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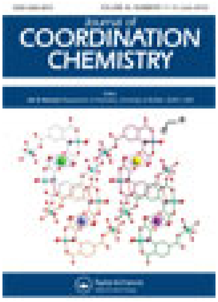

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Exploratory syntheses, structures, and photoluminescent properties of three lead multi-dimensional frameworks

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Exploratory syntheses, structures, and photoluminescent properties of three lead multi-dimensional frameworks

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Three structurally diverse Pb^{II} coordination complexes, $[Pb_3O(OH)(4\text{-sphth})]_2(H_2O)$ (**1**), $[Pb(3,5\text{-Hdhb})]H_2O$ (**2**), and $[Pb_3(4\text{-nphth})_2(OH)_2]$ (**3**) (4-H_3sphth, 4-sulfophthalic acid; 3,5-H_2dhb, 3,5-dihydroxybenzoic acid; 4-H_2nphth, 4-nitrophthalic acid), were synthesized under hydrothermal conditions. X-ray diffraction analyses reveal that **1** is constructed from $[Pb_4O_4]$ cubanes, based on which ladder-shaped structure is built *via* 4-H_3sphth bridge. This is the first Pb_4O_4-containing polymer. The Pb_2O_2 units in **2** are bridged by two parallel 3,5-HDHB ligands along the *a*-axis and two other parallel 3,5-HDHB ligands along the *b*-axis, forming a 3-D framework. For **3**, the crystal structure is built up of a layer motif consisting of corner-sharing pyramidal Pb_3O units, which are linked through Pb corners to form a hexagonal unit. Each PbO_6 polyhedron is connected to three polyhedra (Pb_3O) *via* sharing an edge (two μ_3-oxygen atoms) and two faces (three μ_3-oxygen atoms), thus yielding an infinite 2-D Pb–O–Pb (3,6-net) honeycomb layer. The luminescence of **1**–**3** demonstrates that they may be good candidates for luminescent materials.

Keywords: Lead; 4-Sulfophthalic acid; 3,5-Dihydroxybenzoic acid; 4-Nitrophthalic acid; Pb_4O_4; X-ray analysis; Luminescence

1. Introduction

Design and synthesis of highly connected coordination frameworks has received interest because of their appealing structures and topologies [1–6], their unusual optical, electronic, magnetic, catalytic properties [7–10], and their potential from their antiviral and the inhibition of angiogenesis [11–13]. However, it is difficult to rationally construct such coordination frameworks *via* conventional synthetic methods due to the limited coordination sites around metal centers and the steric hindrance of ligands. Currently, there are two potential routes to highly connected coordination networks: (i) using lanthanides with high coordination numbers and organic linkers with small

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steric hindrance. For example, Long *et al.* reported a series of highly connected lanthanide coordination frameworks with a flexible 4,4′-bipyridine-*N*,*N*′-dioxide [14–16]; (ii) employing metal clusters as secondary building units (SBUs), such as Co_4 and Zn_{11}-based 8-connected bcu networks and a Cd_5-based 10-connected γ-Pu topology [17–19]. Polynuclear cluster SBUs usually possess more outward-connecting sites and larger surface areas, which can readily meet the steric requirement of the organic linkers to afford the resulting highly connected nets.

In contrast to transition metals, lead(II) is commonly found in critical life cycles due to its widespread use in numerous industrial applications [20–22]. Molecular mechanisms of lead(II) toxicity may be involved in several types of proteins [23–25]. Knowledge of Pb(II) coordination properties, including aspects such as the lone pair of electrons, coordination number, and coordination geometry, is crucial for understanding the toxicological properties of lead(II) [26–29]. Lead(II) possess unique coordination preferences and electronic properties, presenting opportunities for the preparation of structures with new and interesting characteristics [27–29].

