Hydrothermal synthesis, characterization and crystal structures of two new layered lead(II) diphosphonates

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Received (in Montpellier, France) 25th February 2003, Accepted 7th April 2003
First published as an Advance Article on the web 14th July 2003

Hydrothermal reactions of *N*-benzyliminobis(methylenephosphonic acid), $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L), with lead(II) chloride and lead(II) acetate resulted in two novel lead(II) phosphonates, namely, $Pb_5(H_2L)_2(HL)_2{\cdot}2H_2O$ (**1**) and $Pb_3(H_2L)_2Cl(H_2O)_3{\cdot}Cl{\cdot}2H_2O$ (**2**). Compound **1** is orthorhombic, *Pbca*, with $Z = 4$. Compound **1** features a layered structure in which the lead(II) ions are bridged by phosphonate groups.Two lead(II) ions (Pb1 and Pb3) are three-coordinated with a distorted tetrahedral geometry in which one apex is occupied by the lone pair of the lead(II) ion, the third lead(II) ion (Pb2) is six-coordinated by six phosphonate oxygen atoms from six ligands. Two ligands are doubly protonated whereas the other two are singly protonated. Compound **2** crystallizes in $I2/a$ with $Z = 4$. In compound **2**, one lead(II) ion is six-coordinated by four phosphonate oxygen atoms from four ligands, one aqua ligand and one chloride anion in a distorted octahedral geometry; the other lead(II) ion is coordinated by four phosphonate oxygen atoms from four ligands and two aqua ligands with a severely distorted octahedral geometry. One phosphonate group of the ligand bridges with five lead(II) ions, whereas the other one is unidentate. The interconnection of the lead(II) ions through bridging phosphonate groups results in the formation of a $\langle 040 \rangle$ layer. In both compounds, the phenyl groups of the ligand are oriented toward the interlayer space.

Metal phosphonates have potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry.[1] Most of these are layered species in which the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers that are separated by hydrophobic regions comprised by the organic moieties.[1] Studies have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, can form this type of layered compound.[1–3] One challenge for studying such materials is that they usually exhibit poor crystallinity, which makes their structural analysis a difficult task. Divalent metal phosphonates usually have a larger solubility in various solvents than do zirconium(IV) or titanium(IV) phosphonates and they are more likely to be obtained in the form of single crystals, thus allowing more systematic structural studies to be carried out. Another method to improve the crystallinity is to put additional functional groups such as crown ether, amine and carboxylate groups into the phosphonic acid.[4–6] Diphosphonic acids in which the two phosphonate groups are attached to diamine groups, ($HO_3PCH_2HNRNHCH_2PO_3H$), can also form metal phosphonates with a variety of structures, such as mononuclear chelate compounds,[7] compounds with 1D chain or 3D network structures based on dimeric units[8] and pillared layered compounds.[4,9]

Only a few structural studies have been reported on metal compounds of aminodiphosphonic acids, $RN(CH_2PO_3H_2)_2$.[10–12] The crystal structure of a copper compound with ethylaminebis(methylphosphonate) was reported by Makaranets *et al.*[10] Recently a series of divalent metal compounds with *N*-methyliminodi(methylenephosphonate) (H_4L') were isolated in our laboratory.[11] With the removal of one proton from the ligand, we isolated two layered compounds with the formula of $M(H_3L')_2{\cdot}2H_2O$ (M = Cd, Mn); replacement of two protons from a ligand by a divalent metal ion resulted in $Zn(H_2L')(H_2O)$ with a double chain structure and a layered lead diphosphonate, $Pb(H_2L')$.[11] Removal of three protons from the ligand afforded $Zn_3(HL')_2$ whose structure features a 3D network.[11] A series of layered zirconium diphosphonates with $(H_2O_3PCH_2)_2NC_nH_{2n+1}$ (n = 1–6 and 8–10) have been synthesized and one compound with $n = 2$ has been structurally characterized by X-ray powder diffraction.[12] In order to understand the effect of the substitute R group and the anions on the structure of the metal phosphonates, we have synthesized a new diphosphonic acid, *N*-benzyliminobis(methylenephosphonic acid), $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L). Hydrothermal reactions of the above ligand with lead(II) chloride and lead(II) acetate resulted in two new layered lead(II) phosphonates, namely, $Pb_5(H_2L)_2(HL)_2{\cdot}2H_2O$ O (**1**) and $Pb_3(H_2L)_2Cl(H_2O)_3{\cdot}Cl{\cdot}2H_2O$ (**2**), which contains both coordinated and non-coordinated chloride anions. Herein we report their synthesis, characterization and crystal structures.

