Two isomeric lead(II) carboxylate-phosphonates: syntheses, crystal structures and characterizations

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Abstract

Two isomeric layered lead(II) carboxylate-phosphonates of N-(phosphonomethyl)-N-methyl glycine ([MeN(CH$_2$CO$_2$H)(CH$_2$PO$_3$H$_2$)] = H$_3$L), namely, monoclinic Pb$_3$L$_2 \cdot$ H$_2$O **1** and triclinic Pb$_3$L$_2 \cdot$ H$_2$O **2**, have been synthesized and structurally determined. Compound **1** synthesized by hydrothermal reaction at 150°C is monoclinic, space group $C2/c$ with $a = 19.9872(6)$, $b = 11.9333(1)$ and $c = 15.8399(4)$ Å, $\beta = 110.432(3)°$, $V = 3540.3(1)$ Å^3, and $Z = 8$. The structure of compound **1** features a $\langle 400 \rangle$ layer in which the lead(II) ions are bridged by both phosphonate and carboxylate groups. The lattice water molecules are located between the layers, forming hydrogen bonds with the non-coordinated carboxylate oxygen atoms. Compound **2** with a same empirical formula as compound **1** was synthesized by hydrothermal reaction at 170°C. It has a different layer structure from that of compound **1** due to the adoption of a different coordination mode for the ligand. It crystallizes in the triclinic system, space group $P\bar{1}$ with cell parameters of $a = 7.1370(6)$, $b = 11.522(1)$, $c = 11.950(1)$ Å, $\alpha = 110.280(2)$, $\beta = 91.625(2)$, $\gamma = 95.614(2)°$, $V = 915.3(1)$ Å^3 and $Z = 2$. The structure of compound **2** features a $\langle 020 \rangle$ metal carboxylate-phosphonate double layer built from 1D lead(II) carboxylate chains interconnected with 1D lead(II) phosphonate double chains. XRD powder patterns of compounds **1** and **2** indicate that each compound exists as a single phase.

1. Introduction

Metal phosphonate chemistry has been an area of interest to both inorganic and materials chemists in recent years due to potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1]. Most of the compounds studied are layered species in which the metal octahedra are bridged by phosphonate tetrahedra to form 2D layers that are separated by the hydrophobic regions of the organic moieties [1]. Studies from our group and others have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, form this type of layered compound [1–3]. In addition to the layered species, metal phosphonates also exhibit a variety of open framework and microporous structures [1]. Materials with open-framework and microporous structures are expected to find their use as hybrid composite materials in electro-optical and sensing application [4]. A variety of functional groups such as crown ether, amine, and carboxylate groups have been attached to the phosphonic acids in search of new inorganic–organic hybrid materials [1,4–14]. Researches on metal compounds with phosphonic acids attached with aza-crown ethers and diaza-crown ether show that those compounds exhibit many unusual structural features such as 1D "macrocyclic leaflets" and porous 3D networks [1,5,6]. A series of novel pillar layered and microporous compounds have been synthesized by hydrothermal reactions of

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phosphonic acids containing a carboxylate group, such as $H_2O_3PCH_2CH_2CO_2H$ and $H_2O_3PCH_2CO_2H$, with different metal salts [4,7,8]. Studies on metal amino-carboxylate-phosphonates are still relatively rare [9–15]. A new layered zirconium diphosphonate fluoride, $ZrHF(O_3PCH_2)_2NHC_3H_6CO_2$, has been reported by the Vivani group and a layered cobalt(II) complex with the phosphonic acid derived from proline were reported recently [9]. Layered or 3D network structures of the alkali metal, Ag(I), Zn(II), Pb(II) and Eu(II) complexes with *N*-(phosphonomethyl)-glycine have also been reported [10]. *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) has been found to be able to form metal phosphonates with 1D chain, 2D layer and 3D porous structures [11–14]. Zinc(II) compounds with *N,N*-bis (phosphonomethyl)amino-acetic acid and *N*-(phospho-nomethyl)-*N*-methyl glycine have been also prepared recently in our laboratory [15]. The structure of the latter zinc(II) amino-carboxylate-phosphonate features a microporous structure built from heptanuclear $Zn_6(Zn)(ligand)_6$ cluster anions [15b]. Lead(II) phosphonates usually have different structures from those of divalent transition metal due to the presence of the lone pair electrons [10,12]. Reactions of *N*-(phosphono-methyl)-*N*-methyl glycine with lead(II) acetate afforded two layered isomers with a same formula of $Pb_3L_2 \cdot H_2O$, namely a monoclinic phase **1**, and a triclinic phase **2**. Isomeric metal phosphonates have not been reported yet, although they exist in metal phosphates and other inorganic salts. Herein we reported their syntheses, characterizations and crystal structures.