Self-assembly of main group metal–organic supramolecular complexes with interesting structures have been reported [30–35]. Organic acid and neutral chelating ligands have important effects on the structures of their complexes [36–40]. In spite of advances in crystal engineering, only a limited number of $[Pb_mO_n]$-containing architectures with highly connected topologies are known [41–44] and their design and synthesis is still a challenge. It is necessary to build more structural paradigms for further demonstrating the nature of such supramolecular systems. For example, a few $[Pb_4O_4]$ cubanes with the bridge of RO^{-1} (R = tBu, $SiMe_3$, and $CHPh_2$) have been reported [45–47] and a series of fascinating structures based on Pb^{II} and carboxylates are also published [48–52]. Such crystalline systems with structural diversity also exhibit important properties of electroluminescence, photovoltaic conversion, and fluorescence [48–52].

As continuation of our work [53–56], we describe the synthesis and structural characterizations of three lead complexes, $[Pb_3O(OH)(4\text{-sphth})]_2(H_2O)$ (**1**), [Pb(3,5-Hdhb)]H_2O (**2**), and $[Pb_3(4\text{-nphth})_2(OH)_2]$ (**3**) (4-H_3sphth, 4-sulfophthalic acid; 3,5-H_2dhb, 3,5-dihydroxybenzoic acid; 4-H_2nphth, 4-nitrophthalic acid). The different architectures of **1**–**3** can be attributed to different structures of the organic acids [36–40].

2. Experimental

2.1. *Materials and methods*

All reagents of analytical grade were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. and used without purification. Elemental analysis was conducted on a Perkin-Elmer 240 C elemental analyzer; infrared (IR) spectra were recorded from 400 to 4000 cm^{-1} on a Perkin-Elmer 2400LSII spectrometer.

Synthesis of 1: A mixture of $Pb(NO_3)$ (0.50 mmol, 0.165 g), 4-H_3sphth (0.50 mmol, 0.12 g), and 2,2′-bipyridine (0.5 mmol, 0.078 g) at a ratio of 1 : 1 : 1 in 15 mL of H_2O was sealed in a Teflon-lined stainless steel vessel, heated at 140°C for 3 days under autogenous pressure, and then cooled to room temperature. Colorless block crystals of **1** were harvested with a yield of 82% based on Pb. Elemental analysis Calcd for $C_{16}H_{10}O_{19}Pb_6S_2$ (%): C, 10.59; H, 0.50. Found: C, 10.36; H, 0.46. IR data

(KBr, cm^{-1}): 3418 s, 3110 ms, 1584 s, 1542 m, 1479 w, 1379 s, 1213 s, 1176 m, 1138 m, 863 m, 783 w, 682 w, 638 m.

Synthesis of 2: The synthetic method is also similar to that of **1** except that 3,5-dihydroxy benzoic acid (0.50 mmol, 0.08 g) replaced 4-H_3sphth. Colorless block crystals were obtained after cooling to room temperature with a yield of 78% based on Pb. Elemental analysis Calcd for $C_7H_6O_5Pb$ (%): C, 22.46; H, 1.60. Found: C, 22.35; H, 1.49. IR data (KBr, cm^{-1}): 3418 s, 3110 ms, 1584 s, 1542 m, 1479w, 1379 s, 1213 s, 1176 m, 1138 m, 863 m, 783 w, 682 w, 638 m.

Synthesis of 3: The synthetic method is also similar to that of **1** except that 4-nitrophthalic acid (0.50 mmol, 0.11 g) replaced 4-H_3sphth. Colorless block crystals were obtained after cooling to room temperature with a yield of 85% based on Pb. Elemental analysis Calcd for $C_{16}H_8N_2O_{14}Pb_3$ (%): C, 18.05; H, 0.75, N, 2.61. Found: C, 17.55; H, 0.66; N, 2.35. IR data (KBr, cm^{-1}): 3418 s, 3110 ms, 1584 s, 1542 m, 1479 w, 1379 s, 1213 s, 1176 m, 1138 m, 863 m, 783 w, 682 w, 638 m.

X-ray crystallography: Intensity data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at 293(2) K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using SADABS based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL-97 package [57]. During the refinement, all atoms were refined anisotropically by full-matrix least-squares calculations based on F^2. Crystallographic data for **1**–**3** are given in table 1. Selected bond lengths and angles are listed in tables 2–4.