Experimental

Materials and methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Solution NMR was recorded on a Varian Unity 500 NMR.

H_3PO_4 was used as ^{31}P standard reference. Thermogravimetric analysis was carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C min^{-1} under a nitrogen atmosphere. IR spectra were taken on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm^{-1} range.

Synthesis of *N*-benzyliminobis(methylenephosphonic acid). The diphosphonic acid was prepared by a Mannich type reaction according to the procedures previously described.[11] Its purity was confirmed by NMR measurements and elemental analysis. ^{31}P NMR shows only one single peak at 8.025 ppm. ^1H NMR: 3.493 ($N–CH_2–PO_3$, d, 4H, $J_{H–P} = 12.0$ Hz), 4.738 ($Ph–CH_2–N$, s, 2H), 7.554 and 7.590 (C_6H_5, d, 5H) ppm. Elem. anal. 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).

Preparation of $Pb_5(H_2L)_2(HL)_2 \cdot 2H_2O$ (1) and $[Pb_3(H_2L)_2Cl(H_2O)_3]Cl \cdot 2H_2O$ (2). Both compounds were synthesized by hydrothermal reactions using a similar method. A mixture of 0.5 mmol of H_4L, 0.5 mmol of lead acetate trihydrate (or lead chloride) and 10.0 ml of deionized water was sealed into a bomb equipped with a Teflon liner and then heated at 180 °C for 4 days. Colorless crystals for compounds **1** and **2** were recovered in *ca.* 62% and 76% yields as a single phase, respectively. Elem. anal. for compound **1**, $C_{36}H_{54}Pb_5N_4O_{26}P_8$: C, 19.06; H, 2.34; N, 2.41%; calcd: C, 19.28; H, 2.43; N, 2.50%. IR data (KBr, cm^{-1}): 3431(m), 3034 (m), 2978(m), 2941(m), 2866(m), 1653(w), 1558(w), 1456(w), 1119 (s), 1041(vs), 908(m), 737(m), 700(w), 634(w), 555(m), 538(m). Elem. anal. for compound **2**, $C_{18}H_{36}Pb_3N_2O_{17}P_4Cl_2$: C, 15.54; H, 2.61; N, 1.94%; calcd: C, 15.77; H, 2.65; N, 2.04%. IR data (KBr, cm^{-1}): 3450(m), 3406(m), 3026(w), 2808(w), 1616(w), 1423(m), 1186(m), 1095(s), 1061(s), 968(m), 739(m), 702(m), 553(m) and 471(m).

X-Ray crystallography

Single crystals of compounds **1** and **2** were mounted on a Bruker Smart CCD and the intensities measured using MoKα radiation ($\lambda = 0.71069$ Å) and a graphite monochromator at room temperature. A hemisphere of data (1271 frames at 5 cm detector distance) was collected by the narrow-frame method with scan widths of 0.30° in ω and exposure times of 10 and 20 s per frame for compounds **1** and **2**, respectively. The first 50 frames were recollected at the end of the data collection session to assess the stability of the crystal; it was found that the decay in intensity was less than 1%. The data were corrected for Lorentz factors, polarization, air absorption and absorption due to variations in the path length through the detector faceplate. An absorption correction based on SADABS was also applied.[13]

The space group was uniquely determined to be *Pbca* (No. 61) for compound **1** and *I*2/*a* (No. 15) for compound **2**. Both structures were solved by direct methods (SHELXTL) and refined by least-squares methods with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms.[13] All hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. The residual extremes of the final refinements are meaningless and are within 1.3 Å of the lead(II) atoms. Some of the data collection and refinement parameters are summarized in Table 1. Important bond lengths and angles for the two compounds are listed in Table 2.

CCDC reference numbers 214482 and 214483. See http://www.rsc.org/suppdata/nj/b3/b302240b/ for crystallographic data in CIF format or other electronic format.