2. Experimental

N-(phosphonomethyl)-*N*-methyl glycine (H_3L) was prepared by a Mannich type reaction according to procedures previously described [15b]. All other chemicals were of reagent grade obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analysis was carried out with a TGA/SBTA851 unit, at a heating rate of 15°C/min under an oxygen atmosphere. The XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated Cu$K\alpha$ radiation in the angular range $2\theta = 5-70°$ with a step size of 0.02° and a counting time of 3 s per step.

2.1. Synthesis of the monoclinic $Pb_3L_2 \cdot H_2O$ 1

Compound **1** was prepared by hydrothermal reactions. A mixture of 0.5 mmol of lead(II) acetate trihydrate (Aldrich), 0.5 mmol of H_3L and 10 mL of deionized water was heated at 150°C for 5 days. The initial and final pH values of the solution are 6.0 and 5.5,

respectively. Colorless crystals of **1** were obtained in a 42.5% yield based on Pb. Elemental analysis for **1**, $C_8H_{16}N_2O_{11}P_2Pb_3$: C, 9.45; H, 1.39; N, 2.97. Calc. C, 9.60; H, 1.61; N, 2.80%.

2.2. Synthesis of triclinic $Pb_3L_2 \cdot H_2O$ 2

Compound **2** was also synthesized by hydrothermal reactions. A mixture of 0.5 mmol of lead(II) acetate trihydrate (Aldrich), 0.5 mmol of H_3L, 0.5 mmol of 3-sulfobenzoic acid monosodium salt (Acros) and 10 mL of distillated water was heated at 170°C for 5 days. The initial and final pH values of the solution are 6.0 and 5.5, respectively. Colorless crystals of **2** were isolated in a 47.0% yield based on Pb. Elemental analysis for **2**, $C_8H_{16}N_2O_{11}P_2Pb_3$: C, 9.38; H, 1.43; N, 2.69. Calc. C, 9.60; H, 1.61; N, 2.80%.

2.3. X-ray crystallography

Single crystals of compounds **1** and **2** were mounted on a Siemens Smart CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). 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 based on ψ scan technique. All structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [16]. All non-hydrogen atoms, except for N(1), C(3), C(4), C(5), O(3) and O(13) atoms for compound **1**, and N(1) and C(6) atoms for compound **2**, are refined with anisotropical thermal parameters. Hydrogen atoms except those for the water molecules were located at the geometrically calculated positions. Crystallographic data and refinement residuals are summarized in Table 1. Important bond distances and angles are listed in Table 2.

CCDC No. 207758 and 207759 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].

3. Results and discussion

The monoclinic form of $Pb_3L_2 \cdot H_2O$ **1** synthesized by hydrothermal reactions at 150°C has a layered structure. As shown in Fig. 1, the asymmetric unit of compound **1** contains three unique Pb(II) ions, two carboxylate-phosphonate ligands and a lattice water molecule. Both Pb(1) and Pb(2) are five coordinated by a tridentate chelating ligand and two phosphonate oxygen atoms from two neighboring ligands. Pb(3) is five-coordinated

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

Compound	**1**	**2**
Empirical formula	$C_8H_{16}N_2O_{11}P_2Pb_3$	$C_8H_{16}N_2O_{11}P_2Pb_3$
M	999.74	999.74
Space group	$C2/c$	$P\bar{1}$
a (Å)	19.9872(6)	7.1370(6)
b (Å)	11.93330(10)	11.5222(10)
c (Å)	15.8399(4)	11.9498(11)
α (°)	90.0	110.280(2)
β (°)	110.432(3)	91.625(2)
γ (°)	90.0	95.614(2)
V (Å^3)	3540.34(14)	915.30(14)
Z	8	2
D_c (g cm^{-3})	3.751	3.627
μ (Mo$K\alpha$) (mm^{-1})	28.702	27.755
F (000)	3536	884
Reflections collected	5553	4708
Unique reflections	3092 ($R_{int} = 6.89\%$)	3163 ($R_{int} = 8.16\%$)
Observed reflections ($I > 2\sigma(I)$)	2390	2608
Goodness-of-fit on F^2	1.154	1.087
R_1, wR_2 ($I > 2\sigma(I)$)	0.0591, 0.1085	0.0514, 0.1185
R_1, wR_2 (all data)	0.0904, 0.1244	0.0693, 0.1320