3. Results and discussion

3.1. *Synthesis and general characterization*

The unique ladder-shaped structure of **1**, based on the Pb_4O_4 units, is obtained from the hydrothermal reaction of $Pb(NO_3)$, 4-H_3sphth, and 2,2′-bipyridine with pH adjusted to 6–7 at 140°C. As continuation of our investigation of Pb_mO_n-containing structures, 2,3(2,4; 2,5; 2,6; 3,4; or 3,5)-pyridine dicarboxylic acids, 3,5-dihydroxybenzoic acid, and 4-nitrophthalic acid are used to replace 4-H_3sphth under the same synthetic environment. As a result, two new complexes, **2** and **3**, are obtained. The Pb_2O_2 units in **2** are bridged by two parallel 3,5-HDHB ligands along the *a*-axis and by two other parallel 3,5-HDHB ligands along the *b*-axis to yield a 3-D framework. For **3**, the crystal structure is built up of a layer motif consisting of corner-sharing pyramidal Pb_3O units, linked through Pb corners to form a hexagonal unit. The different architectures of **1**–**3** can be attributed to the organic acids [36–40].

3.2. *Structures of 1–3*

Single-crystal X-ray diffraction analysis reveals that **1** is constructed from [Pb_4O_4] cubanes, based on which ladder-shaped 1-D structure is built *via* the 4-H_3sphth bridge.

Table 1. Crystallographic data and details of diffraction experiments for **1–3**.

	1	**2**	**3**
Empirical formula	$C_{16}H_{10}O_{19}Pb_6S_2$	$C_7H_6O_5Pb$	$C_{16}H_8N_2O_{14}Pb_3$
Formula weight	1813.50	377.31	1073.81
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pnma*	$P\bar{1}$	*Cc*
Unit cell dimensions (Å, °)			
a	9.633(1)	6.946(3)	7.031(3)
b	20.827(3)	7.181(3)	7.071(3)
c	14.314(2)	9.210(5)	11.090(5)
α	90.00	106.123(6)	91.475(4)
β	90.00	104.948(6)	102.677(4)
γ	90.00	105.678(4)	114.704(4)
Volume (Å^3), *Z*	2871.6(7), 4	396.4(3), 2	484.4(4), 4
Calculated density (g cm^{-3})	4.195	3.161	3.681
Absorption coefficient (mm^{-1})	35.279	21.264	26.092
Reflections collected	14,026	2277	3362
Independent reflection	2605 [*R*(int) = 0.0477]	1380 [*R*(int) = 0.0467]	1690 [*R*(int) = 0.0471]
Refined parameters	203	125	164
Goodness-of-fit on F^{2c}	0.997	1.001	1.000
Final $R^{a,b}$indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0924$	$R_1 = 0.04991$, $wR_2 = 0.1366$	$R_1 = 0.0389$, $wR_2 = 0.0984$
$R^{a,b}$indices (all data)	$R_1 = 0.0354$, $wR_2 = 0.0957$	$R_1 = 0.0520$, $wR_2 = 0.1389$	$R_1 = 0.0420$, $wR_2 = 0.1005$
Largest difference peak and hole (e Å^{-3})	2.210 and −3.187	4.796 and −3.597	2.301 and −2.667

$w = 1/[\sigma^2(F_o^2) + xP + (yP)^2]$; with $P = (F_o^2 + 2F_c^2)/3$ and $x = 0.0407$, $y = 34.2438$ (**1**); $x = 0.0931$, $y = 0.0000$ (**2**); $x = 0.0540$, $y = 0.0000$ (**3**). [c]Goodness-of-fit on $F^2 = [\Sigma w(F_{obsd}^2 - F_{calcd}^2)^2/(n - p)]^{1/2}$, where n = number of reflections, p = parameter used. [a]$R1 = \Sigma||F_{obsd.}| - |F_{calcd.}||/\Sigma|F_{obsd.}|$. [b]$wR_2 = \{\Sigma[w(F_{obsd}^2 - F_{calcd}^2)^2]/\Sigma[w(F_{obsd}^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths and angles for **1**.

