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Two luminescent frameworks constructed from lead(II) salts with carboxylate ligands containing dinuclear lead(II) units

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Abstract

Two luminescent Pb(II) coordination frameworks containing dinuclear lead(II) units, $[Pb(PYDC)(H_2O)]_n$ (**1**) and $[Pb(HPHT)]_n$ (**2**) have been prepared by the self-assembly of lead(II) salts with pyridinecarboxylate and benzenecarboxylate. Single-crystal X-ray diffraction analyses reveal that compound **1** is a three-dimensional architecture consisting of Pb_2O_2 dimeric building units, whereas compound **2** is a two-dimensional layer structure containing one-dimensional lead-oxide chains. The luminescent properties of **1** and **2** have been investigated in the solid state at room temperature, indicating structure-dependent photoluminescent properties of the coordination frameworks.

Keywords: Lead(II); Coordination frameworks; Luminescent properties

1. Introduction

The rational design and synthesis of inorganic–organic hybrid coordination frameworks is one of the most active areas of materials research [1,2]. The increasing interest is justified not only by their unique application as functional materials, but also by their particular structural diversity of the architectures [3]. The resulting architectures and properties mainly depend on the nature of metal centers and the structural characterization of organic ligands used. Until now, much of the effort has been focused on the coordination of transition- and lanthanide-metal ions [4]. However, the analogous chemistry of the heavy metal ions of main group is not profoundly developed despite their important applications in electroluminescent devices or organic light-emitting diode (OELD) technology [5]. Considering the large radius, rich coordination numbers and geometries, the possible occurrence of stereochemically active lone pair of electrons, Pb(II) cation is employed in our present work. On the other hand, the ligands play an important role in exploring the coordination behavior of metal ions. Thus, two ligands have been chosen to explore the coordination chemistry of lead(II). First, 3,4-pyridinedicarboxylic acid (H_2PYDC), possessing rigid ring and multiple coordination modes, was coming into our sight. It is well known that lead(II) is affinitive to oxygen; thus, a large number of lead-carboxylate or -phosphate coordination compounds have been synthesized [6,7]. Exploring the coordination chemistry of lead(II) to ligands possessing oxygen and nitrogen donors would be a fascinating task [8]. Second, an asymmetric and flexible ligand of homophthalic acid (H_2HPHT) was selected. Symmetrical benzene dicarboxylic acids, such as terephthalic acid and 1,3,5-benezetricarboxylic acid, as O-donor ligands, have been widely used to synthesize coordination polymers containing transition-metal ions [9]. However, many asymmetric and flexible benzene carboxylic acids such as homophthalic acid have not been investigated extensively, and the study on the structures constructed from these ligands remains undeveloped [10]. Our aim is to use such ligands to construct lead-organic complexes with interesting topology

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or properties for potential application, and to investigate the different coordination geometries which Pb(II) cations may adopt. Recently, we have reported a heterometallic polymer containing heptanuclear units and one-dimensional lead-oxide chains producing by the hydrothermal reaction of 5-hydroxyisophthalic acid with lead and nickel nitrates [11]. In this paper, the hydrothermal reactions of lead(II) salts with H_2PYDC/H_2HPHT and the characterizations of two novel polymeric complexes, $[Pb(PYDC)(H_2O)]_n$ (**1**) and $[Pb(HPHT)]_n$ (**2**), will be reported.

2. Experimental section

2.1. Materials and general methods

All chemicals were of reagent-grade quality obtained commercially and used without further purification. Elemental analyses were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded on PerkinElmer Spectrum One as KBr pellets in the range 4000–400 cm^{-1}. Fluorescent spectra were measured at room temperature with an Edinburgh FL-FS90 TCSPC system.

