

## 一维链状配位聚合物 $\{[\text{Pb}(\text{PTCP})(2,5\text{-pydc})]_2 \cdot \text{H}_2\text{O}\}_n$ 的水热合成、晶体结构和发光性质研究

王湘成<sup>1</sup> 刘春波<sup>1,2</sup> 李秀颖<sup>1</sup> 李春香<sup>1</sup> 闫永胜<sup>\*,1</sup> 车广波<sup>\*,1,2</sup>

(<sup>1</sup> 江苏大学化学化工学院, 镇江 212013)

(<sup>2</sup> 吉林师范大学环境友好材料制备与应用教育部重点实验室, 四平 136000)

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## Hydrothermal Synthesis, Crystal Structure and Photoluminescence of a 1D Chain Coordination Polymer: $\{[\text{Pb}(\text{PTCP})(2,5\text{-pydc})]_2 \cdot \text{H}_2\text{O}\}_n$

WANG Xiang-Cheng<sup>1</sup> LIU Chun-Bo<sup>1,2</sup> LI Xiu-Ying<sup>1</sup> LI Chun-Xiang<sup>1</sup>

YAN Yong-Sheng<sup>\*,1</sup> CHE Guang-Bo<sup>\*,1,2</sup>

(<sup>1</sup> School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013)

(<sup>2</sup> Key Laboratory of Preparation and Applications of Environmental Friendly Materials  
(MOE), Jilin Normal University, Siping, Jilin 136000)

**Abstract:** A new metal-organic coordination compound framework formulated  $\{[\text{Pb}(\text{PTCP})(2,5\text{-pydc})]_2 \cdot \text{H}_2\text{O}\}_n$  (**1**) (PTCP=2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]-phenanthrene, H<sub>2</sub>pydc=pyridine-2,5-dicarboxylic acid) has been prepared in the hydrothermal condition and characterized by single-crystal X-ray diffraction, elemental analysis, IR and TG. It crystallizes in monoclinic, space group *C2/c* with *a*=2.129 2(4) nm, *b*=1.111 2(2) nm, *c*=2.049 4(4) nm,  $\beta$ =105.02(3)°, *V*=4.683 2(16) nm<sup>3</sup>, *Z*=4, Pb<sub>2</sub>C<sub>52</sub>H<sub>32</sub>N<sub>10</sub>O<sub>9</sub>, *M<sub>r</sub>*=1 355.26, *D<sub>c</sub>*=1.922 g·cm<sup>-3</sup>, *F*(000)=2 600, *S*=0.825, *R*<sub>1</sub>=0.056 2 and *wR*<sub>2</sub>=0.168 9. In the crystal, the Pb atom is five-coordinated by three N and two O atoms. The complex forms a one-dimensional zigzag polymeric chain along the *b* axis which is stacked to furnish a two-dimensional supramolecular layer structure via aromatic  $\pi$ - $\pi$  interactions in the *ab* plane. In addition, hydrogen bonds are observed in the compound which play an important role in forming the final structure. Solid-state fluorescence spectrum of **1** exhibits the maximum emission peak at 621 nm. CCDC: 791183.

**Key words:** lead complex; pyridine-2,5-dicarboxylic acid; crystal structure; photoluminescence

Metal-containing supramolecular has rapidly emerged as a subject of great interest, not only due to their intriguing variety of architectures and topologies<sup>[1-3]</sup>, but also because of the potential applications

such as luminescence<sup>[4]</sup>, nonlinear optics<sup>[5]</sup>, gas adsorption<sup>[6-7]</sup>, ion exchange<sup>[8]</sup>, magnetism<sup>[9]</sup>, catalysis<sup>[10]</sup> and so on. Various of multicarboxylate ligands have been extensively referred to as secondary building unit in the

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\*通讯联系人。E-mail: guangbochejl@yahoo.com, yys@ujs.edu.cn