Pb(1)–O(8)	2.238(8)	Pb(4)–O(9)	2.461(8)
Pb(1)–O(7)	2.506(7)	Pb(4)–Pb(5)	3.641(1)
Pb(2)–O(9)	2.294(7)	Pb(5)–O(10)	2.296(8)
Pb(2)–O(8)	2.321(9)	S–O(3)	1.390(11)
Pb(3)–O(8)	2.342(5)	S–O(2)	1.431(10)
Pb(3)–O(10)	2.346(5)	S–O(1)	1.452(10)
Pb(3)–O(9)	2.381(7)	S–C(1)	1.767(9)
Pb(4)–O(10)	2.238(8)		
O(8)–Pb(1)–O(7)	82.1(2)	O(8)–Pb(3)–O(10)	73.1(2)
O(9)–Pb(2)–O(8)	75.2(2)	O(8)–Pb(3)–O(9)	73.2(3)
O(9)–Pb(2)–Pb(3)	39.09(2)	O(10)–Pb(3)–O(9)	76.3(3)
O(8)–Pb(2)–Pb(3)	38.24(2)	O(10)–Pb(4)–O(9)	76.7(2)

As shown in figures 1 and S1, **1** crystallizes in the space group $P\bar{1}$ with five crystallographically distinct Pb^{2+} ions, Pb(1), Pb(2), Pb(3), Pb(4), and Pb(5), one half of O(8) and O(10), one hydroxide of O(9), one 4-sphth, and one lattice water in an asymmetric unit. The ratio of Pb(1), Pb(2), Pb(3), Pb(4), and Pb(5) is 1 : 1 : 2 : 1 : 1. Pb(2), Pb(3), Pb(3A), and Pb(4) are bound to μ_3-O(8), O(9), O(9A), O(10) to form a $[Pb_4O_4]$ core with metal ions occupying alternating corners of the distorted cubane core;

Table 3. Selected bond lengths and angles for **2**.

O(2)–Pb(1)#1	2.337(10)	Pb(1)–O(2)#1	2.337(10)
O(4)–Pb(1)	2.342(9)	Pb(1)–O(4)#2	2.393(9)
O(4)–Pb(1)#2	2.393(9)		
O(2)#1–Pb(1)–O(4)	85.1(3)	O(4)–Pb(1)–O(4)#2	70.0(3)
O(2)#1–Pb(1)–O(4)#2	81.9(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y,-z$; #2$-x+2,-y+1,-z$.

Table 4. Selected bond lengths and angles for **3**.

O(1)–Pb(2)	2.673(6)	Pb(1)–O(2)#4	2.615(7)
O(2)–Pb(1)#1	2.615(7)	Pb(1)–O(2)#5	2.615(7)
O(3)–Pb(2)	2.665(6)	Pb(1)–O(5)#6	2.635(7)
O(3)–Pb(1)	2.686(7)	Pb(1)–O(5)#2	2.635(7)
O(4)–Pb(2)#2	2.654(8)	Pb(1)–O(3)#7	2.686(7)
O(5)–Pb(2)	2.299(7)	Pb(2)–O(5)#2	2.477(7)
O(5)–Pb(2)#2	2.477(7)	Pb(2)–O(4)#2	2.654(8)
O(5)–Pb(1)#3	2.635(7)		
O(2)#4–Pb(1)–O(5)#6	112.3(2)	O(5)#2–Pb(1)–O(3)	69.9(2)
O(2)#5–Pb(1)–O(5)#6	67.7(2)	O(5)–Pb(2)–O(5)#2	71.8(3)
O(2)#4–Pb(1)–O(5)#2	67.7(2)	O(5)–Pb(2)–O(4)#2	75.5(2)
O(2)#5–Pb(1)–O(5)#2	112.3(2)	O(5)#2–Pb(2)–O(4)#2	75.2(2)
O(2)#4–Pb(1)–O(3)#7	106.1(2)	O(5)–Pb(2)–O(3)	79.0(2)
O(2)#5–Pb(1)–O(3)#7	73.9(2)	O(5)#2–Pb(2)–O(3)	72.6(2)
O(5)#6–Pb(1)–O(3)#7	69.9(2)	O(4)#2–Pb(2)–O(3)	143.8(2)
O(5)#2–Pb(1)–O(3)#7	110.1(2)	O(5)–Pb(2)–O(1)	80.8(2)
O(2)#4–Pb(1)–O(3)	73.9(2)	O(5)#2–Pb(2)–O(1)	133.5(2)
O(2)#5–Pb(1)–O(3)	106.1(2)	O(4)#2–Pb(2)–O(1)	133.1(2)
O(5)#6–Pb(1)–O(3)	110.1(2)	O(3)–Pb(2)–O(1)	65.7(2)

