(II) carbonate with amino-diphosphonic acid and 3-sulfobenzoic acid (or, 1,3,5-benzenetricarboxylic acid). In both compounds, the 2-D inorganic-organic layer is formed by the lead(II) ions that are interconnected through the diphosphonate ligands. The sulfonate group of the carboxylate-sulfonate ligand in complex **1** acts as a pendant group between the 2-D layers, whereas the 1,3,5-benzenetricarboxylate ligands in complex **2** act both as a pendant ligand and as the intercalated species between two metal-diphosphonate layers. It is believed that a wide range of novel open-frameworks and microporous materials can be developed using this ligand-hybrid technique.

Experimental Section

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 TGA/SBTA851 unit at a heating rate of 15 °C/ min under a nitrogen atmosphere. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the 4000−400 cm^{-1} range. ^1H and ^{31}P NMR spectra were recorded on a Varian Unity 500 NMR in D_2O. H_3PO_4 (85%) was used as ^{31}P standard reference. The XRD powder patterns were collected on a Philips X′Pert-MPD diffractometer using graphite-monochromated Cu-K_α radiation in the angular range $2\theta = 5-70°$ with a step size of 0.02° and a counting time of 3 seconds per step.

Preparation of H_4L^1 and H_4L^2: H_4L^1 and H_4L^2 were prepared by a Mannich type reaction according to procedures described previously.[11]

Isopropylamine (100 mmol, 5.911 g) was mixed with hydrochloric acid (16.0 cm^3), deionized water (20 mL) and phosphorous acid (400 mmol, 32.8 g). The mixture was allowed to reflux at 120 °C for 1 h, paraformaldehyde (300 mmol, 9 g) was then added in small portions over a period of 1 h, and the mixture was refluxed for one additional hour. Removal of solvents afforded 16.8 g of a white powder of H_4L^1 (yield 68.1%). Its purity was confirmed by NMR spectroscopic measurements and elemental analysis. ^{31}P NMR spectroscopy shows a single peak at 9.50 ppm. ^1H NMR: $\delta = 1.37$ (CH_3, d, 6 H, $J_{H-H} = 5.5$ Hz), 3.57 ($N-CH_2-PO_3$, d, 4 H, $J_{H-P} = 12.5$ Hz), 4.16 (Me_2-CH-N, sept., 1 H) ppm. Elemental analysis for H_4L^1, $C_5H_{15}NO_6P_2$ (247.12): calcd. C 24.86, H 6.62, N 4.88; found C 24.29, H 6.07, N 5.67.

H_4L^2 was obtained in a yield of 77.5% by a Mannich type reaction using cyclohexylamine (100 mmol, 9.92 g), hydrochloric acid (16.0 cm^3), deionized water (20.0 mL), phosphorous acid (400 mmol, 32.8 g) and paraformaldehyde (300 mmol, 9.0 g), in a similar method to that of H_4L^1. ^{31}P NMR spectroscopy shows a single peak at 8.75 ppm. ^1H NMR: $\delta = 1.16$, 1.36, 1.67, 1.91 and 2.06 (for five CH_2- groups of cyclohexyl, d), 1.51 (CH- of cyclohexyl, t, 1 H), 3.51 ($N-CH_2-PO_3$, d, 4 H, $J_{H,P} = 13.0$ Hz) ppm. Elemental analysis for H_4L^2, $C_8H_{19}NO_6P_2$ (288.54): calcd. C 33.24, H 6.81, N 4.59; found C 33.45, H 6.62, N 5.33.

$Pb_7(3\text{-}O_3S-C_6H_4-CO_2)(L^1)_3(H_2O)_2\cdot 2H_2O$ (1) and $Pb_3(HL^2)(H_2L^2)(H_2BTC)(H_2O)\cdot H_3BTC\cdot H_2O$ (2): A mixture of $PbCO_3$ (1.0 mmol, 0.267 g), H_4L^1 (0.5 mmol, 0.124 g), 3-sulfobenzoic acid monosodium salt (0.5 mmol, 0.112 g) and deionized water (10 mL) was sealed into a bomb equipped with a Teflon liner (20 mL), and then heated at 180 °C for 5 days. Colorless prismatic crystals of complex **1** were recovered in ca. 71% yield based on Pb. Elemental analysis for **1**, $C_{22}H_{45}N_3O_{27}P_6Pb_7S$ (2451.82): calcd. C 10.67, H 1.38, N 1.82; found C 10.77, H 1.84, N 1.71%. IR data (KBr, cm^{-1}): $\tilde{\nu} = 3406$ (s), 2962 (m), 2933 (m), 2875 (m), 2798 (m), 2407 (m), 1732 (m), 1651 (m), 1587 (m), 1531 (s), 1419 (s), 1383 (s), 1302 (m), 1200 (m), 1084 (vs), 1032 (vs), 966 (vs), 839 (m), 752 (m), 679 (m), 588 (s), 557 (s), 507 (m), 480 (m).