2.2. Syntheses of the compounds

2.2.1. Preparation of $[Pb(PYDC)(H_2O)]_n$ (1)

A mixture of $Pb(NO_3)_2$ (0.065 g, 0.20 mmol) and H_2PYDC (0.032 g, 0.20 mmol) in a 1:1 molar ratio in H_2O (10 mL) was transferred to a 25 mL stainless steel reactor with Teflon liner and heated to 160 °C for 72 h, then the reaction system was cooled to room temperature over 48 h. A large amount of yellow prism-shaped crystals of compound **1** were obtained. Yield: 72% (based on Pb). Elemental analysis (%): calcd. for **1** $C_7H_5NO_5Pb$ (390.32): C 21.54, H 1.29, N 3.59; found: C 21.49, H 1.25, N 3.55. IR (KBr, cm^{-1}): 3438(s), 1606(m), 1567(s), 1539(s), 1486(m), 1381(s), 840(s), 719(s), 676(s).

2.2.2. Preparation of $[Pb(HPHT)]_n$ (2)

A mixture of H_2HPHT (0.09 g, 0.5 mmol) and $Pb(NO_3)_2$ (0.166 g, 0.5 mmol) were dissolved in 10 mL water. Then, ethanol was allowed to diffuse into the resultant solution slowly. After two weeks, colorless block-shaped crystals of compound **2** were collected. Yield: 53% (based on Pb). Elemental analysis (%): calcd. for **2** $C_9H_6O_4Pb$ (385.33): C 28.05, H 1.57; found: C 27.89, H 1.62. IR (KBr, cm^{-1}): 3392(m), 3058(m), 1623(m), 1589(m), 1516(s), 1385(s), 1284(s), 854(s), 723(s).

2.2.3. X-ray crystallographic study

X-ray diffraction data of compounds **1** and **2** were collected on a Rigaku diffractometer with a Mercury CCD area detector with graphite-monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. Empirical absorption corrections were applied to the data using the CrystalClear program [12]. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program [13]. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Crystallographic data and structure determination summaries for compounds **1** and **2** are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.

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

	1	**2**
Empirical formula	$C_7H_3NO_5Pb$	$C_9H_6O_4Pb$
Formula weight	388.29	385.33
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2(1)/c$
a (Å)	8.336(2)	13.602(1)
b (Å)	8.705(2)	6.6961(5)
c (Å)	11.750(3)	9.6654(8)
α (deg)	96.171(8)	90
β (deg)	106.50(1)	90.999(5)
γ (deg)	90.650(1)	90
V (Å^3)	812.0(3)	880.2(1)
Z	4	4
$\rho_{calcd.}$ (Mg/m^3)	3.176	2.908
μ (Mo$K\alpha$) (mm^{-1})	20.770	19.149
No. of data collected	6321	5290
No. of unique data (all)	3669 (R(int) = 0.0589)	1542 (R(int) = 0.0773)
No. of observed data [$F > 2(\sigma F)$]	3669	1542
Parameters	253	128
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0654, 0.1618	0.0487, 0.1136
R_1,[a] wR_2[b] (all data)	0.0841, 0.1718	0.0560, 0.1156
GOF	1.061	1.037

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

3. Results and discussions

3.1. Structural description of $[Pb(PYDC)(H_2O)]_n$ (1)

Single-crystal X-ray diffraction analysis reveals that compound **1** is a three-dimensional architecture consisting of Pb_2O_2 dimeric building units. As shown in Fig. 1, the asymmetric unit of compound **1** consists of two crystallographically independent Pb(II) motifs. Pb(1) is five-coordinated by four carboxylate oxygen atoms from three PYDC ligands and one oxygen atom from water molecule. It adopts a highly distorted triangle bipyramid geometry, which is unusual compared to coordination geometry of transition metals. One monodentate carboxylate oxygen and water oxygen atoms occupy the apexes of the pyramid, while the other oxygen atoms comprise the equatorial plane. We presume that the electron geometry can be described as a ψ-octahedral PbO_5 in which the lone pair of electrons on the Pb^{2+} ion occupies the sixth coordination

Table 2
Selected bond lengths (Å) and angles (deg) for compounds **1**[a] and **2**[a]