第一作者: 王湘成, 男, 25 岁, 硕士研究生; 研究方向: 配合物化学。

preparation of such supramolecular frameworks<sup>[11-13]</sup>. Pyridine-carboxylic acids are one series of excellent multicarboxylate ligands which have been widely used to construct novel metal-organic solid materials<sup>[14-16]</sup> because of their outstanding coordination ability and their good hydrogen bonds receptivity. However, to construct an attractive metal-containing supramolecular framework, it should be not only to introduce a good hydrogen bonds acceptor, but also to choose one multifunctional hydrogen bonds donors. As one kind of important elements of *N*-containing heterocyclic ring systems in coordination chemistry, phenanthroline (phen) and its derivatives have been extensive application in organic light-emitting diodes<sup>[17]</sup>, organic optical sensor<sup>[18]</sup>, photoluminescence (PL) material<sup>[19]</sup> and so on. Phen derivative 2-phenyl-1H-1,3,7,8-tetraazacyclopenta[1]phenanthrene (PTCP) combines the excellent properties of coordination,  $\pi \cdots \pi$  stacking interactions and hydrogen-bond donor. Herein, we present the hydrothermal synthesis and structural characterization of a novel lead(II) complex  $[\text{Pb}(\text{PTCP})(2,5\text{-pydc})_2 \cdot \text{H}_2\text{O}]_n$  (**1**) (2,5- $\text{H}_2\text{pydc}$ =pyridine-2,5-dicarboxylic acid) which has not yet been reported in the literatures. Compound **1** is a two-dimensional supramolecular layer structure via aromatic  $\pi$ - $\pi$  interactions in the *ab* plane. The thermalgravimetric analysis (TGA) and the PL of **1** were also investigated.

## 1 Experimental

### 1.1 Chemicals and general methods

PTCP was prepared by the literature method<sup>[20]</sup>. All other reagents were commercially available and were used as received without further purification. Elemental analyses were performed with an Perkin-Elmer 240C element analyzer. IR spectrum (KBr pellets) was

recorded in the 4 000~400  $\text{cm}^{-1}$  range on a Bruker IFS 66V/S FTIR spectrometer. TGA was performed on a TA Instruments with a heating rate of 5  $^\circ\text{C} \cdot \text{min}^{-1}$  under an air atmosphere. The PL spectrum was measured on a Perkin-Elmer LS55 spectrometer.

### 1.2 Synthesis of the complex

A mixture of  $\text{Pb}(\text{NO}_3)_2$  (0.066 g, 0.2 mmol),  $\text{H}_2\text{pydc}$  (0.033 g, 0.2 mmol), PTCP (0.059 g, 0.2 mmol) was dissolved in 16 mL of water and sealed in a 25 mL teflon reactor, which was heated to 165  $^\circ\text{C}$  for 5 days and then cooled to room temperature. Pale yellow single crystals of **1** suitable for X-ray single-crystal diffraction analysis were obtained (yield 78%). Anal. calc. for **1**  $\text{C}_{52}\text{H}_{32}\text{Pb}_2\text{N}_{10}\text{O}_9$  (%): C, 46.15; H, 2.23; N, 10.35. Found (%): C, 46.13; H, 2.28; N, 10.36. Main IR (KBr,  $\text{cm}^{-1}$ ): 3 560(s), 3 064(s), 1 592(s), 1 458(m), 1 390(s), 1 350(s), 1 279(m), 1 070(w), 1 036(w), 818(m), 766(m), 735(w), 700(m), 499(m), 473(w).

### 1.3 Crystal structure determination

Suitable single crystal with dimensions of 0.235 mm×0.137 mm×0.115 mm was mounted on glass fiber and reflection data were collected at room temperature on a Rigaku RAXIS-RAPID single-crystal diffractometer equipped with a graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\,073\,\text{nm}$ ) at 292(2) K by using an  $\omega$  scan mode. The structure was solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using SHELXTL-97 program<sup>[21]</sup>. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of organic ligands were generated geometrically, and the hydrogen atoms of water molecules were located from difference Fourier map. Crystal data and details of the data collection and the structure refinement are given in Table 1.

CCDC: 791183.

Table 1 Crystal date and structure refinement for complex **1**

Formula	$\text{C}_{52}\text{H}_{32}\text{N}_{10}\text{O}_9\text{Pb}_2$	<i>c</i> / nm	2.049 4(4)
Formula weight	1 355.26	$\beta$ / ( $^\circ$ )	105.02(3)
Temperature / K	292(2)	<i>V</i> / $\text{nm}^3$	4.683 2(17)
Crystal system	Monoclinic	<i>Z</i>	4
Space group	<i>C2/c</i>	<i>D<sub>c</sub></i> / ( $\text{g} \cdot \text{cm}^{-3}$ )	1.922
<i>a</i> / nm	2.129 2(4)	<i>F</i> (000)	2 600
<i>b</i> / nm	1.111 2(2)	Crystal size / mm	0.235×0.137×0.115

