

## 苯甲酸与含氮配体构筑的两种铅配合物的 水热合成、结构与性质研究

戴 俊 杨 娟\* 陈 曦  
(河南理工大学理化学学院, 焦作 454003)

**摘要:** 用水热合成方法得到了 2 个二价铅配合物  $[\text{Pb}(\text{BA})_2(\text{phen})] \cdot (\text{HBA})$  (**1**) 及  $[\text{Pb}(2,2'\text{-bipy})(\text{BA})(\text{NO}_3)]_n$  (**2**) (HBA=benzoic acid; phen=1,10-phenanthroline; 2,2'-bipy=2,2'-bipyridine), 对它们进行了元素分析、红外光谱、荧光光谱、粉晶衍射及热分析表征, 并通过 X-射线单晶衍射测定了配合物的单晶结构。X-射线单晶结构解析表明, 配合物 **1** 与 **2** 均属三斜晶系,  $P\bar{1}$  空间群。化合物 **1** 中, 弱  $\text{Pb} \cdots \text{O}$  相互作用、分子间氢键及  $\pi \cdots \pi$  堆积作用共同构筑了配合物 **1** 的三维框架结构。铅的 6s 孤电子具有立体化学活性, 使配位键分布于半球型区域。化合物 **2** 中, 相邻的  $\text{Pb}^{\text{II}}$  离子通过螯合-桥联的硝酸根联结成一维链状结构, 广泛存在的  $\pi \cdots \pi$  堆积作用将邻近的一维链堆积成三维超分子结构。化合物 **2** 中的 6s 孤对电子未显示出立体化学活性, 其配位键近似分布于全球型区域。

**关键词:** 铅配合物; 苯甲酸; 2,2'-联吡啶; 邻菲咯啉; 晶体结构

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## Hydrothermal Syntheses, Crystal Structures and Properties of Two Lead Compounds with Benzoic Acid and N-Donor Ligands

DAI Jun YANG Juan\* CHEN Xi

(Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454003, China)

**Abstract:** Two coordination compounds  $[\text{Pb}(\text{BA})_2(\text{phen})] \cdot (\text{HBA})$  (**1**) and  $[\text{Pb}(2,2'\text{-bipy})(\text{BA})(\text{NO}_3)]_n$  (**2**) (HBA: benzoic acid; phen: 1,10-phenanthroline; 2,2'-bipy: 2,2'-bipyridine) have been synthesized by hydrothermal methods and characterized by elemental analysis, IR spectra, fluorescence, powder X-ray diffraction and thermal analysis, and the crystal structures were determined by single-crystal X-ray diffraction. Both compounds crystallize in the Triclinic system, space group  $P\bar{1}$ . In compound **1**, the weak  $\text{Pb} \cdots \text{O}$  interactions, intermolecular H-bond and  $\pi \cdots \pi$  stacks construct the complex into stable 3D framework. The lone pairs of electrons are clearly active and the coordination sphere of  $\text{Pb}^{\text{II}}$  ions is hemidirected. In compound **2**, the adjacent  $\text{Pb}^{\text{II}}$  ions are linked by nitrate groups in the chelating-bridging coordination mode, resulting in a 1D chain structure. The extensive  $\pi \cdots \pi$  interactions connect the neighboring 1D chains into 3D supramolecular structure. The lone pairs of  $\text{Pb}^{\text{II}}$  are inactive and the coordination sphere is holodirected in compound **2**. CCDC: 803044, **1**; 803057, **2**.

**Key words:** lead complex; benzoic acid; 2,2'-bipy; phen; crystal structure

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\*通讯联系人。E-mail: yangjuan0302@yahoo.cn

The constructions of metal-organic frameworks (MOFs) have received considerable attention due to their versatile topological structures and potential applications in many fields, such as adsorption, catalysis, separation, and so on<sup>[1-3]</sup>. In order to fabricate stable inorganic-organic framework complexes possessing weak interactions, the rigid multidentate ligands with O atoms or N atoms are generally used<sup>[4-6]</sup>. 2,2'-bipyridine (2,2'-bipy), 1,10-phenanthroline (phen), benzoic acid and its derivatives are all excellent rigid multidentate ligands.

Benzoic acid and its derivatives are especially interesting not only because of their various coordination modes to metal ions, resulting from completely or partially deprotonated sites allowing for the large diversity of topologies<sup>[7]</sup>, but also because of their abilities to act as H-bond acceptors and donors to assemble various supramolecular structures. On the other hand, the chelating aromatic amine ligands 2,2'-bipy and phen as co-ligands can effectively increase the thermal stability and fluorescent properties, due to the  $\pi \cdots \pi$  stacks between the neighboring benzene and pyridine rings.

