

## 邻菲啰啉衍生物与柔性二羧酸构筑的铅(II)配位聚合物: 合成、结构与表征

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**摘要:** 通过水热合成的方法得到了一个新的化合物 $[\text{Pb}_2(\text{L1})_2(\text{L2})_2]$ , 并对该化合物进行了元素分析、红外、热重和单晶 X-射线表征( $\text{H}_2\text{L1}$  为丁二羧酸阴离子,  $\text{L2}$  为邻菲啰啉衍生物)。该化合物属于单斜晶系, 空间群  $P2_1/c$ , 晶胞参数:  $a=0.795\ 40(10)\ \text{nm}$ ,  $b=2.649\ 0(3)\ \text{nm}$ ,  $c=1.996\ 9(2)\ \text{nm}$ ,  $\beta=99.784(2)^\circ$ ,  $V=4.1463(9)\ \text{nm}^3$ ,  $Z=4$ ,  $R=0.038\ 0$ ,  $wR=0.084\ 5$ 。在该化合物中, 丁二羧酸阴离子连接着铅原子形成一维链状结构。此外, 链与链之间的  $\pi-\pi$  相互作用使一维链形成了三维超分子结构。最后,  $\text{N-H}\cdots\text{O}$  氢键进一步地稳定了此三维超分子结构。

**关键词:** 晶体结构; 配位聚合物; 丁二羧酸; 邻菲啰啉衍生物

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## Synthesis, Structure and Characterization of Pb(II) Coordination Polymer Constructed by 1,10-Phenanthroline Derivative and Succinic Acid

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**Abstract:** A coordination polymer,  $[\text{Pb}_2(\text{L1})_2(\text{L2})_2]$  (**1**) ( $\text{H}_2\text{L1}$ =succinic acid and  $\text{L2}$ =2-(4-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline), has been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, TGA and single-crystal X-ray diffraction. Crystal data:  $\text{C}_{46}\text{H}_{30}\text{F}_2\text{N}_8\text{O}_8\text{Pb}_2$ , monoclinic, space group  $P2_1/c$ ,  $a=0.795\ 40(10)\ \text{nm}$ ,  $b=2.649\ 0(3)\ \text{nm}$ ,  $c=1.996\ 9(2)\ \text{nm}$ ,  $\beta=99.784(2)^\circ$ ,  $V=4.146\ 3(9)\ \text{nm}^3$ ,  $Z=4$ ,  $R=0.038\ 0$ ,  $wR=0.0845$ . In **1**, each  $\text{L1}$  anion in a bis-chelating mode bridges  $\text{Pb(II)}$  atoms to afford a one-dimensional (1D) chain structure. Neighboring 1D chains are linked together by  $\pi-\pi$  stackings among  $\text{L2}$  ligands to yield a 3D supramolecular architecture. Finally, the  $\text{N-H}\cdots\text{O}$  hydrogen-bonding interactions further stabilize the 3D supramolecular structure of **1**.

**Key words:** crystal structure; coordination polymer; succinic acid; 1,10-phenanthroline derivative

## 0 Introduction

Recently, extensive attention has been focused on

the design and synthesis of coordination polymers for their fascinating motifs and potential applications<sup>[1-5]</sup>.

Up to now, a wide range of one-, two- and three-

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dimensional infinite solid-state coordination architectures have been reported in the last decade<sup>[6-8]</sup>. Particularly, aromatic multi-benzenecarboxylate ligands together with N-based ligands have been extensively utilized in the construction of mixed-ligand coordination polymers<sup>[9-17]</sup>. Nevertheless, the coordination chemistry and structural properties of coordination polymers constructed by fatty carboxylates and chelating N, N-based ligands have been documented relatively little to date<sup>[8-17]</sup>. The succinic acid (H<sub>2</sub>L1), as a good candidate for the construction of coordination polymer, has two -CH<sub>2</sub>-spacers. Therefore, it can coordinate with metals in a flexible coordination mode and yield fascinating architectures.

On the other hand, 1,10-phenanthroline (phen) and its derivatives have been used to construct supramolecular architectures owing their excellent coordination ability and large conjugated system that can easily form  $\pi$ - $\pi$  interactions<sup>[8,10]</sup>. However, the combination of the phen derivatives and the different fatty dicarboxylates has not been well studied in coordination chemistry<sup>[11]</sup>. In this work, we report a new Pb(II) coordination polymer based on L1 anion and 2-(4-fluorophenyl)-1H-imidazo [4,5-f] [1,10] phenanthroline (L2), [Pb<sub>2</sub>(L1)<sub>2</sub>(L2)<sub>2</sub>] (**1**).