Compound **1**			
Pb(1)–O(1)	2.513(14)	Pb(1)–O(7A)	2.606(11)
Pb(1)–O(3B)	2.624(10)	Pb(1)–OW1	2.646(14)
Pb(1)–O(8A)	2.730(13)	Pb(2)–O(5)	2.441(13)
Pb(2)–O(7C)	2.586(10)	Pb(2)–O(3D)	2.621(11)
Pb(2)–O(2)	2.738(12)	Pb(2)–OW2	2.757(13)
Pb(2)–N(2E)	2.796(14)		
O(1)–Pb(1)–O(7A)	78.5(4)	O(1)–Pb(1)–O(3B)	71.4(4)
O(7A)–Pb(1)–O(3B)	65.9(3)	O(1)–Pb(1)–OW1	141.4(4)
O(7A)–Pb(1)–OW1	77.3(4)	O(3B)–Pb(1)–OW1	71.5(4)
O(1)–Pb(1)–O(8A)	79.3(4)	O(7A)–Pb(1)–O(8A)	49.0(3)
O(3B)–Pb(1)–O(8A)	112.4(3)	OW1–Pb(1)–O(8A)	105.9(4)
O(5)–Pb(2)–O(7C)	74.1(4)	O(5)–Pb(2)–O(3D)	77.7(4)
O(7C)–Pb(2)–O(3D)	66.2(3)	O(5)–Pb(2)–O(2)	97.8(4)
O(7C)–Pb(2)–O(2)	161.2(4)	O(3D)–Pb(2)–O(2)	129.5(3)
O(5)–Pb(2)–OW2	142.0(4)	O(7C)–Pb(2)–OW2	72.4(4)
O(3D)–Pb(2)–OW2	72.8(4)	O(5)–Pb(2)–N(2E)	121.2(4)
O(7C)–Pb(2)–N(2E)	92.6(4)	O(3D)–Pb(2)–N(2E)	147.9(4)
O(2)–Pb(2)–N(2E)	76.9(4)	OW2–Pb(2)–N(2E)	78.0(4)
Compound **2**			
Pb(1)–O(2A)	2.410(11)	Pb(1)–O(3B)	2.610(8)
Pb(1)–O(3C)	2.625(8)	Pb(1)–O(4D)	2.629(8)
Pb(1)–O(4B)	2.630(8)	Pb(1)–O(1)	2.752(9)
O(2A)–Pb(1)–O(3B)	115.1(3)	O(2A)–Pb(1)–O(3C)	77.3(3)
O(3B)–Pb(1)–O(3C)	120.4(2)	O(2A)–Pb(1)–O(4D)	79.6(3)
O(3B)–Pb(1)–O(4D)	71.7(2)	O(3C)–Pb(1)–O(4D)	156.8(3)
O(2A)–Pb(1)–O(4B)	95.8(3)	O(3B)–Pb(1)–O(4B)	50.2(2)
O(3C)–Pb(1)–O(4B)	71.4(2)	O(4D)–Pb(1)–O(4B)	112.9(2)
O(2A)–Pb(1)–O(1)	151.8(3)	O(3B)–Pb(1)–O(1)	76.3(3)
O(3C)–Pb(1)–O(1)	74.9(3)	O(4D)–Pb(1)–O(1)	128.4(2)
O(4B)–Pb(1)–O(1)	71.1(3)		

[a] Symmetry codes: for **1** (A) $-x$, $-y+2$, $-z$; (B) $-x$, $-y+2$, $-z+1$; (C) $-x$, $-y+1$, $-z$; (D) $-x$, $-y+1$, $-z+1$; (E) $x-1$, y, z. **2** (A) $-x+2$, $y-1/2$, $-z+3/2$; (B) x, $-y+1/2$, $z-1/2$; (C) $-x+2$, $-y+1$, $-z+2$; (D) $-x+2$, $-y$, $-z+2$.