Most of these works have been focused on coordination complexes containing group  $d^{10}$  transition metal ions and lanthanide ions, not only for their novel structures, but also for their good photoluminescent properties<sup>[8-9]</sup>. However, the investigation of coordination chemistry of main-group Lead remains largely unexplored. The Pb(II) ions can adopt diverse coordination numbers from 2 to 10 and rich coordination geometry deriving from large radius like lanthanide ions and the possible occurrence of a stereochemically active lone pair of electrons<sup>[10]</sup>. In general, the coordination sphere of Pb(II) ion can be classified as a hemi- or holodirected configuration, which is important in the structure assembly<sup>[11-12]</sup>, electron charge transfer, and photophysical or photochemical properties<sup>[13-14]</sup>. Therefore, the combination of Pb(II) and aromatic carboxylate ligands was used to study the configuration activity of valence-shell electron lone pairs and their diverse structural topologies. We have recently reported the Pb(II) complexes with substituted benzoic acid ligands<sup>[6,15]</sup>. As a

continuation of these work, we selected benzoic acid ligand and 2,2'-bipy or phen as co-ligand, and obtained two new Pb(II) compounds  $[\text{Pb}(\text{BA})_2(\text{phen})] \cdot (\text{HBA})$  (**1**) and  $[\text{Pb}(2,2'\text{-bipy})(\text{BA})(\text{NO}_3)]_n$  (**2**) prepared by hydrothermal method. The crystal structures, weak interactions and properties of the compounds are reported in this paper.

## 1 Experimental

### 1.1 Reagents and instruments

$\text{Pb}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ , benzoic acid, 2,2'-bipy, phen were A.R. grade and used without further purification. Infrared spectra were collected on a Bruker TENSor37 spectrometer with KBr pellets in the  $4000 \sim 400 \text{ cm}^{-1}$  regions. Elemental (C, H and N) analysis was performed on a Perkin-Elmer 2400LS analyzer. The melting points were determined on a XT4A microscopic melting point meter (Beijing Keyi). The UV-Vis spectra were recorded in anhydrous methanol solvent ( $c = 1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ) by a Hitachi U-3010 spectrophotometer. The luminescent spectra were recorded at room temperature on a Varian Cary Eclipse spectrofluorometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2500 X-ray diffractometer using  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 0.154056 \text{ nm}$ ) under ambient conditions. Thermogravimetric analyses were conducted on a Perkin Elmer TG-7 with a heating rate of  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  from 20 to  $700 \text{ }^\circ\text{C}$  under a  $\text{N}_2$  atmosphere.

### 1.2 Syntheses of compounds 1 and 2

Compound **1** was prepared from a mixture  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  (0.05 g, 0.13 mmol), HBA (0.10 g, 0.83 mmol), phen (0.08 g, 0.41 mmol) and distilled water (15 mL) in a 25 mL Teflon-lined autoclave under autogenous pressure at 403 K for 6 d. After cooling to room temperature, colorless prism crystals **1** were collected by filtration and washed with distilled water in 36% yield (based on Pb). m.p.  $246.5 \sim 248.5 \text{ }^\circ\text{C}$ . Anal. calcd. for  $\text{C}_{33}\text{H}_{24}\text{N}_2\text{O}_6\text{Pb}$ (%): C, 52.73; H, 3.20; N, 3.73. Found (%): C, 52.62; H, 3.13; N, 3.68.

Compound **2** was prepared by the same synthetic method except using  $\text{Pb}(\text{NO}_3)_2$  and 2,2'-bipyridine instead of  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  and phen, respectively.

Colorless prism crystals of **2** were obtained with a yield of 53% (based on Pb). m.p. 218~220 °C. Anal. calcd. for  $C_{17}H_{13}N_3O_3Pb$ (%): C, 37.36; H, 2.38; N, 7.69. Found (%): C, 37.05; H, 2.47; N, 7.26.

### 1.3 X-ray crystal structure determination

The X-ray diffraction measurements for **1** and **2** were performed on Bruker SMART APEX II CCD diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) by using  $\varphi$ - $\omega$  scan mode at 296(2) K. Empirical absorption correction was applied to the intensity data using the SADABS program<sup>[16]</sup>. The

structures were solved by direct methods and refined by full-matrix least-square on  $F^2$  using the SHELXTL-97 program<sup>[17]</sup>. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms bonded to carbon atoms were placed in calculated positions and treated in a riding-model approximation. The carboxylic hydrogen atoms were located in a difference Fourier map. Details of the crystal parameters, data collection and refinements for **1** and **2** are summarized in Table 1.