## 1 Experimental

### 1.1 General

All materials were analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; IR spectrum was obtained on a Perkin-Elmer 2400LSII spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer in the range from 40 to 800 °C under nitrogen gas.

### 1.2 Synthesis and crystal growth

A mixture of H<sub>2</sub>L1 (1 mmol), Pb(NO<sub>3</sub>)<sub>2</sub> (1 mmol) and L2 (1 mmol) were dissolved in distilled water (10 mL) and ethanol (3 mL), which was heated at 170 °C in a Teflon-lined stainless steel autoclave for 4 days. After the mixture had been cooled to room temperature at a rate of 10 °C · h<sup>-1</sup>, crystals of **1**

suitable for single-crystal X-ray diffraction analysis were collected by filtration, washing several times with distilled water and drying in air at ambient temperature. Yield: 19% based on Pb(II). Anal. for C<sub>46</sub>H<sub>30</sub>F<sub>2</sub>N<sub>8</sub>O<sub>8</sub>Pb<sub>2</sub> (%): Calcd.: C 43.33, H 2.37, N 8.79; Found: C 43.21, H 2.17, N 8.63. IR (KBr, cm<sup>-1</sup>):  $\nu$ =3471s, 1 643m, 1 564m, 1 481w, 1 415m, 1 218w, 1 132s, 991w, 826w, 743w, 618w, 542w.

### 1.3 X-ray structure determination

A single crystal with dimension of 0.15 mm×0.12 mm×0.11 mm was selected and mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromatized Mo K $\alpha$  ( $\lambda$ =0.071 073 nm) radiation by using an  $\omega$ -2 $\theta$  scanning method at a temperature of 20 ±2 °C. Out of the total 21284 reflections collected in the 1.29 ≤  $\theta$  ≤ 25.05° range, 7332 were independent with  $R_{\text{int}}$ =0.0509, of which 5380 were considered to be observed ( $I > 2\sigma(I)$ ) and used in the succeeding refinement.

Absorption corrections were applied by using a multi-scan technique. The structure was solved by Direct Method with SHELXS-97 program<sup>[18]</sup> and refined with SHELXL 97<sup>[19]</sup> by full-matrix least-squares techniques on  $F^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. All H atoms were positioned geometrically (N-H=0.086 nm and C-H=0.093 nm) and refined as riding, with  $U_{\text{iso}}$  (H) values set at 1.2 times  $U_{\text{eq}}$  (carrier). The maximum residual electron density is 1 910 e · nm<sup>-3</sup> at 0.099 nm from Pb. The residual electron density can be interpreted as Fourier truncation error. The final  $R$ =0.038 0 and  $wR$ =0.084 5 ( $w=1/[\sigma^2(F_o^2)+(0.042\ 6P)^2+0.000\ 0P]$ , where  $P=(F_o^2+2F_c^2)/3$ ).  $S$ =0.968,  $(\Delta\rho)_{\text{max}}$ =1.909,  $(\Delta\rho)_{\text{min}}$ =−0.540 e · nm<sup>-3</sup> and  $(\Delta/\sigma)_{\text{max}}$ =0.003.

## 2 Results and discussion

### 2.1 Description of crystal structure

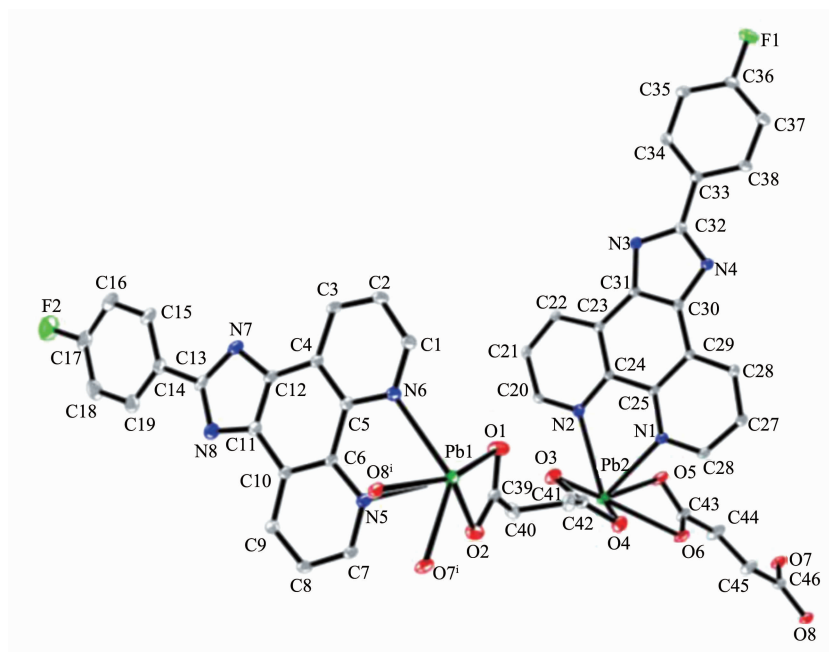
Selected bond lengths and angles for **1** are given in Table 1. As shown in Fig. 1, the asymmetric unit of **1** has two crystallographically independent Pb(II) atoms, two unique L1 anions, and two unique L2 ligands. Each Pb(II) atom is six-coordinated by two