Table 1 Crystal data and structure refinement for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{36}H_{54}Pb_5N_4O_{26}P_8$	$C_{18}H_{36}Cl_2N_2O_{17}P_4Pb_3$
M	2242.54	1368.84
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (No. 61)	*I*2/*a* (No. 15)
a/Å	13.0056(2)	9.8986(2)
b/Å	13.755(1)	31.4972(4)
c/Å	30.0991(4)	10.9253(4)
β/°	90	95.290(1)
U/Å^3	5384.4(1)	3391.8(2)
Z	4	4
μ(Mo-Kα)/mm^{-1}	15.909	15.274
Data collected	17 434	5499
Independent data	4790	2967
R_{int}	0.0832	0.0430
Observed data [$I > 2\sigma(I)$]	3646	2609
R_1 [$I > 2\sigma(I)$]	0.0516	0.0548
wR_2 [$I > 2\sigma(I)$]	0.1137	0.1519
R_1 (all data)	0.0776	0.0623
wR_2 (all data)	0.1287	0.1616

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|, wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Results

Crystal structure of $Pb_5(H_2L)_2(HL)_2 \cdot 2H_2O$, 1

As shown in Fig. 1, the asymmetric unit of compound **1** contains three lead(II) ions, two ligand molecules and a lattice water molecule. Pb1 is three-coordinated by three phosphonate oxygen atoms from three ligands; Pb3 is also coordinated by three phosphonate oxygen atoms but from two ligands only. The coordination geometry of Pb1 and Pb3 can be described as distorted tetrahedron with one apex occupied by the lone pair electrons of the lead(II) ion. Pb2 occupies a position of −1 symmetry; it is six-coordinated by six phosphonate oxygen atoms from six ligands in a distorted octahedral geometry. The Pb–O distances are in the range of 2.305(9) to 2.636(9) Å (Table 2), comparable with those reported in other lead phosphonates.[11,14] An analysis of bond valences with these short Pb–O distances reveals that the valences are 1.59 (Pb1), 1.97 (Pb2) and 1.52 (Pb3), thus secondary coordination (weak bonds) should also be considered for Pb1 and Pb3.[15] Pb1 has three longer contacts with N2 [2.991(9) Å], O32 [2.829(9) Å, symmetry code: $1/2 - x$, $1/2 + y$, z] and O21 [3.106(9) Å], whereas Pb3 atom forms four weak bonds with O11 and O13 [3.025(9) and 2.836(9) Å, respectively, symmetry code: $-x$, $-y$, $1 - z$], O22 (2.931 Å; $-1/2 + x$, $-1/2 - y$, $1 - z$) as well as O33 [3.108(9) Å]. With these weak bonds included in the calculations, the valences are 1.90 and 1.92, respectively, for Pb1 and Pb3, which are close to the expected value.

One ligand (P1, P2) is doubly protonated and based on the P–O distance, the N1 and O23 atoms are most likely to be protonated; the other ligand (P3, P4) is singly protonated and we deem that O43 with a long P–O distance is most likely to be protonated. Two phosphonate groups (P1, P3) bridge with three lead(II) ions, one phosphonate group(P2) is unidentate and the fourth one (P4) connects with two lead(II) ions using the O41 atom. The bridging of the lead(II) ions by phosphonate groups resulted in the formation of ⟨001⟩ and ⟨002⟩ layers (Fig. 2 and Fig. 3), these two types of layers are similar and are related by the mirror symmetry at 1/4*c*. The distance between these two layers is half the length of the *c* axis (15.05 Å). The phenyl rings are oriented toward the interlayer space. Within the layer, there are a number of hydrogen bonds formed between non-coordinated phosphonate oxygen atoms and the lattice water molecules (Table 2).