CCDC: 803044, **1**; 803057, **2**.

**Table 1** Crystallographic data and structure refinement of complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	$C_{33}H_{24}N_2O_6Pb$	$C_{17}H_{13}N_3O_3Pb$
Formula weight	751.73	546.49
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ / nm	1.007 25(8)	0.653 89(11)
$b$ / nm	1.056 97(8)	0.850 52(14)
$c$ / nm	1.554 77(17)	1.554 8(3)
$\alpha$ / (°)	93.414(2)	84.566(3)
$\beta$ / (°)	102.836(2)	86.593(3)
$\gamma$ / (°)	117.972(1)	83.729(2)
$Z$	2	2
$V$ / nm <sup>3</sup>	1.399 3(2)	0.854 6(3)
$D_c$ / (g·cm <sup>-3</sup> )	1.784	2.124
$\mu$ (Mo $K\alpha$ ) / mm <sup>-1</sup>	6.08	9.90
$F(000)$	732	516
Crystal size / mm	0.26×0.18×0.15	0.23×0.21×0.15
$\theta$ range for data collection / (°)	1.4 to 26.5	2.7 to 25.0
Reflections collected	8 277	4 385
Independent reflections ( $R_{int}$ )	5 710 (0.020)	2 981 (0.030)
Observed reflections ( $I>2\sigma(I)$ )	4 950	2 769
Final GooF	1.02	1.02
$R_1, wR_2$ ( $I>2\sigma(I)$ )	0.029 3, 0.071 2	0.037 0, 0.097 1
$R_1, wR_2$ (all data)	0.037 1, 0.073 9	0.039 5, 0.098 8
Largest different peak and hole / (e·nm <sup>-3</sup> )	731, -730	2 695, -2 786

## 2 Results and discussion

### 2.1 Structure description

#### 2.1.1 Crystal structure of compound **1**

The asymmetric unit of compound **1**,  $[Pb(BA)_2(phen)] \cdot (HBA)$ , consists of a Pb<sup>II</sup> cation, two BA ligands, one phen ligand and one free HBA, as shown in

Fig.1. Selected bond distances and angles of compound **1** are listed in Table 2. The Pb<sup>II</sup> ion is chelated by two N atoms of phen with distances of 0.256 4(3) and 0.263 2(4) nm and four O atoms of BA ligands with Pb-O distances varying from 0.233 7(3) to 0.292 8(4) nm. Among the Pb-O bonds, two longer Pb1-O4 and Pb1-O2 distance of 0.292 8(4) and 0.282 2(3) nm belongs to

Table 2 Selected bond distances (nm) and bond angles ( $^{\circ}$ ) for complexes **1** and **2**

1					
Pb1-O1	0.233 7(3)	Pb1-O2	0.282 2(3)	Pb1-O3	0.236 1(4)
Pb1-O4	0.292 8(4)	Pb1-N1	0.263 2(4)	Pb1-N2	0.256 4(3)
O1-Pb1-O3	84.82(14)	O1-Pb1-N2	88.82(12)	O3-Pb1-N2	75.08(11)
O1-Pb1-N1	85.71(12)	O3-Pb1-N1	137.85(11)	N2-Pb1-N1	63.74(12)
O1-Pb1-O2	49.51(10)	O3-Pb1-O2	121.87(13)	N2-Pb1-O2	127.06(11)
N1-Pb1-O2	79.89(11)				
2					
Pb1-O1	0.243 2(5)	Pb1-N2	0.244 1(6)	Pb1-N1	0.247 1(5)
Pb1-O2	0.261 9(6)	Pb1-O4	0.287 1(6)	Pb1-O3	0.292 8(6)
Pb1-O3 <sup>i</sup>	0.289 3(6)	Pb1-O5 <sup>ii</sup>	0.288 7(7)		
O1-Pb1-N2	85.6(2)	O1-Pb1-N1	80.21(18)	N2-Pb1-N1	66.18(18)
O1-Pb1-O2	51.83(16)	N2-Pb1-O2	77.48(18)	N1-Pb1-O2	121.47(18)
N2-Pb1-O4	72.48(18)	N1-Pb1-O4	76.30(19)	O2-Pb1-O4	133.87(16)
N2-Pb1-O3	110.35(18)	N1-Pb1-O3	73.97(19)	O4-Pb1-O3	43.33(16)
O1-Pb1-O5 <sup>ii</sup>	120.12(20)	N2-Pb1-O5 <sup>ii</sup>	85.50(19)	O2-Pb1-O5 <sup>ii</sup>	68.42(19)
O4-Pb1-O5 <sup>ii</sup>	74.99(19)	O3-Pb1-O5 <sup>ii</sup>	98.23(19)	O1-Pb1-O3 <sup>i</sup>	85.60(19)
N1-Pb1-O3 <sup>i</sup>	83.81(17)	O2-Pb1-O3 <sup>i</sup>	118.16(17)	O4-Pb1-O3 <sup>i</sup>	105.12(17)
O3-Pb1-O3 <sup>i</sup>	61.80(17)	O5 <sup>ii</sup> -Pb1-O3 <sup>i</sup>	123.69(18)		