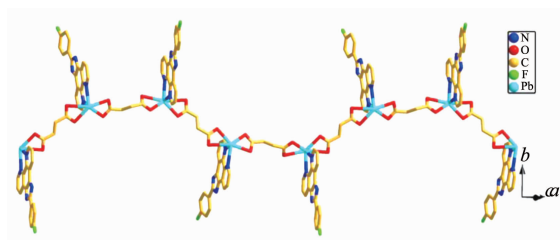
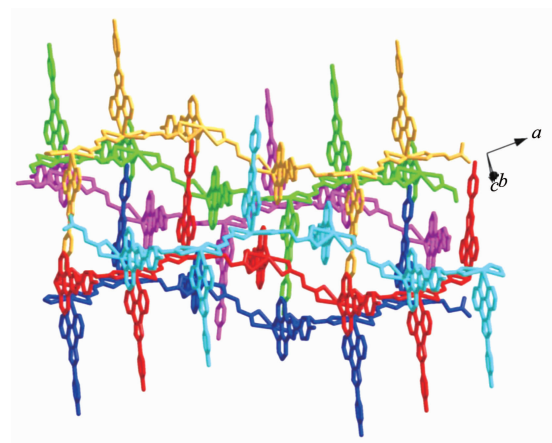
**Table 1** Selected bond distances (nm) and angles (°)

Pb(1)-O(1)	0.2703(5)	Pb(1)-O(2)	0.2449(5)	Pb(1)-O(7)i	0.2490(5)
Pb(1)-O(8) <sup>i</sup>	0.2674(5)	Pb(1)-N(5)	0.2469(6)	Pb(1)-N(6)	0.2556(6)
Pb(2)-O(5)	0.2680(5)	Pb(2)-O(6)	0.2523(4)	Pb(2)-N(1)	0.2446(5)
Pb(2)-O(4)	0.2535(5)	Pb(2)-O(3)	0.2558(5)	Pb(2)-N(2)	0.2578(6)
O(2)-Pb(1)-N(5)	73.81(19)	O(2)-Pb(1)-O(7)i	91.86(17)	N(5)-Pb(1)-O(7)i	80.06(18)
O(2)-Pb(1)-N(6)	110.28(19)	N(5)-Pb(1)-N(6)	65.06(19)	O(7)i-Pb(1)-N(6)	129.76(16)
O(2)-Pb(1)-O(8) <sup>i</sup>	134.74(17)	N(5)-Pb(1)-O(8)i	75.55(16)	O(7)i-Pb(1)-O(8)i	50.33(14)
N(6)-Pb(1)-O(8) <sup>i</sup>	85.29(15)	O(2)-Pb(1)-O(1)	49.51(18)	N(5)-Pb(1)-O(1)	92.88(19)
O(7)i-Pb(1)-O(1)	140.77(16)	N(6)-Pb(1)-O(1)	78.56(17)	O(8)i-Pb(1)-O(1)	163.07(17)
N(1)-Pb(2)-O(6)	78.85(17)	N(1)-Pb(2)-O(4)	75.34(17)	O(6)-Pb(2)-O(4)	89.96(16)
N(1)-Pb(2)-O(3)	84.92(18)	O(6)-Pb(2)-O(3)	140.59(17)	O(4)-Pb(2)-O(3)	51.03(17)
N(1)-Pb(2)-N(2)	65.44(17)	O(6)-Pb(2)-N(2)	125.69(16)	O(4)-Pb(2)-N(2)	116.66(17)
O(3)-Pb(2)-N(2)	77.00(16)	N(1)-Pb(2)-O(5)	73.75(18)	O(6)-Pb(2)-O(5)	50.11(15)
O(4)-Pb(2)-O(5)	133.15(17)	O(3)-Pb(2)-O(5)	153.81(17)	N(2)-Pb(2)-O(5)	80.34(15)