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, w$R_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$.

by two carboxylate and three phosphonate oxygen atoms from five ligands. The Pb(1)–O(12a) (symmetry operator: $\frac{1}{2} - x$, $-\frac{1}{2} - y$, $-z$) bond of 2.811 (15) Å, is much weaker than the remaining Pb–O bonds ranging from 2.269(15) to 2.704(15) Å. Such weak Pb–O bonds have been reported in other lead(II) phosphonates or carboxylates, and they are necessary to satisfy the valence of the lead(II) ion [10c,12,17]. The Pb–N distances are in the range of 2.577(18)–2.598(19) Å, comparable to those reported in other lead(II) phosphonates [10c,12]. The coordination geometry around Pb(2) and Pb(3) atoms can be described as a distorted tetragonal pyramid. The lone pair electrons of the Pb(II) ion occupy the free side of square plane, completing an octahedron. The lone pair electrons of Pb(1) occupy one corner of the square plane. One phosphonate group (P(1)) acts as a pentadentate metal linker and bridges with five Pb(II) ion (with the weak Pb–O bonds included), whereas the other phosphonate group (P2) connects with four Pb(II) ions. O(12), O(13) and O(23) each bridges two metal ions. All carboxylate groups are unidentate. The lattice water molecule forms a hydrogen bond with a non-coordinated carboxylate oxygen (O(1)) (Table 2).

The interconnection of the lead(II) ions via bridging phosphonate ligands resulted in the formation of a ⟨400⟩ metal carboxylate phosphonate layer (Fig. 2). Within the 2D layer, the Pb(1) and Pb(2) carboxylate chains along c-axis are sandwiched between the Pb(3) phosphonate chains along the c-axis. The lattice

water molecules are located at the interlayer space and form hydrogen bonds with non-coordinated carboxylate oxygen atoms (Fig. 3, Table 2). The interlayer distance is one half of the length of the a-axis (about 10 Å) and the thickness of the 2D layer is ca. 6.6 Å.

The triclinic $Pb_3L_2 \cdot H_2O$ **2** was synthesized by hydrothermal reactions at 170°C with addition of 3-sulfobenzoic acid monosodium salt. We still do not understand the role 3-sulfobenzoic acid monosodium salt played on the formation of compound **2**. As shown in Fig. 4, Pb(1) and Pb(2) each is six-coordinated by one tridentate chelating carboxylate-phosphonate ligands and three phosphonate oxygen atoms from three neighboring [PbL] units with one of the Pb–O bonds elongated due to the "lone pair" electrons of the Pb(II) ion, which is slightly different from that in compound **1**. The coordination geometry around the Pb(II) ions is a severely distorted octahedron. Unlike that in compound **1**, the Pb(1)L and Pb(2)L units in compound **2** are bridged by a pair of μ^2-phosphonate oxygen atoms (O(21) and O(12)), to form a four-membered ring. Pb(3) forms three normal Pb–O bonds with one carboxylate and two phosphonate oxygen atoms from three neighboring [PbL] units. The Pb–O distances range from 2.332(14) to 2.435(14) Å, comparable to those in compound **1** as well as those reported in other lead(II) phosphonates [10c,12]. Bond valence calculations indicate that the valence associated with these three Pb(3)–O bonds is 1.49, cover only 75% of the assumed oxidation state of Pb(II), hence secondary bonding should also be considered [17]. Pb(3) forms three addition weak Pb–O bonds with three carboxylate (O(3a) and O(2a), symmetry operator: $-x, 1 - y, 2 - z$, and O(4)). These weak Pb–O bonds range from 2.759(17) to 2.843(16) Å. With these weak bonds included in the calculation, the valence for Pb(3) is 1.96, which is in good agreement with the expected value. The coordination geometry around the Pb(3) atom can be best described as a distorted octahedron. Two types of rings are formed, one is a 4-membered ring formed by Pb(1), O(12), Pb(2), and O(21) atoms, the other one is a 6-membered ring contains Pb(1), O(1), Pb(3a), O(23), P(2) and O(21) atoms.