Symmetry codes used to generate equivalent atoms in compound **2**: <sup>i</sup> 1-x, -y, 1-z; <sup>ii</sup> -x, -y, 1-z.

weak secondary bond, which are shorter than the sum of van der Waals radii of lead and oxygen (0.344 nm)<sup>[18]</sup>. The O atoms from one of carboxylate ligands (O3 and O4) are almost coplanar with the N atoms of the phen ligand (N1 and N2), with a dihedral angle of

10.49 (12) $^{\circ}$ . Therefore, if we consider that the second carboxylate ligand occupies just one coordination site, the coordination environment of Pb<sup>II</sup> may be described as pseudo-square-pyramidal.

In the crystal **1**, there exist the weak interactions of Pb(II) with oxygen atoms of an adjacent molecule, via weak Pb $\cdots$ O coordinated bonds with Pb $\cdots$ O<sup>i</sup> (symmetry code: <sup>i</sup> 1-x, 1-y, 1-z) distance 0.320 6 (4) nm. Each Pb<sup>II</sup> ion is linked to another inversion-related Pb<sup>II</sup> center by two O atoms of benzoate groups to give rise to a centro-symmetric dimeric unit (Fig.2). The Pb1 $\cdots$ Pb1<sup>i</sup> intermolecular separation is 0.386 4(4) nm, indicating the weak metal-metal interaction. Moreover, the intermolecular hydrogen bond exists between the carboxyl H atom of solvent HBA and metal-coordinated carboxylate O atom (Fig.2). Additionally, there also exists inter-molecular  $\pi\cdots\pi$  stacks in the crystal **1**. As shown in Fig.3, the benzoate ring ( $C_g$ ) and neighboring phen ring ( $C_g^{ii}$ ) are parallel and the shortest centroid-centroid distance is 0.363 1(7) nm. The phen ring ( $C_g^*$ ) and the adjacent ring ( $C_g^{iii}$ ) are parallel highly with the

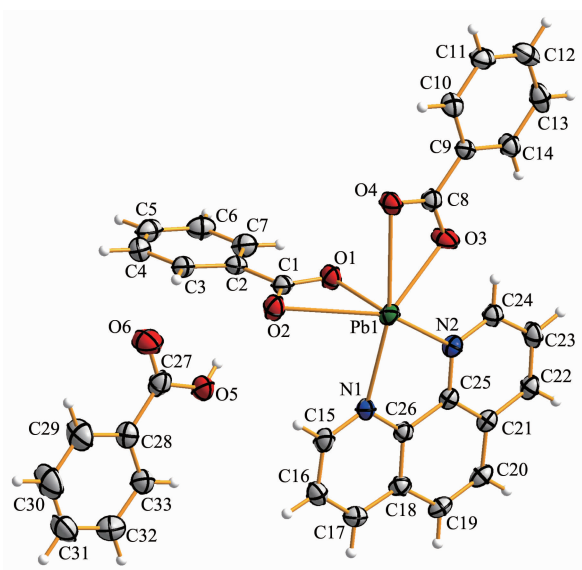


Fig.1 Asymmetric unit of compound **1** with the atom numbering

shortest centroid-centroid distance of 0.360 3(7) nm. Consequently, the three-dimensional framework is generated not only by coordination bonds and weak interactions but also by intermolecular H-bonds and  $\pi \cdots \pi$  stacking interactions (Fig.3).