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

Pb(1) and Pb(5) are connected by O(8) and O(10). Furthermore, Pb(1) and Pb(5) are bridged by two syn-anti bridging carboxylates (O(6) and O(7)) from two 4-H_3sphth. Pb(5) is further coordinated by two monodentate carboxylates from two other 4-H_3sphth ligands, forming a unique ladder-shaped structure along the *a*-axis (figure 2). Pb–O distances are 2.299(7)–2.686(7) Å, falling in the range for Pb–O covalent bonds (2.46 to 2.96 Å) [58, 59]. To the best of our knowledge, such a 1-D structure containing lead-oxide cubane among Pb^{II}-organic frameworks has not been reported.

Moreover, X-ray analysis reveals that there are relatively weak contacts between Pb(1) and O(1) and O(3) in the sulfo group at 2.98(1)–3.04(1) Å, expanding into a 3-D network with pores of 7.2×3.9 and $5.9 \times 4.7\,Å^2$, which are occupied by lattice water molecules (Supplementary material, figure S1). Relative weak hydrogen bonding among lattice water molecules, hydrogen on O(9), and carboxylate oxygen atoms leads to a consolidation of the structure with $O \cdots O$ distances of 2.61(2)–2.81(2) Å.

The single-crystal X-ray diffraction analysis reveals that **2** crystallizes in the triclinic system space group *P1*. The asymmetric unit of **2** consists of one Pb^{II}, one 3,5-HDHB, and one lattice water. Each Pb^{II} is in a distorted octahedral coordination, supplied by three carboxylate oxygen atoms from two 3,5-HDHB, and three phenol oxygen atoms from three other 3,5-HDHB ligands (figure 3). Three "weak" Pb–O bonds (Pb(1)–O(1)

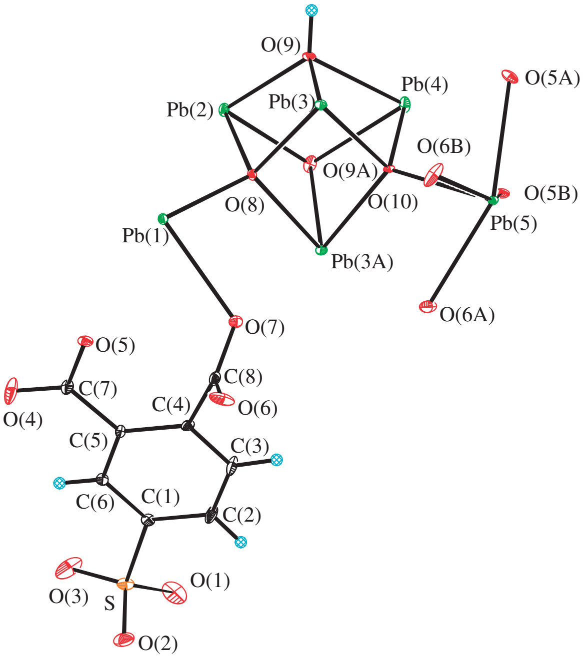

Figure 1. ORTEP view of **1** (30% thermal ellipsoids) showing the atom-labeling scheme. Symmetry-related atoms are indicated by Pb1A, etc. Symmetry code A: x, $-y+3/2$, z; B: $x+1$, y, z.