Each phosphonate group is tetradentate and connects with four lead(II) ions, whereas each carboxylate group is tridentate and bridges with three metal ions. This type of coordination mode is different from that in compound **1**. The interconnection of lead(II) ions through bridging carboxylate and phosphonate groups results in the formation of a ⟨020⟩ double layer (Fig. 5). The double layer is built from 1D Pb(3) carboxylate chains along a-axis interconnected with the 1D metal phosphoante double chain of Pb1 and Pb2 along a-axis (Fig. 5). In the metal carboxylate chain, each pair of lead(II) ions is bridged by a pair of carboxylate groups, forming

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

1

Pb(1)–O(21)	2.269(15)	Pb(1)–O(2)	2.476(17)
Pb(1)–N(1)	2.577(18)	Pb(1)–O(13)	2.642(14)
Pb(1)–O(12)#1	2.811(15)	Pb(2)–O(4)	2.420(13)
Pb(2)–O(13)#2	2.437(13)	Pb(2)–O(23)	2.592(16)
Pb(2)–N(2)	2.598(19)	Pb(2)–O(12)#3	2.661(15)
Pb(3)–O(22)	2.378(16)	Pb(3)–O(23)#4	2.379(15)
Pb(3)–O(2)	2.533(15)	Pb(3)–O(4)#5	2.594(14)
Pb(3)–O(11)#6	2.704(15)		

Hydrogen bonds:

O(1)···O(1w)	2.83(3)		
O(21)–Pb(1)–O(2)	84.3(6)	O(21)–Pb(1)–N(1)	88.4(6)
O(2)–Pb(1)–N(1)	65.0(5)	O(21)–Pb(1)–O(13)	89.2(5)
O(2)–Pb(1)–O(13)	133.8(5)	N(1)–Pb(1)–O(13)	69.1(5)
O(21)–Pb(1)–O(12)#1	160.6(6)	O(2)–Pb(1)–O(12)#1	76.3(5)
N(1)–Pb(1)–O(12)#1	83.4(5)	O(13)–Pb(1)–O(12)#1	104.2(4)
O(4)–Pb(2)–O(13)#2	74.4(5)	O(4)–Pb(2)–O(23)	135.5(5)
O(13)#2–Pb(2)–O(23)	92.5(5)	O(4)–Pb(2)–N(2)	67.3(5)
O(13)#2–Pb(2)–N(2)	86.1(5)	O(23)–Pb(2)–N(2)	69.5(5)
O(4)–Pb(2)–O(12)#3	89.1(5)	O(13)#2–Pb(2)–O(12)#3	163.0(4)
O(23)–Pb(2)–O(12)#3	102.5(5)	N(2)–Pb(2)–O(12)#3	91.6(5)
O(22)–Pb(3)–O(23)#4	82.1(6)	O(22)–Pb(3)–O(2)	89.4(6)
O(23)#4–Pb(3)–O(2)	69.1(6)	O(22)–Pb(3)–O(4)#5	87.7(6)
O(23)#4–Pb(3)–O(4)#5	84.7(5)	O(2)–Pb(3)–O(4)#5	153.8(5)
O(22)–Pb(3)–O(11)#6	150.8(6)	O(23)#4–Pb(3)–O(11)#6	72.2(6)
O(2)–Pb(3)–O(11)#6	93.9(5)	O(4)#5–Pb(3)–O(11)#6	76.6(5)