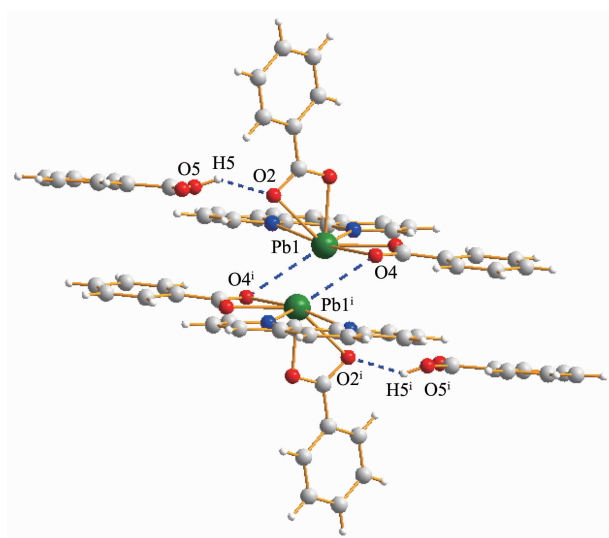


Fig.2 Dimer structure of complex **1**, formed by the weak Pb $\cdots$ O interactions

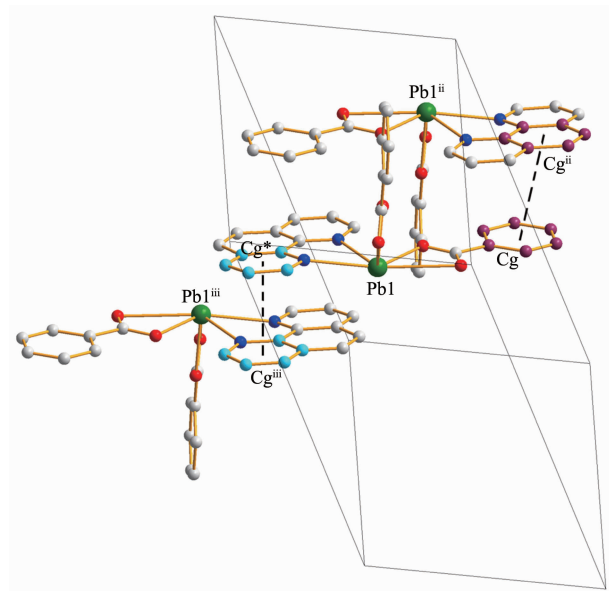


Fig.3 3D supramolecular framework of compound **1** assembled by  $\pi$ - $\pi$  stacking interactions

### 2.1.2 Crystal structure of compound **2**

The asymmetric unit of compound **2**, [Pb(2,2'-bipy)(BA)(NO<sub>3</sub>)], contains one crystallographically independent Pb(II), one 2,2'-bipy, one benzoate and one

nitrate ligand. As illustrated in Fig.4a, the coordination environment of Pb cation and the linkage modes of nitrate groups are well denoted. The Pb(II) ion is eight-coordinated by two N atoms from one 2,2'-bipy (Pb-N 0.244 1 (4)~0.247 1 (5) nm), two O atoms from one benzoate anion (Pb-O 0.243 2(5)~0.261 9(6) nm) and four O atoms from three nitrate groups (Pb-O 0.287 1(6)~0.292 8(6) nm). These four Pb-O contacts are much longer than the Pb-O bonds in the chelating mode, which also points out to weak interactions. Such comparable long Pb-O bond distances can be easily found in recent references, for example, 0.305 8 nm in [Pb<sub>2</sub>(2,2'-bipy)<sub>2</sub>( $\mu$ -4,4'-bipy)(NO<sub>3</sub>)<sub>4</sub>]<sup>[19]</sup> and 0.307 2 nm in [Pb<sub>3</sub>(BTC)<sub>2</sub>]<sup>[20]</sup>. Among four Pb $\cdots$ O weak interactions, two of them are in chelating mode and the other two are in bridging mode. The coordination bonds and weak interactions lead to a distorted dodecahedron coordination environment of Pb<sup>II</sup> ion (Fig.4b).