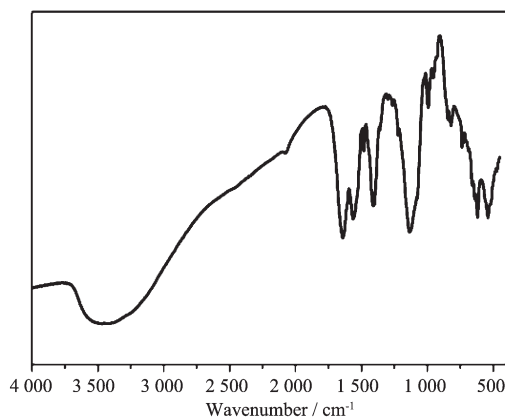
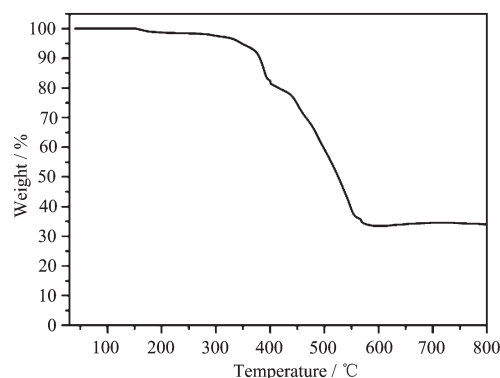
Symmetry code: <sup>i</sup>  $x-2, -y+1/2, z-1/2$ **Table 2** Hydrogen bonds for complex **1** (nm) and angles (°)

D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
N(7)-H(7A)...O(5) <sup>ii</sup>	0.086	0.211	0.2909(8)	154.0
N(3)-H(3A)...O(8) <sup>iii</sup>	0.086	0.207	0.2836(7)	148.5

Symmetry codes: <sup>ii</sup>  $-x+2, -y+1, -z+2$ ; <sup>iii</sup>  $-x+3, y+1/2, -z+5/2$ Symmetry code: (i)  $x-2, 1/2-y, z-1/2$ **Fig.1** View of the coordination environments of Pb(II) atoms in **1** (displacement ellipsoids at the 15% probability level)

Fig.2 View of the one-dimensional chain structure of **1**Fig.3 View of the three-dimensional supramolecular architecture of **1** formed by  $\pi$ - $\pi$  interactions

nitrogen atoms from one L2 ligand, and four carboxylate oxygen atoms from two different L1 anions. The Pb-O distances range from 0.244 9 (5) to 0.268 0 (5) nm, which are comparable to the reported Pb-O distances found in related coordination polymer [Pb(ndc)(ptcp)] $\cdot$ 0.5H<sub>2</sub>O (ndc=1,4-naphthalenedicarboxylate and ptcp=2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta [1]phenanthrene)<sup>[6]</sup>. Each L1 anion coordinates with two Pb(II) atoms in a bis-chelating mode. In this fashion, the L1 anions bridge neighboring Pb (II) atoms to

Fig.4 IR spectrum of the complex **1**Fig.5 TG curve of complex **1**

generate a 1D chain structure (Fig.2). Interestingly, the L2 ligands are attached on both sides of the chain. Moreover, neighboring 1D chains are linked together by  $\pi$ - $\pi$  stackings between the quinoline ring systems [N1/C20-C31 at ( $x, y, z$ ) and N5/C1-C12 ( $1-x, 1-y, 2-z$ )] of the L ligands (centroid-to-centroid distance of ca. 0.354 nm and face-to-face distance of 0.347 nm) among L2 ligands from neighboring chains to yield a fascinating 3D supramolecular architecture (Fig.3). As listed in Table 2, the N-H  $\cdots$  O hydrogen-bonding interactions further consolidate the 3D supramolecular architecture of **1**.

## 2.2 IR analysis

The solid-state IR spectrum of **1** is shown in the region of 4 000~400  $\text{cm}^{-1}$  (Fig.4). The strong peaks at 1 643 and 1 564  $\text{cm}^{-1}$  correspond to the asymmetric and symmetric vibrations of carboxylate groups of the L1. The broad band at 3 471  $\text{cm}^{-1}$  may come from the stretching vibrations of N-H bond of L2 ligand. The C-N and C=N stretching vibrations of L2 ligand are observed at 1 132 and 1 415  $\text{cm}^{-1}$ <sup>[20]</sup>.

## 2.3 Thermogravimetric analysis

In order to characterize the compound more fully in terms of thermal stability, thermogravimetric property of compound **1** was performed. The experiment was conducted under N<sub>2</sub> atmosphere with a heating rate of 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$  from room temperature to 800  $^{\circ}\text{C}$  (Fig.5). The first weight loss in 150~405  $^{\circ}\text{C}$  (Obsd. 17.6%, Calcd. 18.2%) can be attributed to the release of L1 anion. The next weight loss from 405 to 575  $^{\circ}\text{C}$  corresponds to the decomposition of L ligand (Obsd. 48.2%, Calcd. 49.3%).

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