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

Compound **1**			
Pb(1)–O(31)	2.305(9)	Pb(1)–O(11)#1	2.322(8)
Pb(1)–O(13)	2.423(8)	Pb(2)–O(33)#2	2.462(9)
Pb(2)–O(33)#3	2.462(9)	Pb(2)–O(21)#4	2.495(9)
Pb(2)–O(21)	2.495(9)	Pb(2)–O(41)#4	2.636(9)
Pb(2)–O(41)	2.636(9)	Pb(3)–O(12)	2.300(9)
Pb(3)–O(32)#5	2.319(9)	Pb(3)–O(41)#5	2.507(9)
O(1w)···N(1)#6 (H bond)	2.796	O(1w)···O(22) (H bond)	2.691
O(1w)···O(43)#5 (H bond)	2.663	O(23)···O(42)#4 (H bond)	2.566
O(31)–Pb(1)–O(11)#1	83.1(4)	O(31)–Pb(1)–O(13)	92.4(3)
O(11)#1–Pb(1)–O(13)	79.3(3)	O(33)#2–Pb(2)–O(33)#3	180.0(5)
O(33)#2–Pb(2)–O(21)#4	89.1(3)	O(33)#3–Pb(2)–O(21)#4	90.9(3)
O(33)#2–Pb(2)–O(21)	90.9(3)	O(33)#3–Pb(2)–O(21)	89.1(3)
O(21)#4–Pb(2)–O(21)	180.0(1)	O(33)#2–Pb(2)–O(41)#4	75.0(3)
O(33)#3–Pb(2)–O(41)#4	105.0(3)	O(21)#4–Pb(2)–O(41)#4	80.4(3)
O(21)–Pb(2)–O(41)#4	99.6(3)	O(33)#2–Pb(2)–O(41)	105.0(3)
O(33)#3–Pb(2)–O(41)	75.0(3)	O(21)#4–Pb(2)–O(41)	99.6(3)
O(21)–Pb(2)–O(41)	80.4(3)	O(41)#4–Pb(2)–O(41)	180.0(1)
O(12)–Pb(3)–O(32)#5	79.2(3)	O(12)–Pb(3)–O(41)#5	90.2(3)
O(32)#5–Pb(3)–O(41)#5	83.6(3)	Pb(3)#3–O(41)–Pb(2)	105.2(3)
Compound **2**			
Pb(1)–O(12)#1	2.480(8)	Pb(1)–O(12)#2	2.552(9)
Pb(1)–O(22)	2.574(8)	Pb(1)–O(13)#3	2.658(9)
Pb(1)–O(1W)	2.679(8)	Pb(1)–Cl(1)	3.055(4)
Pb(2)–O(13)#4	2.557(8)	Pb(2)–O(13)	2.557(8)
Pb(2)–O(11)#5	2.561(8)	Pb(2)–O(11)#6	2.561(8)
Pb(2)–O(2W)#4	2.692(9)	Pb(2)–O(2W)	2.692(9)
Cl(2)···O(2w) (H bond)	3.145	Cl(2)···O(2w)#4 (H bond)	3.145
Cl(2)···O(3w)#1 (H bond)	3.224	Cl(2)···O(3w)#8 (H bond)	3.224
N(1)···O(23) (H bond)	3.010	N(1)···O(23)#1 (H bond)	2.973
O(21)···O(3w) (H bond)	2.576	O(23)···O(2w)#1 (H bond)	2.884
O(1w)···O(22)#9 (H bond)	2.788	O(1w)···O(22)#2 (H bond)	2.788
O(12)#1–Pb(1)–O(12)#2	69.6(3)	O(12)#1–Pb(1)–O(22)	81.3(3)
O(12)#2–Pb(1)–O(22)	81.9(3)	O(12)#1–Pb(1)–O(13)#3	140.2(3)
O(12)#2–Pb(1)–O(13)#3	115.7(3)	O(22)–Pb(1)–O(13)#3	137.6(3)
O(12)#1–Pb(1)–O(1W)	70.2(2)	O(12)#2–Pb(1)–O(1W)	77.4(3)
O(22)–Pb(1)–O(1W)	149.2(2)	O(13)#3–Pb(1)–O(1W)	72.8(2)
O(12)#1–Pb(1)–Cl(1)	80.9(2)	O(12)#2–Pb(1)–Cl(1)	149.4(2)
O(22)–Pb(1)–Cl(1)	101.6(2)	O(13)#3–Pb(1)–Cl(1)	82.3(2)
O(1W)–Pb(1)–Cl(1)	85.6(2)	O(13)#4–Pb(2)–O(13)	136.4(4)
O(13)#4–Pb(2)–O(11)#5	83.9(3)	O(13)–Pb(2)–O(11)#5	105.9(3)
O(13)#4–Pb(2)–O(11)#6	105.9(3)	O(13)–Pb(2)–O(11)#6	83.9(3)
O(11)#5–Pb(2)–O(11)#6	154.1(4)	O(13)#4–Pb(2)–O(2W)#4	77.6(3)
O(13)–Pb(2)–O(2W)#4	68.0(3)	O(11)#5–Pb(2)–O(2W)#4	140.4(3)
O(11)#6–Pb(2)–O(2W)#4	65.5(3)	O(13)#4–Pb(2)–O(2W)	68.0(3)
O(13)–Pb(2)–O(2W)	77.6(3)	O(11)#5–Pb(2)–O(2W)	65.5(3)
O(11)#6–Pb(2)–O(2W)	140.4(3)	O(2W)#4–Pb(2)–O(2W)	75.2(4)
Pb(1)–Cl(1)–Pb(1)#7	86.3(1)	Pb(1)#7–O(1W)–Pb(1)	102.5(4)