2

Pb(1)–O(12)	2.461(14)	Pb(1)–O(1)	2.519(14)
Pb(1)–O(21)	2.533(14)	Pb(1)–N(1)	2.599(16)
Pb(1)–O(22)#1	2.631(13)	Pb(1)–O(13)#2	2.776(14)
Pb(2)–O(21)	2.466(15)	Pb(2)–O(12)	2.527(14)
Pb(2)–O(13)#3	2.571(15)	Pb(2)–N(2)	2.621(18)
Pb(2)–O(4)	2.625(16)	Pb(2)–O(23)#4	2.819(13)
Pb(3)–O(11)	2.332(14)	Pb(3)–O(1)#4	2.356(15)
Pb(3)–O(23)#4	2.435(14)	Pb(3)–O(3)#5	2.759(17)
Pb(3)–O(4)	2.780(16)	Pb(3)–O(2)#5	2.843(16)
O(12)–Pb(1)–O(1)	101.3(5)	O(12)–Pb(1)–O(21)	71.1(5)
O(1)–Pb(1)–O(21)	78.9(5)	O(12)–Pb(1)–N(1)	72.0(5)
O(1)–Pb(1)–N(1)	64.8(5)	O(21)–Pb(1)–N(1)	120.5(5)
O(12)–Pb(1)–O(22)#1	77.6(5)	O(1)–Pb(1)–O(22)#1	153.1(5)
O(21)–Pb(1)–O(22)#1	124.6(4)	N(1)–Pb(1)–O(22)#1	89.9(5)
O(12)–Pb(1)–O(13)#2	161.1(5)	O(1)–Pb(1)–O(13)#2	97.4(5)
O(21)–Pb(1)–O(13)#2	115.8(4)	N(1)–Pb(1)–O(13)#2	114.3(5)
O(22)#1–Pb(1)–O(13)#2	84.5(4)	O(21)–Pb(2)–O(12)	71.2(5)
O(21)–Pb(2)–O(13)#3	77.4(4)	O(12)–Pb(2)–O(13)#3	94.8(5)
O(21)–Pb(2)–N(2)	72.5(5)	O(12)–Pb(2)–N(2)	140.9(5)
O(13)#3–Pb(2)—N(2)	91.1(5)	O(21)–Pb(2)–O(4)	87.1(5)
O(12)–Pb(2)–O(4)	100.4(5)	O(13)#3–Pb(2)–O(4)	153.4(5)
N(2)–Pb(2)–O(4)	63.5(5)	O(21)–Pb(2)–O(23)#4	154.5(4)
O(12)–Pb(2)–O(23)#4	103.6(5)	O(13)#3–Pb(2)–O(23)#4	128.1(4)
N(2)–Pb(2)–O(23)#4	102.7(5)	O(4)–Pb(2)–O(23)#4	69.0(5)
O(11)–Pb(3)–O(1)#4	77.8(7)	O(11)–Pb(3)–O(23)#4	77.6(5)
O(1)#4–Pb(3)–O(23)#4	83.9(5)	O(11)–Pb(3)–O(3)#5	78.8(5)
O(1)#4–Pb(3)–O(3)#5	87.3(6)	O(23)#4–Pb(3)–O(3)#5	156.1(5)
O(11)–Pb(3)–O(4)	77.5(6)	O(1)#4–Pb(3)–O(4)	148.7(5)
O(23)#4–Pb(3)–O(4)	72.3(5)	O(3)#5–Pb(3)–O(4)	106.3(5)
O(11)–Pb(3)–O(2)#5	159.6(5)	O(1)#4–Pb(3)–O(2)#5	91.9(6)
O(23)#4–Pb(3)–O(2)#5	83.9(4)	O(3)#5–Pb(3)–O(2)#5	118.7(4)
O(4)–Pb(3)–O(2)#5	105.0(4)		

