



# Influence of the steric effect of flexible isomeric phenylenediacetic acids on the resultant lead(II) coordination polymers



Yunlong Wu, Yanqing Zhao, Guo-Ping Yang\*, Yanjun Guo, Yao-Yu Wang\*, Qi-Zhen Shi

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, PR China

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## ABSTRACT

To study the steric effect of the flexible dicarboxylate ligands on the resultant formations of coordination polymers (CPs), four new Pb<sup>II</sup> CPs [Pb(1,2-pda)(H<sub>2</sub>O)]<sub>n</sub> (**1**), [Pb(1,3-pda)]<sub>n</sub>·nH<sub>2</sub>O (**2**), [Pb<sub>2</sub>(1,4-pda)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub>·2nH<sub>2</sub>O (**3a** and **3b**) have been produced by the isomeric phenylenediacetic acids (H<sub>2</sub>pda). The X-ray crystallography study reveals that CP **1** is a two-dimensional (2D) 4-connected *sql* (4<sup>4</sup>.6<sup>2</sup>) network via the weak Pb···O interactions built on 1D chain-like structure. CP **2** crystallizes in orthorhombic system with chiral space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, showing a 4-connected *sra* (4<sup>2</sup>.6<sup>3</sup>.8) framework where a left-handed helical motif is formed by Pb<sup>II</sup> ions and *trans*-1,3-pda ligands. More interestingly, CPs **3a** and **3b** are two true 3D polymorphs and have the different morphology. Topologically, the framework of **3a** exhibits a 4-connected *lon* 6<sup>6</sup> motif, while that of **3b** is a (4,6)-connected *fsh* (4<sup>3</sup>.6<sup>3</sup>)<sub>2</sub>(4<sup>6</sup>.6<sup>6</sup>.8<sup>3</sup>) net. It is found that the three isomeric pda anions display the various coordination fashions in four CPs. The different structural arrangements show that the steric effect of the isomeric H<sub>2</sub>pda tectons has a positive role in directing the final products of Pb<sup>II</sup> CPs. Also, the fluorescent properties of the CPs were studied in the solid state at room temperature.

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## 1. Introduction

Over the past decades, the prosperous realm of crystal engineering and supramolecular chemistry has achieved the significant success in producing various coordination polymers (CPs), and their available or potential utilities as functional solids [1]. It is well-known that the various multicarboxylate tectons have been commonly employed as the molecular building blocks (MBBs) to build different kinds of CPs for their excellent coordination abilities and versatile coordination conformations [2]. More importantly, the elaborate modifications of the groups, rigidity/flexibility, length, and symmetry of the ligands maybe produce kinds of solid crystalline CPs. Among them, the isomeric phenylenediacetic acids (H<sub>2</sub>pda) should be the excellent tectons to build new CPs with special properties as well as interesting nets [3]. There are two flexible methylene (–CH<sub>2</sub>–) spacers in the H<sub>2</sub>pda ligands, the carboxylic groups of the ligands can thus bend freely and adopt diverse coordination fashions to meet the coordination requirement of different metal ions in the assembly process. Thereby, the assembly of H<sub>2</sub>pda ligands with different metal centers must be

very appealing to the synthetic chemists and materials scientists in crystal chemistry.

On the other hand, compared with the reported CPs based on the transition metal or rare earth metal ions, the CPs containing Pb<sup>II</sup> ions have been relatively less explored up to date [4]. However, as we all know, the Pb<sup>II</sup> ion is of great importance in some practical fields, such as photovoltaic conversion, electroluminescent devices, and fluorescence etc. [5]. As a heavy *p*-block metal ion, Pb<sup>II</sup> ion may provide a nice opportunity to isolate unusual CPs with proper ligands for its larger ionic radius, flexible coordination environments and variable stereochemical activities. In our previous works, we have mainly focused our attention on the construction of CPs based on the transition metal ions with flexible isomeric H<sub>2</sub>pda ligands [6]. However, the systematic study of the steric effect of H<sub>2</sub>pda tectons on the formations of CPs containing the same center metal ions is not well documented in a separate research work so far. Thus, we herein report on the syntheses, structures, and properties of four CPs by the employment of isomeric H<sub>2</sub>pda ligands with Pb<sup>II</sup> ions, namely [Pb(1,2-pda)(H<sub>2</sub>O)]<sub>n</sub> (**1**), [Pb(1,3-pda)]<sub>n</sub>·nH<sub>2</sub>O (**2**), [Pb<sub>2</sub>(1,4-pda)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub>·2nH<sub>2</sub>O (**3a** and **3b**). It is found that the three isomeric pda anions exhibit the various coordination fashions in four CPs. The different structural motifs show that the steric effect of such flexible H<sub>2</sub>pda ligands has a positive role in governing the final architectures of Pb<sup>II</sup> CPs. In addition, the fluorescent properties of four CPs were also studied in the solid state at room temperature.

\* Corresponding authors.

E-mail addresses: [ygp@nwu.edu.cn](mailto:ygp@nwu.edu.cn) (G.-P. Yang), [yyaoyu@nwu.edu.cn](mailto:yyaoyu@nwu.edu.cn) (Y.-Y. Wang).

## 2. Experimental section

### 2.1. Materials and physical measurements

All the reagents for the synthesis were commercially available and used without further purification. The isomeric phenylenediacetic acids ( $H_2pda$ ) were bought from Alfa Aesar. The FT-IR spectra were recorded with a BRUKER EQUINOX-55 spectrometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Elemental analyses (C and H) were determined with a PE-2400 Elemental analyzer. Thermogravimetric analyses were performed on a NETZSCH STA 449C micro-analyzer in a nitrogen atmosphere at a heating rate of  $10\text{ min}^{-1}$  between ambient temperature and  $650\text{ }^\circ\text{C}$ . Luminescent spectra for the solid samples were recorded with a Hitachi F-4500 fluorescence spectrophotometer at the room temperature.