Symmetry transformations used to generate equivalent atoms: For compound **1**: #1: $-x, -y, -z+1$; #2: $-x+1/2, y+1/2, z$; #3: $x+1/2, -y-1/2, -z+1$; #4: $-x+1, -y, -z+1$; #5: $x-1/2, -y-1/2, -z+1$; #6: $1-x, 1+y, z$. For compound **2**: #1: $-x-1/2, y, -z+1$; #2: $x, -y+1/2, z+1/2$; #3: $x, y, z+1$; #4: $-x+1/2, y, -z$; #5: $-x+1/2, -y+1/2, -z+1/2$; #6: $x, -y+1/2, z-1/2$; #7: $-x-1/2, y, -z+2$; #8: $x, y, z-1$; #9: $-1/2-x, 1/2-y, 3/2-z$.

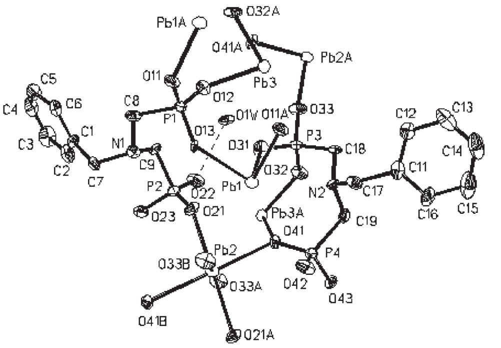

Fig. 1 ORTEP representation of the asymmetric unit of compound **1**. Thermal ellipsoids are drawn at 50% probability.

Crystal structure of $Pb_3(H_2L)_2Cl(H_2O)_3 \cdot Cl \cdot 2H_2O$, 2

Compound **2** has a metal-to-ligand ratio of 3:2. It contains both coordinated and non-coordinated chloride anions, which is uncommon for metal phosphonates. As shown in Fig. 4, the asymmetry unit of compound **2** has two lead(II) ions. Pb1 is octahedrally coordinated by four phosphonate oxygen atoms from four ligands, an aqua ligand and a chloride anion, whereas Pb2 lies on a position of two-fold symmetry and is six-coordinated by four phosphonate oxygen atoms from four ligands and two aqua ligands. Both the $Pb(1)O_5Cl$ and $Pb(2)O_6$ octahedra are severely distorted due to the presence of the lone pair electrons of the lead(II) ion. The Pb–O(phosphonate) distances range from 2.480(8) to 2.658(9) Å, the Pb–O(aqua) distances are slightly longer [2.679(8) and 2.692(9) Å], and the Pb–Cl bond length is 3.055(4) Å (Table 2). One phosphonate group (P1) of the ligand is pentadentate, bridging with five lead(II) ions, whereas the other one is unidentate (Fig. 4). By the requirement of charge balance, each ligand should carry two negative charges, thus the ligand is doubly protonated. Based on the P–O distances as well as the coordination mode, we deem that N1 and O21 are the most likely to be protonated.