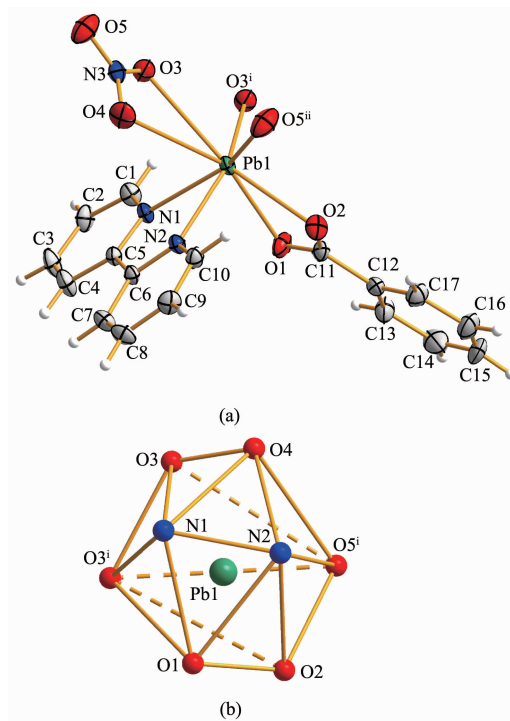
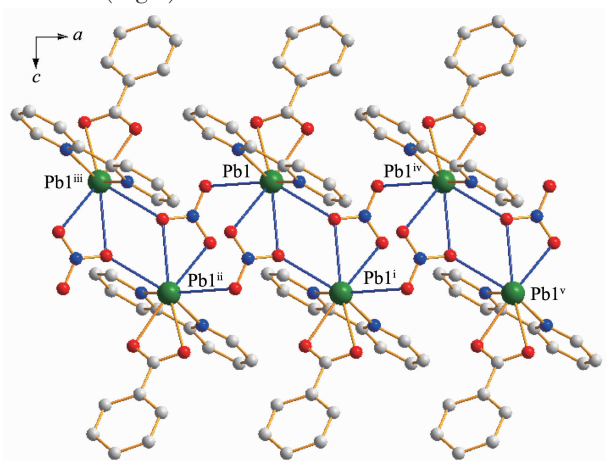


Fig.4 (a) Asymmetric unit of compound **2**; (b) Coordination polyhedron of Pb<sup>II</sup> in compound **2**

The adjacent Pb<sup>II</sup> ions are linked by nitrate groups resulting in an infinite chain structure along *b* axis (Fig. 5). The bridging nitrate ligands adopt the  $\mu_3$ - $\eta^1\eta^2\eta^1$  mode, that is, one chelating and two bridging, leading to

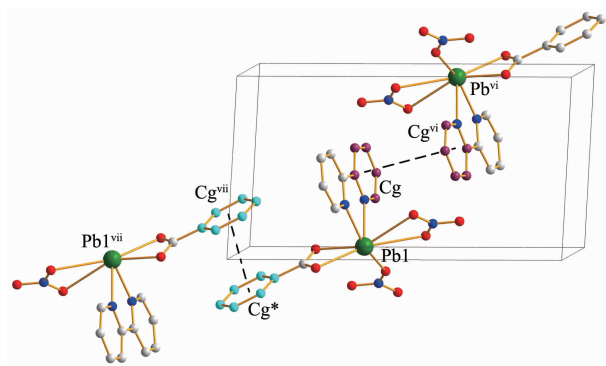


the central  $\text{Pb}_2\text{O}_2$  and  $\text{Pb}_2\text{O}_4\text{N}_2$  cores. The distances between two adjacent  $\text{Pb}^{\text{II}}$  ions are 0.499 5(8) nm for  $\text{Pb1} \cdots \text{Pb1}^{\text{i}}$  (symmetry code:  $^{\text{i}} 1-x, -y, 1-z$ ) and 0.575 7(8) nm for  $\text{Pb1} \cdots \text{Pb1}^{\text{ii}}$  (symmetry code:  $^{\text{ii}} -x, -y, 1-z$ ). And the angle of  $\text{Pb1}^{\text{i}} \cdots \text{Pb1} \cdots \text{Pb1}^{\text{ii}}$  is  $74.54(5)^\circ$ . Additionally, the excellent coordinating ability and large conjugated systems of 2,2'-bipy and benzoate ligands allow to forming  $\pi \cdots \pi$  stacking interactions. There are two kinds of inter-molecular  $\pi \cdots \pi$  interactions between 2,2'-bipy and benzoate ligands belonging to the neighboring chains, with the shortest centroid-centroid distance of 0.375 9(8) and 0.367 8(8) nm, which assemble the 1D chains into 3D supramolecular structure (Fig.6).



Symmetry codes:  $^{\text{i}} 1-x, -y, 1-z$ ;  $^{\text{ii}} -x, -y, 1-z$ ;  $^{\text{iii}} -1+x, y, z$ ;  $^{\text{iv}} 1+x, y, z$ ;  $^{\text{v}} 2-x, -y, 1-z$ ; H atoms are omitted for clarity

Fig.5 1D chain of compound **2** viewed down the  $b$  axis



Symmetry codes:  $^{\text{vi}} 1-x, 1-y, 1-z$ ;  $^{\text{vii}} 1-x, -y, -z$

Fig.6 3D supramolecular structure of compound **2** assembled by  $\pi$ - $\pi$  stacking interactions