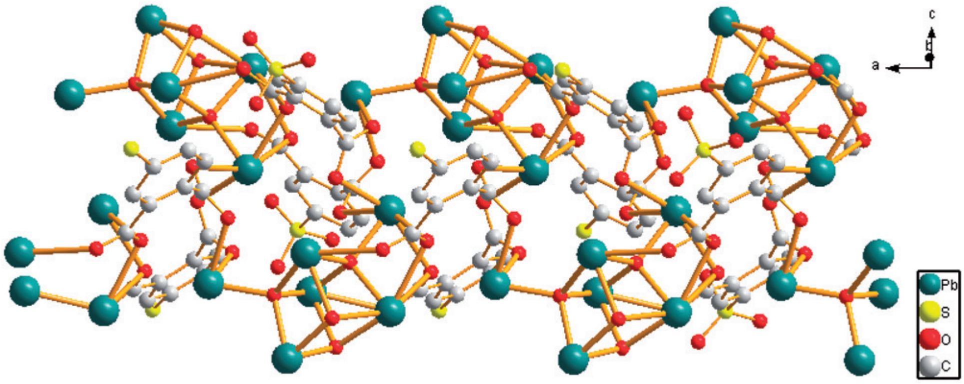

Figure 2. The 1-D framework of **1** along the *a*-axis, showing the adjacent [Pb_4O_4] units are further assembled into a 1-D framework.

2.806(6), Pb(1)–O(1A) 2.852(6) Å, Pb(1)–O(3) 2.782(6) Å) fit hemidirected structural categories [60, 61], suggesting the presence of a stereochemically active lone electron pair around Pb^{II}. Two Pb's are linked by two μ-O of 3,5-HDHB, forming two planar four-membered rings, Pb(1)–O(1)–Pb(1A)–O(1A) and Pb(1)–O(4)–Pb(1A)–O(4A). The two four-membered rings link to form a 1-D Pb–O chain through a corner-sharing Pb polyhedron, shown in figures 4 and S2, where the angle between the two neighboring

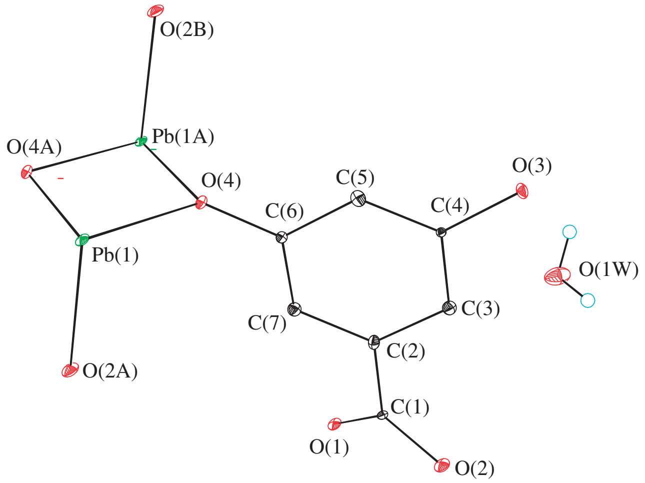

Figure 3. ORTEP view of **2** (30% thermal ellipsoids) showing the atom-labeling scheme. Symmetry-related atoms are indicated by Pb1A, etc. Symmetry code A: x, $-y+3/2$, z; B: $x+1$, y, z.

planes is 81.88(1)°. Pb_2O_2 units are bridged by two parallel 3,5-HDHB ligands along the *a*-axis and by two other parallel 3,5-HDHB ligands along the *b*-axis yielding a 3-D framework, shown in figures 4, S4, and S5. In **2**, 3,5-HDHB is a hexi-connector linking six Pb^{II} centers through one μ-O, one μ2-O, and one O^{-}_{COO} in the *bc* plane (figure S3). The 3-D framework contains two alternate 1-D channels (A and B) with approximate dimensions of 7.6 × 4.7 Å (channel A) and 9.2 × 5.7 Å (channel B) parallel to the *a*- and *c*-axis. Such biporous materials with two (or more) distinct channels make simultaneous isolation or transportation of two different guests possible [62–64]. The guest water molecules, occupying two kinds of channels with hydrogen bonding interactions of O(1W)–H(1W)···O1 (3.10(1) Å), O(1W)–H(2W)···O(2) (2.81(1) Å), and O(3)–H(3)···O(1W) (2.66(1) Å), lead to a consolidation of the packing structure.