The interconnection of the above two types of octahedral *via* bridging ligands results in the formation of a ⟨040⟩ layer (Fig. 5). The layers at $y = 1/4b$ and $y = 3/4b$ are not identical, but are related by a mirror plane at $y = 1/2b$ (Fig. 6). This kind of arrangement is similar to that of compound **1**. The interlayer distance of 15.75 Å is slightly longer than that of compound **1**. The phenyl groups occupy the interlayer space, which is similar to what is observed in compound **1**, forming big tunnels along *a*. The lattice water molecules and uncoordinated chloride ions are located in these tunnels, forming a hydrogen-bonded 3D network with aqua ligands and non-coordinated phoshonate oxygen atoms (Table 2).

Thermogravimetric analysis

The TGA diagram for compound **1** indicates three main steps of weight loss. The first step is the loss of two lattice water molecules, which started at 85 °C and is completed at 266 °C. The following two steps are overlapped: first, the release of water molecule formed by the condensation of hydrogen phosphonate groups, which started at about 267 °C; second, the burning of the organic group, which continued up to 800 °C. The total weight loss is 26.2%, which is in agreement with the calculated weight loss of 24.9% if the final products are assumed to be $Pb_2P_2O_7 + 3Pb(PO_3)_2$. Metaphosphates are

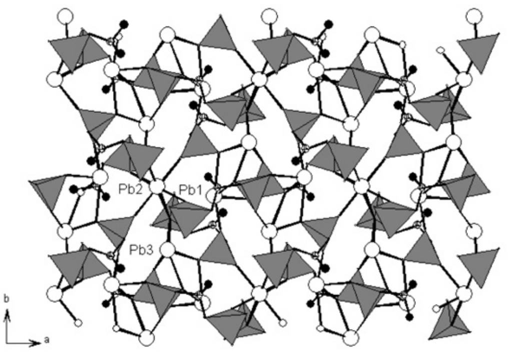

Fig. 2 ⟨002⟩ lead phosphonate layer of compound **1**. C–PO_3 tetrahedra are in grey. Pb, N, O and C atoms are shown as open (large), octanded, open (small) and black circles, respectively. For the sake of clarity, the phenyl groups of the ligand have been omitted.

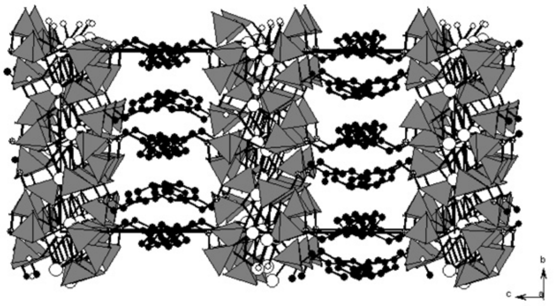

Fig. 3 View of the crystal structure of compound **1** along the *a* axis. C–PO_3 tetrahedra are in grey. Pb, N, O and C atoms are shown as open (large), octanded, open (small) and black circles, respectively.

usually found if the P/M ratio is larger than 1.[11] The TGA diagram of compound **2** shows four major weight losses. The first step is the loss of two lattice water molecules, which is completed at 167 °C. The second step corresponds to the loss of three aqua ligands and the chloride anions. There are two processes taking place between 320 °C and 550 °C; first, the release of water molecules formed by the condensation of hydrogen phosphonate groups; second, the pyrolysis of the organic group. However, these two processes overlap. The final product is $Pb_2P_2O_7 + Pb(PO_3)_2$,in a 1:1 molar ratio; the total weight loss of 27.9% is slightly less than the calculated weight loss of 30.3%, thus the decomposing process is not complete at 800 °C.

Discussion

Reaction of *N*-benzyliminobis(methylenephosphonic acid) (H_4L) with lead(II) acetate and lead(II) chloride yields two different layered materials, whose structures differ from the layered lead(II) compounds with *N*-methyliminobis(methylenephosphonic acid) (H_4L'), $Pb(H_2L')$. $Pb(H_2L')$ has a double layered structure in which the layers are held together *via* hydrogen bonds. In both $Pb_5(H_2L)_2(HL)_2{\cdot}2H_2O$ (**1**) and $Pb_3(H_2L)_2Cl(H_2O)_3{\cdot}Cl{\cdot}2H_2O$ (**2**), the interlayer interaction is the van der Waals force. One axial length (stacking direction of the layers) is similar for all three compounds, whereas the other two axial lengths are quite different. Compound **1** contains two types of ligands with different charges, −2 and −3, respectively, whereas in compound **2** the ligand has two negative charges. The coordination modes for the ligands are also quite different in these three compounds. In compound **1**, the −2 charged ligand bridges with four lead(II) ions with one phosphonate group being terdentate and the other unidentate, whereas the −3 charged ligand connects with five lead(II) ions, one phosphonate group is also terdentate, but the other one bridges with two lead(II) ions by using a μ_2 phosphonate oxygen atom. Each ligand in $Pb(H_2L')$ chelates with a lead(II) ion bidentately and in the mean time also bridges with three other lead(II) ions. We deem that these structural differences are mainly caused by the different organic substitute groups as well as the anions used.