### 2.1.3 Lone pair stereochemical properties

The stereochemical activity of  $6s^2$  outer electrons is always an interesting issue. Shimoni-Livny and co-

works classify  $\text{Pb}^{\text{II}}$  complex geometries as holo- and hemidirected<sup>[21]</sup>. In compound **1**, there is an obvious gap in the coordination sphere of  $\text{Pb}^{\text{II}}$  ions, even though considering the secondary  $\text{Pb} \cdots \text{O}$  interactions, for example, the bond angle of  $\text{O3-Pb1-O4}^{\text{i}}$  (symmetry code:  $^{\text{i}} 1-x, 1-y, 1-z$ ) is  $140.58(14)^\circ$ . Thus, the lone pairs of electrons are clearly active and the coordination sphere of  $\text{Pb}^{\text{II}}$  ions is hemidirected (Fig.7a). In compound **2**, the coordination sphere of  $\text{Pb}^{\text{II}}$  ion features small holes or gaps; therefore the coordination spheres can be considered as somewhat holodirected (Fig.7b).

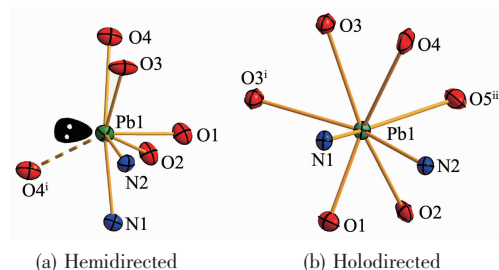


Fig.7 Schematic representation of the  $\text{Pb}^{\text{II}}$  coordination sphere of compounds **1** and **2**, respectively

## 2.2 IR analysis

In the IR spectrum of compound **1**, the strong absorption at around  $1701\text{ cm}^{-1}$  demonstrates the existence of free benzoic acid. The IR spectrum shows typical asymmetric and symmetric carboxylate stretching bonds at  $1554$  and  $1456\text{ cm}^{-1}$ . The  $\Delta\nu(\nu(\text{COO})_{\text{as}} - \nu(\text{COO})_{\text{s}})$  is  $98\text{ cm}^{-1}$ , indicating that the carboxylates act as bidentate chelating coordination mode. The absorption peaks at  $1427$ ,  $854$  and  $730\text{ cm}^{-1}$  could be assigned to the characteristic bonds of phen ligand coordinated with  $\text{Pb}^{\text{II}}$  (free phen  $1421$ ,  $853$  and  $739\text{ cm}^{-1}$ ).

In the IR spectrum of compound **2**, the absence of characteristic bands at  $1700\text{ cm}^{-1}$  attributed to the protonated carboxylic group indicates the complete deprotonation of HBA ligand upon reaction with  $\text{Pb}$  ions. The strong bonds at  $1548$  and  $1462\text{ cm}^{-1}$  should be assigned to  $\nu(\text{COO})_{\text{as}}$  and  $\nu(\text{COO})_{\text{s}}$  stretching vibration. The  $\Delta\nu$  of  $86\text{ cm}^{-1}$  suggests carboxylates act as bidentate chelating mode. The vibration bonds at  $1608$ ,  $1007$  and  $781\text{ cm}^{-1}$  could be assigned to the characteristic peaks of 2,2'-bipy. Compared to those of free 2,2'-bipy ( $1585$ ,  $995$  and  $760\text{ cm}^{-1}$ ), these peaks shift to some extent, indicating the coordination interactions with

Pb<sup>II</sup>. The compound **2** has their characteristic IR absorptions at 1 439 and 1 316 cm<sup>-1</sup> due to the metal bound nitrate groups<sup>[22-23]</sup>. Consequently, the IR analyses of compound **1** and **2** are consistent with their crystal structures.

### 2.3 UV absorption and PL spectra

The UV spectra of compound **1** and free ligands were recorded in methanol solution. UV spectra exhibit the strong absorption peaks at around 263 nm for phen ligand and 228 nm for benzoate ligands, corresponding to  $\pi \rightarrow \pi^*$  transitions. The UV spectrum of compound **1** shows the intense absorption peaks at 275 nm and the shape of **1** is nearly the same as that of free phen. Similarly, the UV spectrum of **2** shows absorption peak at 289 nm (free 2,2'-bipy at 281 nm). Compared with that of free ligand, the red-shift probably attributes to the chelating of phen or 2,2'-bipy with Pb<sup>II</sup> ions, which obviously enhances the conjugation of compounds.