Continued Table 1

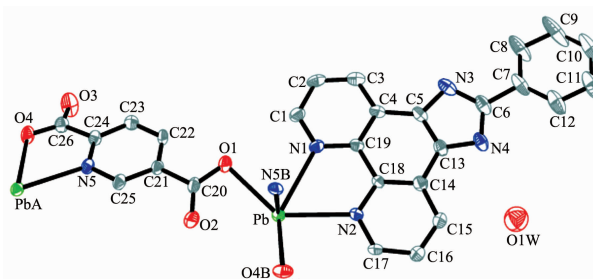
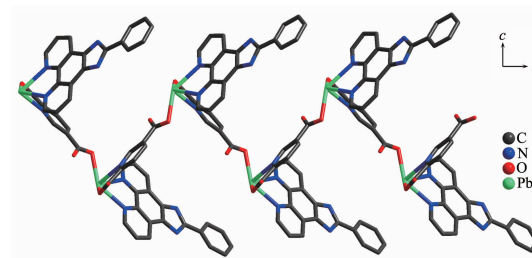
$\theta / (^{\circ})$	3.10 to 27.48	Data / restraints / parameters	5 347 / 33 / 333
Limiting indices	$-27 \leq h \leq 27, -14 \leq k \leq 14, -26 \leq l \leq 26$	Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.056\ 2, wR_2=0.168\ 9$
Reflections collected / unique ( $R_{int}$ )	19 305 / 5 347 (0.072 2)	Largest diff. peak and hole / ( $e \cdot nm^{-3}$ )	1 276, -3 582
Goodness of fit on $F^2$	0.825		

## 2 Results and discussion

### 2.1 Description of crystal structure

Compound **1** crystallizes in the monoclinic space group  $C2/c$ . As shown in Fig.1, each Pb(II) ion is coordinated by two O atoms from 2,5-pydc<sup>2-</sup> ligands and three N atoms in which two N atoms come from the chelated PTCP ligand and another from 2,5-pydc<sup>2-</sup> ligand. The average distance of Pb-O is 0.247 0 nm, while Pb-N bond distances range from 0.246 5 to 0.268 1 nm (Table 2). In **1**, each 2,5-pydc<sup>2-</sup> links two Pb(II) ions by means of bridging and chelating coordination mode, and the adjacent Pb atoms are bridged through 2,5-pydc<sup>2-</sup> ligands to obtain a one-dimensional zigzag chain with the Pb-Pb-Pb angle of 78.29° along the  $b$  axis, as shown in Fig.2. The PTCP ligands and the adjacent 2,5-pydc<sup>2-</sup> ligands are almost arranged with perpendicularity, with the C(6)-Pb-C(22) angles of 86.29(1)°. Simultaneously, by introducing an extended benzene ring into the phenanthroline system, PTCP has more larger  $\pi$ -conjugated plane which can construct strong  $\pi \cdots \pi$  stacking interactions. In complex **1**, the adjacent chains running parallel to one another and the  $\pi$ - $\pi$  interactions between PTCP molecules link them to a two-dimensional supramolecular layer, as shown in Fig.3 (face-to-face distance of 0.350 1 nm, centroid-to-centroid distance of 0.350 3 nm). In addition, imidazole rings of PTCP ligands can provide one hydrogen bonding donors and one N

accepter which lead to two strong hydrogen bonds. One is the intermolecular N  $\cdots$  O hydrogen bonds which forms between N(3) atom of PTCP and the O(3) atom of 2,5-pydc<sup>2-</sup> ligand (N(3)-H(3)A  $\cdots$  O(3)A, symmetry code: A:  $-x+1, y+1, -z+1/2$ ), and the other happens between the water molecular and N(4) (O(1W)-H(1)B  $\cdots$  N(4)). Some weak C-H  $\cdots$  O and C-H  $\cdots$  N hydrogen bonds are also observed and the details are listed in Table 3, which further consolidating the current architectures.

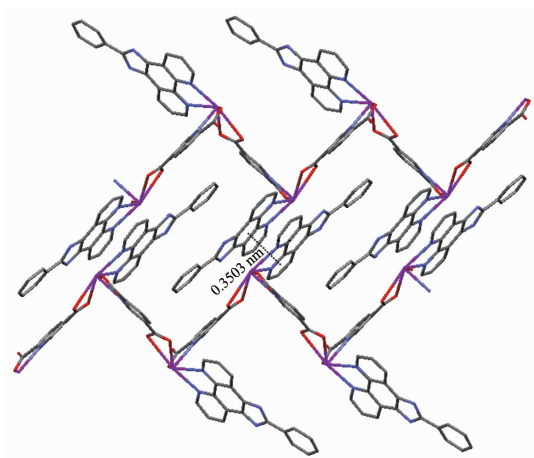
Symmetry codes: A:  $-x+1, y+1, -z+1/2$ ; B:  $-x+3/2, y+1/2, -z+1/2$ Fig.1 Coordination environments of Pb atoms in complex **1**, all the hydrogen atoms are omitted for clarityFig.2 One-dimensional zigzag chain of complex **1** along the  $b$  axisTable 2 Selected bond lengths (nm) and angles ( $^{\circ}$ )