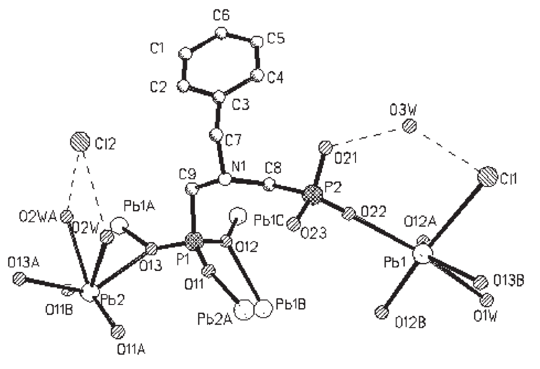

Fig. 4 ORTEP representation of the asymmetric unit of compound **2**. Thermal ellipsoids are drawn at 50% probability.

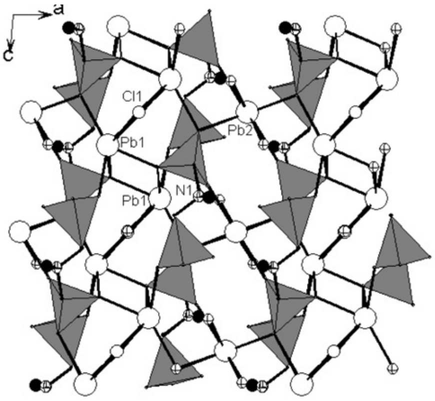

Fig. 5 ⟨040⟩ lead phosphonate layer of compound **2**. C–PO_3 tetrahedra are in grey. Pb, Cl, N, O and C atoms are shown as open (large), open (small), octanded, crossed and black circles, respectively. For the sake of clarity, the phenyl groups of the ligand have been omitted.

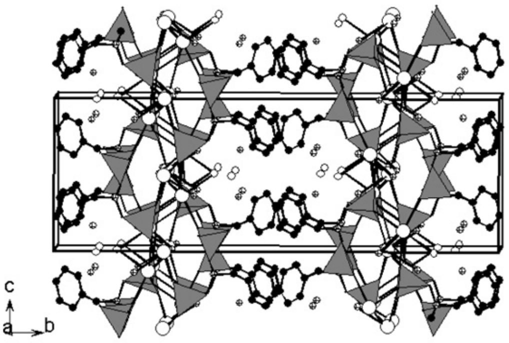

Fig. 6 View of the crystal structure of compound **2** along the *a* axis. C–PO_3 tetrahedra are in grey. Pb, Cl, N, O and C atoms are shown as open (large), open (small), octanded, crossed and black circles, respectively.

Reaction of lead(II) chloride with the diphosphonic acid gave a solution with considerable acidity, thus some chloride anions remain in the coordination sphere or outside the coordination sphere for the sake of charge balance. When the lead(II) acetate is used instead of the chloride, the solution is only slightly acidic, hence, more protons of the ligand can be removed, which in turn allows the ligand to bridge with more lead(II) ions. Since the interlayer space is occupied by the benzyl groups, no interlayer hydrogen bonds can be formed. Also due to the larger size of the benzyl group than the methyl group, the interlayer distances of compounds **1** and **2** are much larger than that of $Pb(H_2L')$ (7.69 Å). To understanding the effect of the substitute group on the structures of the metal phosphonates more clearly, other transition metal ions such as Cd(II) and Zn(II) ions as well as other diphosphonic acids bearing different substitute organic groups have been examined and the results will be reported later.

Acknowledgements

This project is supported by the Innovative Project, the Introduction of Overseas Elitists Program by the Chinese Academy of Sciences and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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