Symmetry transformations used to generate equivalent atoms: For **1**: #1−x+1/2, −y−1/2, −z; #2−x+1/2, y+1/2, −z−1/2; #3x, y+1, z; #4−x+1/2, −y+1/2, −z; #5x, −y+1, z+1/2; #6x, −y, z+1/2. For **2**: #1−x+1, −y+1, −z+1; #2x+1, y, z; #3−x, −y+1, −z+1; #4x−1, y, z; #5−x, −y+1, −z+2.
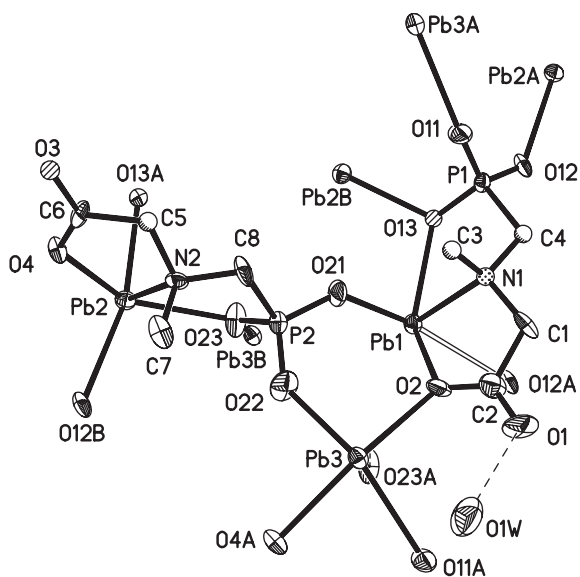
Fig. 1. ORTEP representation of the selected unit of **1**. The thermal ellipsoids for the atoms refined with anisotropical thermal parameters are drawn at 50% probability. The open lines represent weak Pb–O contacts. Hydrogen bond is represented by a dashed line.
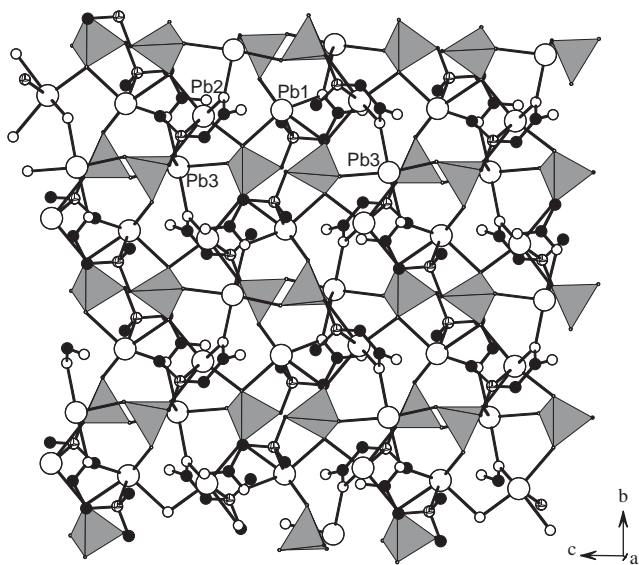

Fig. 3. View of the structure of **1** down the *b*-axis. C-PO$_3$ tetrahedra are shaded in gray. Pb, N, C and O atoms are represented as open (large), octand, black and open (small) circles, respectively.

Fig. 2. A $\langle 400 \rangle$ layer of **1**. C-PO$_3$ tetrahedra are shaded in gray. Pb, N, C and O atoms are represented as open (large), octand, black and open (small) circles, respectively.
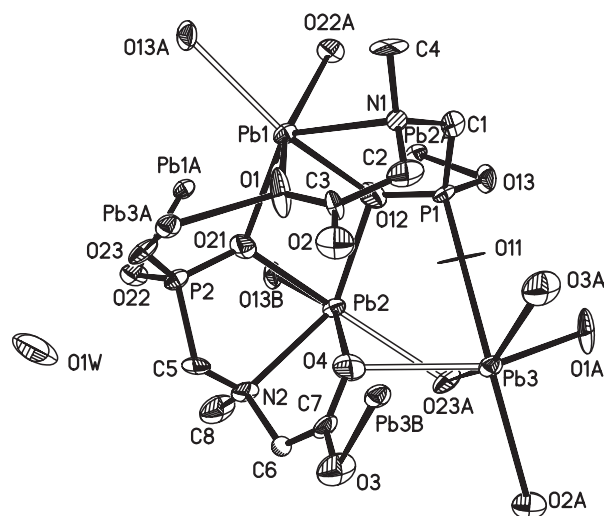
Fig. 4. ORTEP representation of the selected unit of **2**. The thermal ellipsoids for the atoms refined with anisotropical thermal parameters are drawn at 50% probability. The open lines represent weak Pb–O contacts.

an 8-membered ring. Similar to that in compound **1**, the lattice water molecules are located in the middle of the interlayer space (Fig. 6). The interlayer distance of 11.5 Å is much larger than that in compound **1**. The thickness of the layer is calculated to be about 9.1 Å, which is also much larger than that in compound **1**.