site on the equatorial plane [7a,8b]. The Pb(1)–O distances range from 2.51(2) to 2.73(2) Å and the Pb–OW1 distance is 2.65(1) Å, similar to those reported for other lead(II) carboxylates and phosphonates [6,7,14]. However, the six-coordinate Pb(2) is in a distorted octahedron geometry with the two apical positions occupied by monodentate carboxylate oxygen atoms and the four basal positions occupied by two monodentate carboxylate oxygen atoms, one pyridyl nitrogen atom and one oxygen atom from water molecule. The average Pb–N and Pb–O distances are 2.80(1) and 2.63(1) Å, respectively. Similar to that of Pb(1), the electron geometry around Pb(2) can be described as ψ-pentagonal bipyramidal PbO_6 in which the seventh coordination site is occupied by the lone pair electrons of the Pb(II) ion. Although the two independent PYDC ligands both act as tetradentate ligands, they exhibit different coordination modes as illustrated in Scheme 1a and Scheme 1b. The nitrogen atoms are coordinated to Pb(II) centers in Scheme 1b, whereas left uncoordinated in Scheme 1a.

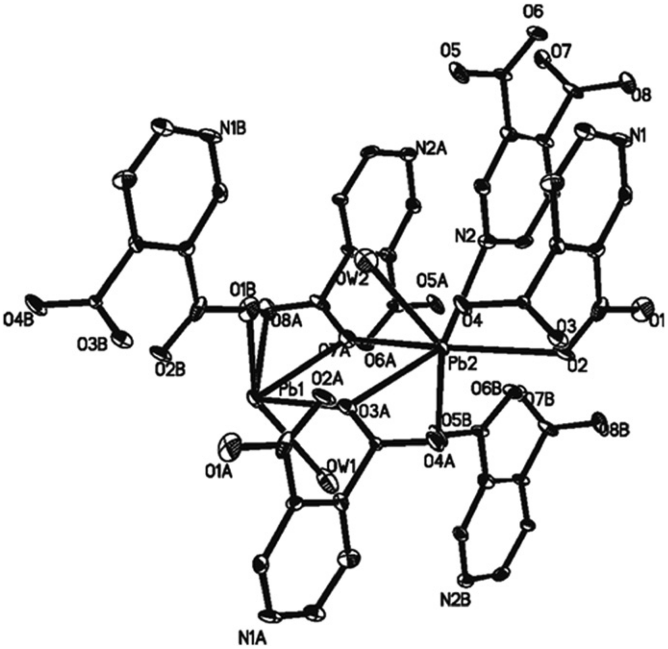
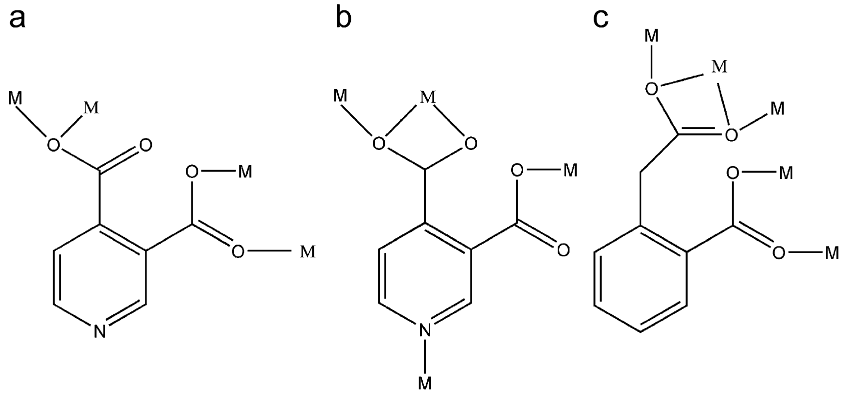


Fig. 1. The coordination environment of the two Pb(II) ions in compound **1** with the thermal ellipsoids at 30% probability level. All the H atoms are omitted for clarity.