Pb-N(1)	0.268 1(6)	Pb-N(2)	0.260 8(7)	PbA-N(5)	0.246 5(6)
Pb-O(1)	0.248 0(6)	PbA-O(4)	0.246 1(7)		
O(4)B-Pb-N(5)B	67.0(2)	O(4)B-Pb-O(1)	125.0(3)	N(5)B-Pb-O(1)	77.1(2)
O(4)B-Pb-N(2)	82.2(2)	N(5)B-Pb-N(2)	85.0(2)	O(1)-Pb-N(2)	135.5(2)
O(4)B-Pb-N(1)	133.64(19)	N(5)B-Pb-N(1)	80.8(2)	O(1)-Pb-N(1)	75.0(2)
N(2)-Pb-N(1)	61.98(19)				

Symmetry codes: A:  $-x+3/2, y-1/2, -z+1/2$ ; B:  $-x+3/2, y+1/2, -z+1/2$ .

**Table 3** Distances and angles of hydrogen bonds for complex **1**

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠(DHA) / (°)
N(3)-H(3)A...O(3)A	0.086	0.192	0.277 4	174.8
O(1W)-H(1)B...N(4)	0.087	0.260	0.317 6	124.5
C(1)-H(1)...O(1)	0.093	0.234	0.302 0	129.9
C(12)-H(12)...N(4)	0.093	0.257	0.290 5	101.7
C(15)-H(15)...O(1W)	0.093	0.256	0.330 8	137.7
C(22)-H(22)...O(1)	0.084	0.222	0.274 8	121.0

Symmetry code: A:  $-x+1, y+1, -z+1/2$ .**Fig.3** 2D layer structure of **1** formed through  $\pi\cdots\pi$  stacking interactions

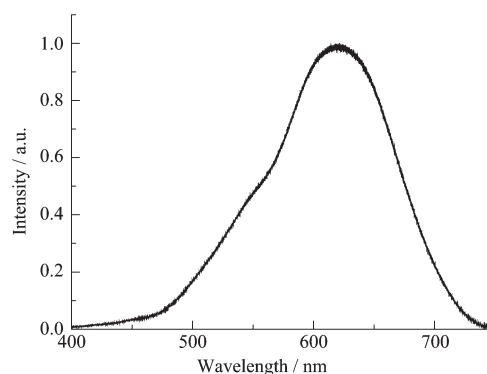
## 2.2 Thermal analysis

To further fully characterize compound **1**, its thermal stability was examined using TG. TGA displayed that compound **1** underwent a three-step weight loss. The first weight loss of 1.35% (cal. 1.33%) is assigned to the liberation of one uncoordinated water molecule which occurred in the range of approximate 100~150 °C. A plateau retains between 150 and 370 °C. The second weight loss of 24.09% (cal. 24.40%) between 370 and 420 °C is ascribed to the loss of 2,5-pydc<sup>2-</sup> ligand. The last loss of 43.84% (cal. 43.79%) occurs from 420 to 600 °C, which corresponds to the loss of PTCP ligand. After the decomposition, a residue of lead oxide in 30.72% (calcd 30.48%) is left.

## 2.3 PL property

The solid-state PL spectrum of **1** at room temperature is depicted in Fig.4. Compound **1** exhibits an intense red emission with a maximum peak at 621 nm upon excitation at 355 nm. In order to understand the nature of this emission band, the PL property of free

PTCP ligand was analyzed, showing that the emission for PTCP is at 475 nm ( $\lambda_{\text{ex}}=393$  nm), which can be assigned to the  $\pi^*\rightarrow n$  transition<sup>[22]</sup>. On complexation of the ligand with Pb<sup>2+</sup> ion, the emission arising from PTCP ligands were not observable. The emission of **1** can be assigned to a metal-centered transition involving the *s* and *p* metal orbitals, as proposed by Vogler<sup>[23-24]</sup>.

**Fig.4** Photoluminescent spectrum of **1** in the solid state at room temperature

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