Single-crystal X-ray diffraction reveals that **3** crystallizes in the triclinic system with space group *P1*. The asymmetric unit consists of 1.5 Pb^{II} and one 4-nitrophthalic acid (figure 5). The crystal structure is built up of a layer motif consisting of corner-sharing pyramidal Pb_3O units, which are linked through Pb^{II} corners to form a hexagonal unit (figure 6). Each PbO_6 polyhedron is connected to three polyhedra, by sharing an edge (through two μ_3-oxygen atoms) and two faces (through three μ_3-oxygen atoms), thus forming an infinite 2-D Pb–O–Pb (3,6-net) honeycomb layer. Both sides of the honeycomb layers are decorated with CHDC rings (figure S6). The projected CHDC rings on each side of the layer are of same crystallographic type. These layers are stacked, along the *a*-axis, in such a way that the projected rings on the neighboring layers are of same type, but with opposite orientation. Both Pb^{II} ions are six-coordinate, Pb(1) with distorted octahedral coordination and Pb(2) a pentagonal pyramid. The Pb(1)–O bond lengths are 2.161(1)–2.884(1) Å, and Pb(2)–O, 2.229(1)–2.859(1) Å.

Thermal gravimetric analyses (TGA) under flowing N_2 were carried out to examine the stability of **1**–**3** (figures S7–S9). The TGA curve of **1** shows water loss at 50°C and the structure begins to decompose above 310°C. The first weight loss of 0.50% is in accord with the loss of lattice water (calculated: 0.49%), while the second weight loss corresponds to the removal of all organic components to yield PbO (found: 24.59%;

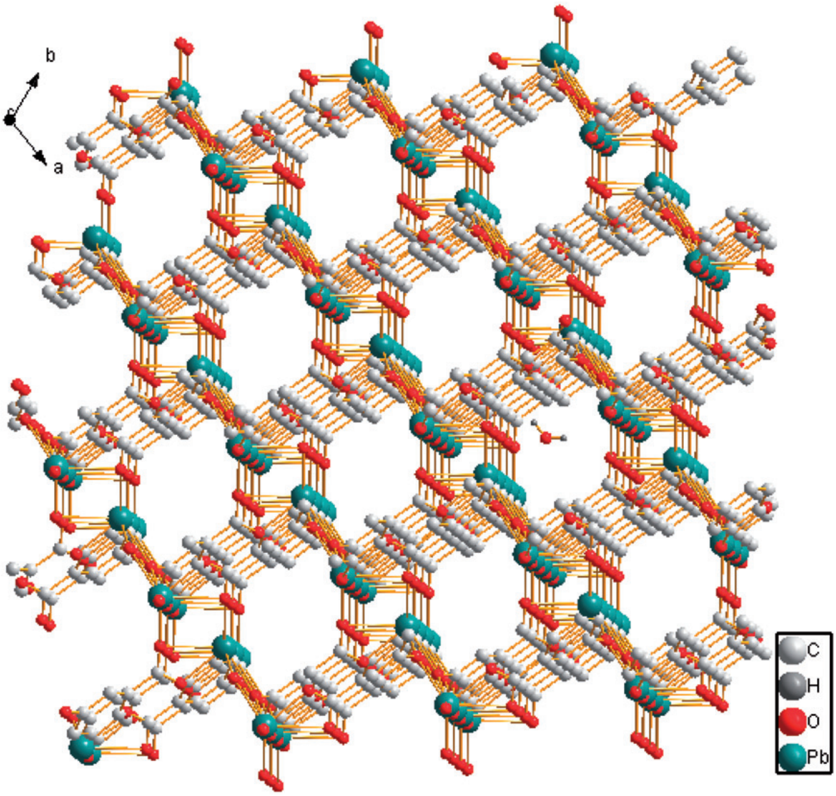

Figure 4. The 3-D framework of **2** containing two alternate 1-D channels (A and B) with different sizes and shapes.