The fluorescent properties of the pure ligand and compound **1** were investigated in methanol solvent at room temperature. As could be seen in Fig.8, benzoic acid and phen display their characteristic emission peaks at 325 nm (curve c,  $\lambda_{\text{ex}}=228$  nm) and 378 nm (curve b,  $\lambda_{\text{ex}}=263$  nm), respectively. The emissions of free ligands may be attributed to the  $\pi \rightarrow \pi^*$  transitions. There is an intense emission at 404 nm (curve a,  $\lambda_{\text{ex}}=275$  nm) for compound **1**, which is red-shifted about 26 nm compared with that of free phen. Similarly, compound **2** has obvious emission peak at 409 nm. According to the previous literature<sup>[24]</sup>, the emissions of compounds **1** and **2** can be assigned to the enhanced conjugation through the chelating with Pb<sup>II</sup> ions or a

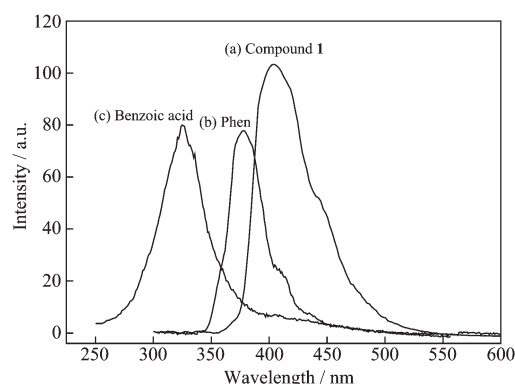


Fig.8 Luminescence spectra of compound **1** and its ligands

metal-perturbing intraligand transition.

### 2.4 PXRD and thermal analysis

The XRD powder pattern of compounds **1** and **2** were collected at  $2\theta$  from 5° to 50°, which are shown in Fig.9. The experimental patterns are in good agreement with those simulated from the single crystal diffraction data, indicating the high phase purity of as-synthesized.

To further characterize compounds **1** and **2**, their thermal stability was examined using TG in 20~700 °C under a N<sub>2</sub> atmosphere. Fig.10 displayed compound **1** underwent a three-step weight loss. The first weight loss of 16.02% (calcd. 16.23%) is assigned to the liberation of one uncoordinated benzoic acid molecule which occurs in the range of 130~180 °C. The second weight loss of 23.65% (calcd. 23.94%) between 266 and 375 °C is ascribed to the loss of phen ligand. The last loss of 30.01% (calcd. 32.10 %) occurs from 375 to 580 °C, which corresponds to the loss of benzoate ligands. The final product after 580 °C is mainly Lead monoxide according to the residual weight.

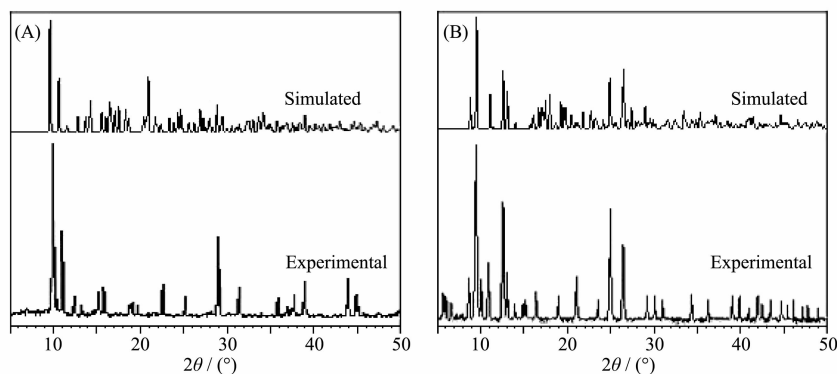
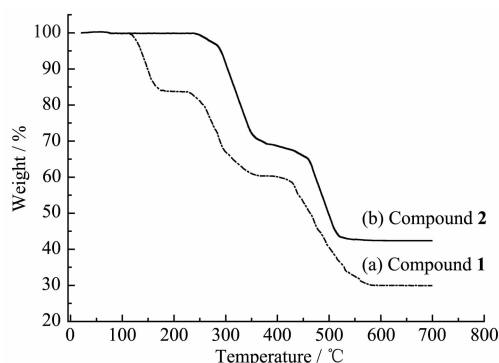


Fig.9 Simulated and experimental XRD patterns for compounds **1** (A) and **2** (B)

Fig.10 TG curves of compounds **1** and **2**

TG analysis of compound **2** shows that it is thermally stable up to 240 °C and proves no solvent molecules in polymer. Above this temperature, a two-step weight loss is observed up to 575 °C. The first weight loss of 31.03% is in accordance with the loss of one nitrate and benzoate ligand (calcd. 33.49 %). The second loss is assigned to the liberation of one 2,2'-bipy. The final experimental residual percentage (42.65%) is consistent with the calculated value of 40.81%, which indicates the final product is likely PbO.

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