As shown in Fig. 1, Pb(1) atoms are linked to Pb(2) by the O(3A) and O(7A) atoms of the PYDC ligands, forming a nearly planar four-membered ring with O–Pb–O bond angles of 65.90° and 66.24° and Pb–O–Pb bond angles of 112.9° and 114.7°, respectively. This Pb_2O_2 unit is essentially symmetric with the Pb–O distances 2.62(1) and 2.62(1) for O(3) and 2.61(1) and 2.59(1) Å for O(7). The Pb–(μ-O) bond lengths are comparable to those found in other $Pb_2(\mu\text{-}OR)_2$ systems [15]. The associated nonbonded Pb(1)···Pb(2) distance is about 4.373 Å. The dinuclear Pb_2O_2 units are bridged by PYDC ligands through carboxylate oxygen atoms, leading to a two-dimensional layered coordination network, as illustrated in Fig. 2. It is noted that the PYDC ligands adopt the coordination mode like V style just using carboxylate groups. Such two-dimensional layers are further interconnected through the remaining nitrogen atoms of pyridine rings to form a three-dimensional infinite network. Within the two-dimensional layer, there are two types of ring. One is the four-membered ring formed by Pb_2O_2 unit, and the other is the 14-membered ring formed by two lead(II) ions and two bridging PYDC ligands (Pb–(O–C–C–C–C–O)2–Pb). The latter rings form open channels along the *a*-axis (Fig. 3). The pyridine rings between the channels are orientated absolutely parallel to each other. The shortest distance between two neighboring pyridine ring centers is 3.65 Å; therefore it is expected that there is π–π interaction between these pyridine rings.

3.2. Structural description of [Pb(HPHT)]$_n$ (**2**)

The X-ray analysis of compound **2** reveals a two-dimensional layer structure containing one-dimensional lead-oxide chains. As shown in Fig. 4, the asymmetric unit of compound **2** consists of one unique Pb(II) ion compared



Scheme 1. The coordination modes of PYDC and HPHT ligands in compounds **1** and **2**.

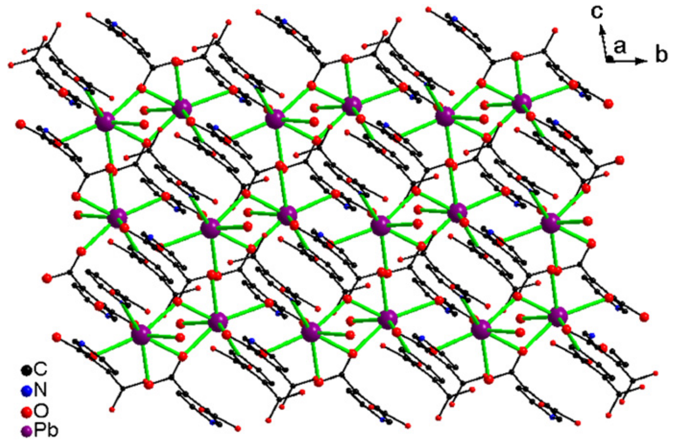


Fig. 2. View of the two-dimensional network of compound **1**, in which the dinuclear Pb_2O_2 units have been shown.

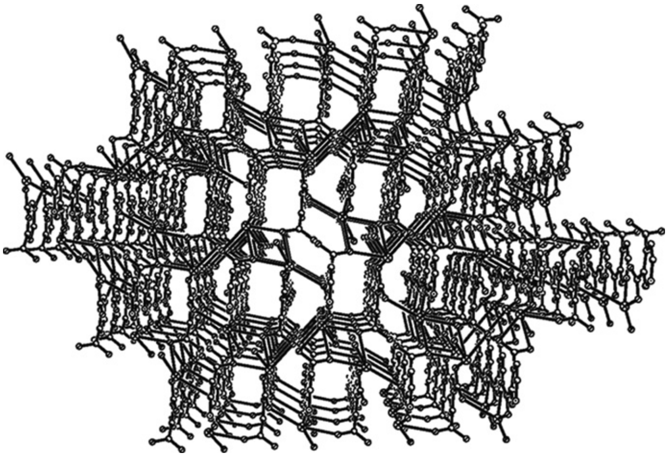


Fig. 3. Perspective view of the three-dimensional packing structure of compound **1** along the *a*-axis.