A mixture of $PbCO_3$ (1.0 mmol, 0.267 g), H_4L^2 (0.5 mmol, 0.144 g), 1,3,5-benzenetricarboxylic acid (0.5 mmol, 0.105 g) and deionized water (10 mL) was sealed into a bomb equipped with a Teflon liner (20 mL), and then heated at 180 °C for 5 days. Prismatic colorless crystals of complex **2** were recovered in ca. 60% yield based on Pb. Elemental analysis for **2**, $C_{34}H_{48}N_2O_{26}P_4Pb_3$

(1646.19): calcd. C 23.93, H 2.42, N 1.62; found C 24.79, H 2.92, N 1.70%. IR data (KBr, cm^{-1}): $\tilde{\nu}$ = 3428 (s), 3021 (s), 2979 (s), 2940 (s), 2862 (s), 2648 (s), 2542 (s), 1878 (m), 1722 (vs), 1614 (s), 1576 (s), 1454 (s), 1381 (s), 1281 (vs), 1111 (vs), 1051 (vs), 987 (s), 933 (s), 777 (m), 744 (s), 692 (s), 621 (m), 526 (m), 442 (m).

Crystal Structure Determination: Single crystals of complexes **1** and **2** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz polarization, as well as for absorption, by ψ scan technique. Both structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[15] All non-hydrogen atoms, except for N(2), C(2), C(3), C(14), C(15), C(22) and C(23) in complex **1**, and C(23) in complex **2,** were refined with anisotropic thermal parameters. Those atoms refined with isotropic thermal parameters were non-positive if refined anisotropically; this was caused by the problem resulting from correcting the absorption due to the presence of very heavy Pb atoms. The final difference Fourier maps showed featureless residual peaks of 3.16 e·Å^{-3} (for complex **1**, 0.91 Å from Pb(2) atom) and 3.56 e Å^{-3} (for complex **2**, 1.02 Å from Pb(1) atom), respectively. All hydrogen atoms were located at geometrically calculated positions. The hydrogen atoms for the water molecules were not included in the refinements. The large standard deviations for the bond lengths in complex **1** are due to the poor quality of the single crystals, which is very common for metal phosphonates; efforts were made to isolate better quality crystals, however they were unsuccessful. Crystallographic data and structural refinements are summarized in Table 3. Important bond lengths and angles are listed in Tables 1 and 2 for complexes **1** and **2**, respectively.

Table 3. Crystal data and structure refinement for complexes **1** and **2**
($R1 = F_o - F_c / F_o$, $wR2 = \{w[(F_o)^2 - (F_c)^2]^2/w[(F_o)^2]^2\}^{1/2}$)

Compound	1	2
Empirical formula	$C_{22}H_{45}N_3O_{27}P_6Pb_7S$	$C_{34}H_{48}N_2O_{26}P_4Pb_3$
Molecular mass	2451.82	1646.19
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No. 2)
a (Å)	10.1796(4)	7.1392(1)
b (Å)	14.9014(6)	15.5844(1)
c (Å)	16.4192(6)	21.3980(1)
α/°	80.314(1)	105.658(1)
β/°	77.032(1)	90.757(1)
γ/°	85.037(1)	96.214(1)
V/Å^3	2389.43(16)	2276.65(4)
Z	2	2
D_c/g·cm^{-3}	3.408	2.401
μ(Mo-K_α)/mm^{-1}	24.902	11.301
F (000)	2188	1560
Reflections collected	12523	11815
Unique reflections	8397 (R_{int} = 0.081)	7925 (R_{int} = 0.0495)
Observed data [$I > 2\sigma(I)$]	6427	6850
No. of parameters refined	560	618
Goodness-of-fit on F^2	1.083	1.195
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0634, 0.1459	0.0627, 0.1532
$R1$, $wR2$ (all data)	0.0925, 0.1656	0.0746, 0.1600

CCDC-217199 and -217200 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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