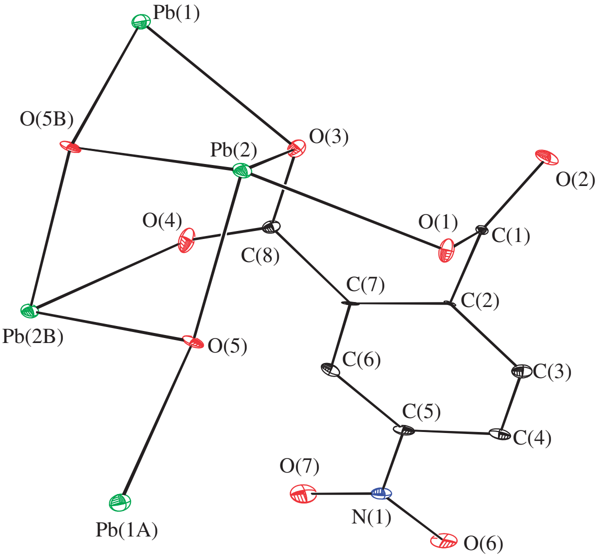

Figure 5. ORTEP view of **3** (30% thermal ellipsoids) showing the atom-labeling scheme. Symmetry-related atoms are indicated by Pb1A, etc. Symmetry code A: x, $-y+3/2$, z; B: $x+1$, y, z.

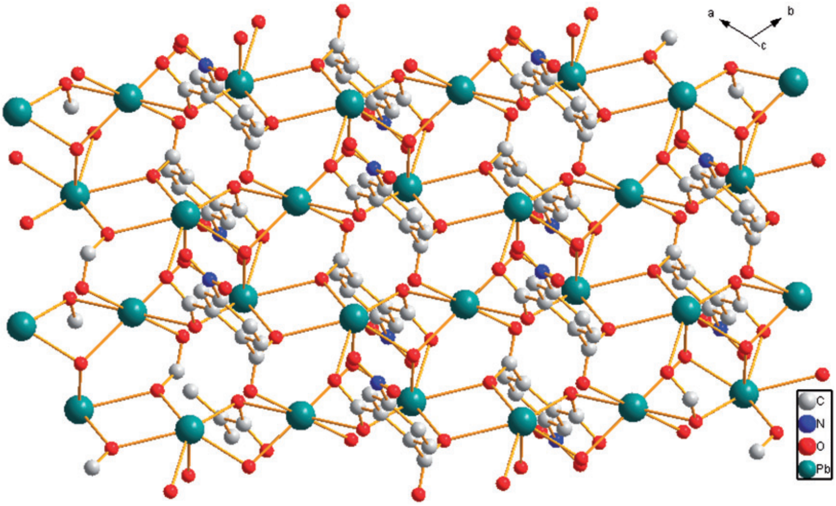

Figure 6. The infinite 2-D Pb–O–Pb (3,6-net) honeycomb layer of **3**.

Calcd: 27.16%). For **2** and **3**, the organic components are decomposed at 394 and 411 K, respectively.

The fluorescence spectra of **1**–**3** and related free ligands were examined in the solid state at room temperature (figures S10–S12). The polymeric structures give significant enhancement of fluorescence intensity, probably due to enhanced rigidity of **1**–**3** [65]. Therefore, the fluorescence behaviors of **1**–**3** are best ascribed to ligand-to-metal charge-transfer [66–68]. The strong orange-yellow fluorescence emissions suggest that these complexes may be used as an emitter for an electroluminescence device or as potential material for a light-emitting diode [36].

4. Conclusions

Three [Pb_mO_n]-containing architectures with 4-sulfophthalic acid, 3,5-dihydroxybenzoic acid, and 4-nitrophthalic acid bridges have been hydrothermally synthesized under similar synthetic conditions. The structural differences of **1**–**3** highlight the effects of organic acids on framework formation of the complexes. The luminescence of **1**–**3** demonstrate that they may be candidates for luminescent materials. Further research on the rational design and construction of lead(II) compounds with interesting structures as well as physical properties is currently underway in our laboratory.

Supplementary material

For **1**–**3**, further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: +44-(0)1223-762-910; Fax: +44-(0)1223-336-033; Email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit], on quoting the depository number CCDC-787178 for **1**, 809178 for **2**, and 809179 for **3**. An additional plot, thermogravimetric spectra, fluorescence spectra, and X-ray data file (CIF) are available free of charge *via* the Internet at http://ees.elsevier.com.

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