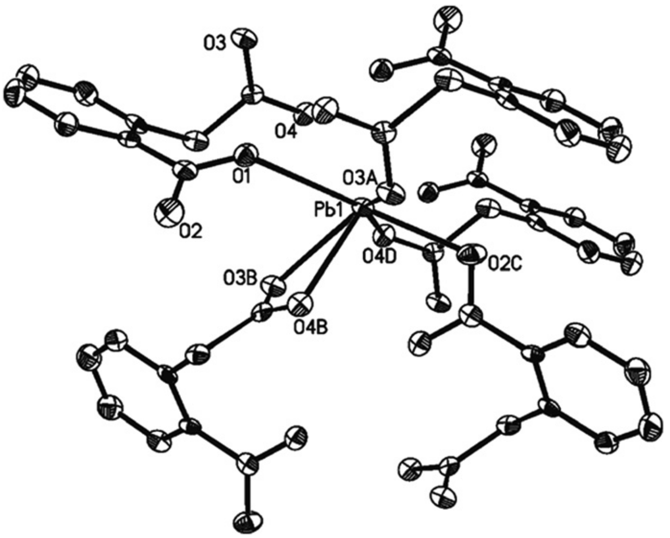


Fig. 4. The coordination environment around Pb(II) ion in compound **2** with the thermal ellipsoids at 30% probability level. All the H atoms are omitted for clarity.

to compound **1** and five HPHT ligands. Pb(II) is six-coordinated by six carboxylate oxygen atoms from five HPHT ligands. The Pb–O distances are in the range 2.411–2.752 Å, with an average value of 2.610 Å. It adopts a highly distorted pentagonal pyramid geometry, which is unusual compared to ordinary transition metals as we depicted above. Obviously, the electron geometry can be described as a ψ-pentagonal bipyramidal $\{PbO_6\}$ with the lone pair of electrons on the Pb^{2+} ion completing the seventh coordination site at the apical position [7a,8b]. The HPHT ligand links two Pb(II) ions, in which the formate group of HPHT anion bridges two Pb(II) ions, while acetate group chelates one Pb(II) ion and also bridges two Pb(II) ions. Thus the HPHT ligand behaves as a μ_5-bridge connecting five Pb(II) atoms through one bidentate formate group and μ_3–η^2:η^2 acetate group as illustrated in Scheme 1c. To the best of our knowledge, this type of coordinating mode is not observed in the previously reported HPHT complexes. Two Pb(II) ions connected by two bridging ethylic carboxylate groups with interatomic distance of 4.019 Å form binuclear Pb_2O_2 basic building unit of the whole structure. The associated nonbonded Pb(1)···Pb(1A) distance (4.019 Å) is closer to the sum of van der Walls radii (3.20 Å) compared to that of compound **1** and other reported lead(II) compounds [16]. With significant difference from compound **1**, the Pb_2O_2 ring inclined to fold with the torsion angle of

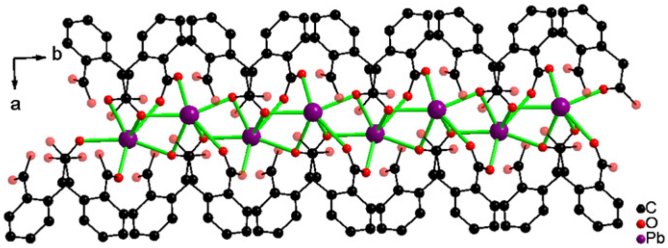


Fig. 5. View of the one-dimensional lead-oxide chain in compound **2** along the *c*-axis.