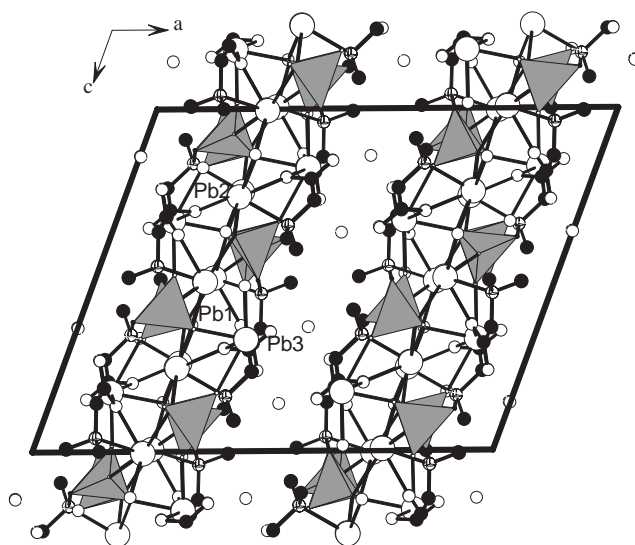The different structures of compounds **1** and **2** have also been indicated by their different powder patterns. Their XRD powder patterns match well with the ones simulated from single crystal structural data, thus both compounds **1** and **2** were obtained as a single phase.

The TGA diagrams for **1** and **2** are similar and show two steps of weight losses. The first weight loss is the release of a lattice water molecule. The observed weight losses are 1.6% and 2.0%, respectively, for compounds **1** and **2**. The second step is the oxidation of organic groups which covers a temperature range from 320°C to 702°C for **1**, and 380°C to 585°C for **2**. The final product is a mixture of Pb$_2$P$_2$O$_7$ (ICDD
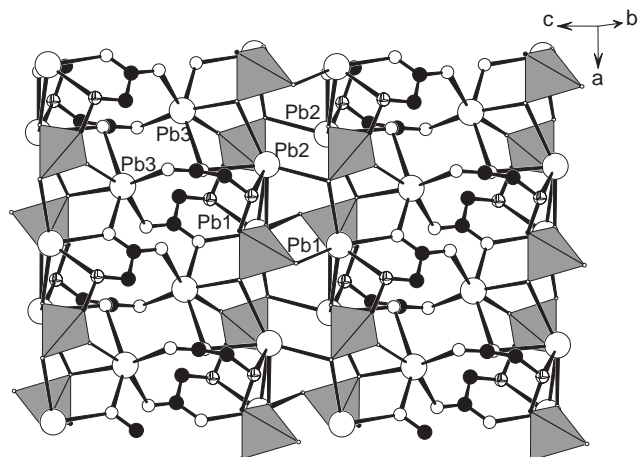
Fig. 5. A $\langle 020 \rangle$ double layer of **2**. C-PO$_3$ tetrahedra are shaded in gray. Pb, N, C and O atoms are represented as open (large), octand, black and open (small) circles, respectively.
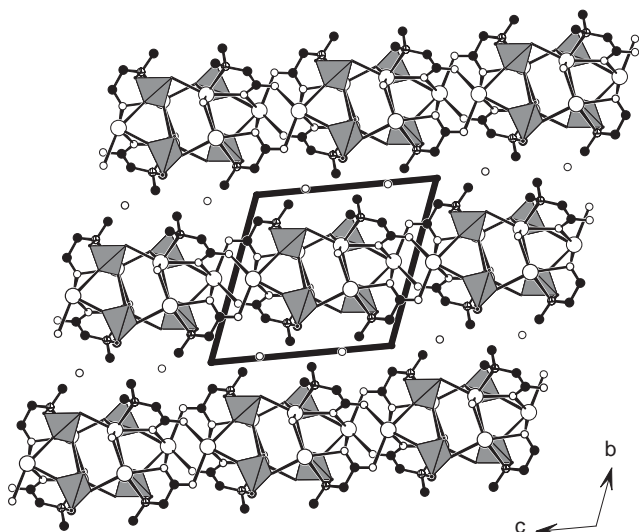

Fig. 6. View of the structure of **2** down *a*-axis. C-PO$_3$ tetrahedra are shaded in gray. Cd, N, C and O atoms are represented as open (large), octanded, black and open (small) circles, respectively.

PDF No. 27-1203) and PbO (ICDD PDF No. 5-0561) in a molar ratio close to 1:1 based on XRD powder patterns. The total weight loss of is 82.3% for **1** and 81.7% for **2**, respectively, which is in good agreement with the calculated weight loss of 81.2%.

4. Conclusions

Reactions of *N*-(phosphonomethyl)-*N*-methyl glycine with different divalent metal salts afforded four divalent metal carboxylate-phosphonate hybrid compounds [15b,18]. To the best of our knowledge, they are the first examples of isomers in metal phosphonates.

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