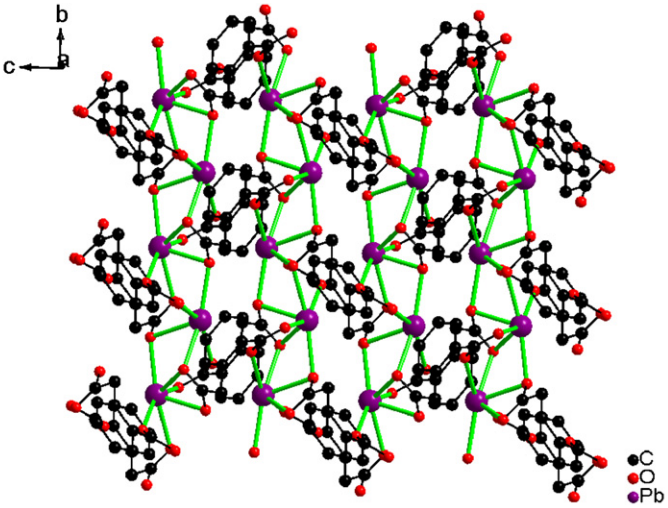


Fig. 6. View of the two-dimensional layer structure in compound **2**.

(Pb1–O3A···O4A–Pb1A) 141.5°, which mainly depended on the flexible arm of HPHT ligand. $\{PbO_6\}$ polyhedrons are connected together via edge-sharing fashion giving rise to a zigzag one-dimensional lead-oxide chain (Fig. 5). The HPHT spacers stretch the one-dimensional chain into the final two-dimensional layer structure completing the coordination sphere of Pb(II) ions, as shown in Fig. 6. The benzene rings of the ligand are orientated toward the interlayer space. The shortest distance between two neighboring benzene ring centers is 4.34 Å; therefore it is expected that there is no π–π interaction between these benzene rings (Fig. 7).

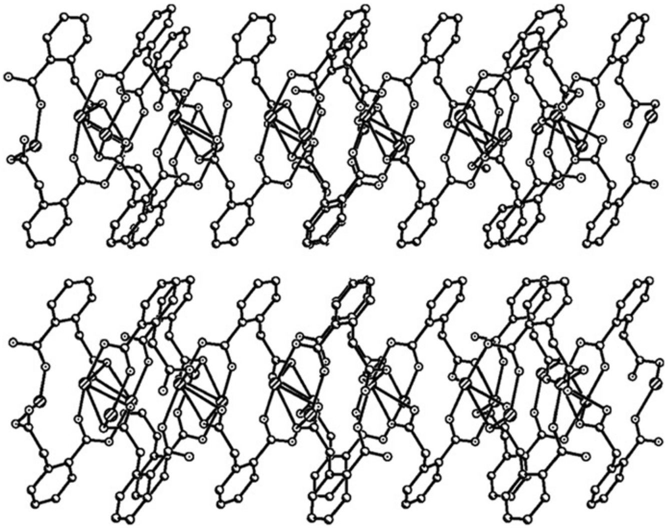


Fig. 7. View of the interlayer space between two-dimensional layers in compound **2** along the *b*-axis.

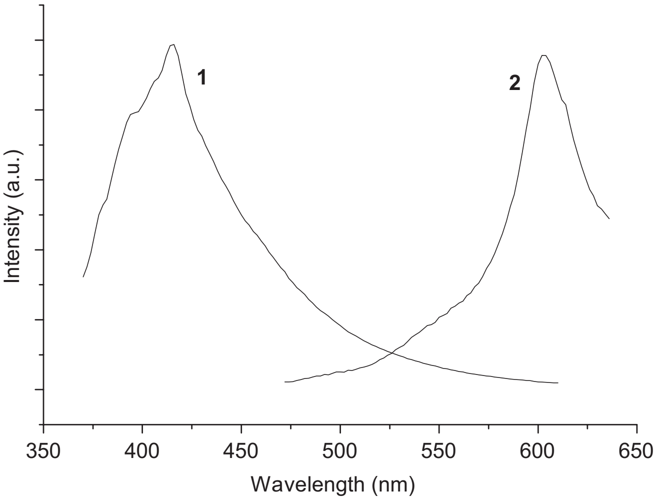


Fig. 8. The solid-state emission spectrum of compound **1** ($\lambda_{ex} = 303$ nm) and **2** ($\lambda_{ex} = 364$ nm) at room temperature.

3.3. Vibrational spectroscopic study

The FT-IR spectrum of compound **1** exhibits a strong and broad absorption centered at 3438 cm^{-1}, which can be ascribed to the presence of water molecules in the structure. Characteristic bands of carboxyl groups at 1567 cm^{-1} for the asymmetric stretching and at 1539 and 1381 cm^{-1} for symmetric stretching, indicate the presence of chelating and bridging coordination modes in compound **1** [17]. The asymmetric and symmetric stretching vibrations of compound **2** at 1589, 1516 and 1385 cm^{-1} show that the carboxylate groups employ the chelating and monodentate coordination geometry, which is consistent with the crystal structures of **2**.

3.4. Luminescent properties

Although the photoluminescence properties of transition-metal complex was of interest in numerous investigations for several decades, s^2-metal complexes are not well studied [18]. The luminescent properties of **1** and **2** have been investigated in solid state at room temperature. The emission spectra of both compounds are dominated by an intense and broad emission band. Compound **1** exhibits an intense emission with a maximum at ca. 415 nm upon excitation at 303 nm. In the case of **2**, photoluminescence with a maximum emission at ca. 602 nm upon excitation at 364 nm is observed (Fig. 8). In order to assign the two emission bands, luminescent measurements were taken for both free ligands and it was found that the strongest emission peak for H_2PYDC is located at ca. 370 nm ($\lambda_{ex} = 276$ nm), whereas for H_2HPHT it is at ca. 455 nm ($\lambda_{ex} = 370$ nm) [19]. The strongest emission peak of compound **1** (415 nm) is very close to the free ligand (370 nm). In addition, a series of lead(II) β-diketonates compounds showing typical intraligand (IL) phosphorescence has been reported [20a]. Therefore, this emission band might be attributed to the intraligand (IL) emission from the PYDC ligand [20]. The bathochromic shift and enhancement of PYDC ligand in compound **1** compared to free ligand may be attributed to the coordination bond between the ligand and Pb(II), which increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state [21]. The emission wavelength of compound **2** occurs at a much lower energy of 602 nm, which is much longer than that of the free ligand (455 nm). The low-energy emissions associated with large Stokes shifts have been commonly observed for other s^2–metal complexes, which can be assigned to a metal-centered transition involving the *s* and *p* metal orbital as proposed by Vogler [18b,c]. Thus the emission band of **2** can be assigned to a metal-centered $s \rightarrow p$ transition. In addition, the dinuclear Pb_2O_2 cluster in the structure has a short $Pb(1)\cdots Pb(1A)$ distance (4.019 Å) compared to compound **1** and other reported lead(II) compounds [16]. The emissions of compound **2** may be assigned partly to the delocalized cluster state of the oxygen-bridged lead ions [7b,16b,22]. As described above, it can be concluded that the different emission spectra of **1** and **2** can be significantly influenced by their crystal structures.

4. Conclusions

In summary, the self-assembly of lead(II) salts with pyridinecarboxylate and benzenecarboxylate affords two luminescent Pb(II) coordination frameworks containing dinuclear lead(II) units, $[Pb(PYDC)(H_2O)]_n$ (**1**) and $[Pb(HPHT)]_n$ (**2**). This paper investigated the microscopic features of molecular packing and the luminescent properties of the two compounds, that differ from each other. Compound **1** is a three-dimensional architecture consisting of Pb_2O_2 dimeric building units, whereas compound **2** is a two-dimensional layer structure containing one-dimensional lead-oxide chains. In addition, the occurrence of stereochemically active lone pair of electrons usually leads to the rich coordination numbers and asymmetric coordination geometry of Pb(II). Compounds **1** and **2** display different fluorescent emissions at room temperature, indicating structure-dependent photoluminescent properties of the coordination frameworks.

5. Supplementary data

CDCC 632185 and 632186 contain the supplementary crystallographic data for $[Pb(PYDC)(H_2O)]_n$ and $[Pb(HPHT)]_n$. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retriving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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