### 2.2. Preparation of four CPs

**[Pb(1,2-pda)(H<sub>2</sub>O)]<sub>n</sub> (1).** A mixture of  $Pb(OAc)_2 \cdot 3H_2O$  (19.0 mg, 0.05 mmol) and 1,2- $H_2pda$  (9.7 mg, 0.05 mmol) in 15 mL water was adjusted to  $pH=7$  with 0.5 M KOH solution and then sealed in 25 mL Teflon-lined stainless steel autoclaves. The resulting solution was heated to  $160\text{ }^\circ\text{C}$  for 72 h and then cooled to room temperature at a rate of  $0.2\text{ }^\circ\text{C min}^{-1}$  and gave some block colorless crystals. Yield: 51%. Elemental analysis calc. (%) for  $C_{10}H_{10}O_5Pb$  (1): C, 28.78; H, 2.41. Found: C, 28.47; H, 1.61. FT-IR (KBr pellet,  $cm^{-1}$ ): 3449s, 3059w, 3018w, 2909w, 1520s, 1396s, 1310m, 1278m, 1208m, 1175w, 1094w, 1047w, 931w, 872w, 818w, 750m, 708m, 630w, 580w.

**[Pb(1,3-pda)]<sub>n</sub> · nH<sub>2</sub>O (2).** The synthetic procedure was adopted as that of CP 1 except that 1,2- $H_2pda$  ligand was replaced by the isomeric 1,3- $H_2pda$  ligand (9.7 mg, 0.05 mmol). Yield: 46%. Elemental analysis calc. (%) for  $C_{10}H_{10}O_5Pb$  (2): C, 28.78; H, 2.41. Found: C, 29.29; H, 1.73. FT-IR (KBr pellet,  $cm^{-1}$ ): 3444s, 2956m, 2915m, 1613m, 1547s, 1426m, 1398s, 1270m, 1174m, 1086w, 974w, 936m, 807w, 729m, 688w, 625m, 553w.

**[Pb<sub>2</sub>(1,4-pda)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub> · 2nH<sub>2</sub>O (3a, 3b).** The synthetic procedures are similar to those of CPs 1 and 2 except that different reaction temperature. The detailed information has been reported in the recent communication [6c]. Elemental analysis calc. (%) for 3a: C, 28.17; H, 2.60. Found: C, 28.97; H, 2.29. FT-IR (KBr pellet,  $cm^{-1}$ ): 3360s, 1546s, 1389s, 1283m, 1206w, 1157w, 1050w, 942w, 838w, 728m, 708m, 679m, 621m, 522w, 428w. 3b: C, 28.17; H, 2.60. Found: C, 28.46; H, 2.42. FT-IR ( $cm^{-1}$ ): 3386s, 1548s, 1388s, 1282m, 1204m, 1152w, 1019w, 941m, 869w, 768w, 726m, 707m, 618m, 562w, 520w, 425w.

### 2.3. Crystal structure determinations

Single-crystal X-ray diffraction analyses of four CPs were carried out on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated  $MoK\alpha$  radiation ( $\lambda=0.71073\text{ \AA}$ ) by using  $\phi/\omega$  scan technique at  $296(2)\text{ K}$  (for 1, and 2) and  $273(2)\text{ K}$  (for 3a and 3b). The structures were determined by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on  $F^2$  was carried out using SHELXS-97 and SHELXL-97 [7]. Hydrogen atoms of water molecules were located by Fourier map, and then refined by riding mode. CP 2 was refined using twin model with the Flack value of 0.48(4), which may indicate the formation of twinned crystals. During refinement of CP 2, some restraints were applied including distance restraint (DFIX) and thermal restraints (DELU, and SIMU) which have been used in some unreasonable atoms. The crystallographic data and experimental details for the structural analyses

are summarized in Table S1. Selected bond lengths and angles are listed in Table S2 (ESI†). CCDC-1000309 and 1000310 contain the supplementary crystallographic data for CPs 1 and 2.

## 3. Results and discussion

### 3.1. General syntheses

The mixture solution of  $Pb^{II}$  ions and phenylenediacetic acid gave the precipitation quickly *via* the aqueous reaction, which makes the growth of good crystalline materials difficult. In this work, therefore, the one-pot hydrothermal method was adopted for the syntheses of targeted CPs. By designing and carrying out a series of parallel experiments, the reaction temperatures have finally been chosen as depicted in Section 2. It is found that the products are not sensitive to the reaction temperature except that CPs 3a and 3b. The major reason might be attributed to the relatively larger distances of two carboxylate of 1,4-pda ligand, which can participate the coordination with metal ions easily to produce the different CPs.

### 3.2. Description of crystal structures

**[Pb(1,2-pda)(H<sub>2</sub>O)]<sub>n</sub> (1).** Single-crystal X-ray diffraction analysis indicates that CP 1 crystallizes in triclinic  $P\bar{1}$  space group and shows a 1D chain-like structure. The asymmetric building unit of 1 contains one  $Pb^{II}$  center, one 1,2-pda anion and one coordination water molecule. Each  $Pb^{II}$  ion is surrounded by five oxygen atoms, which belong to three different carboxylate groups and one aqua ligand (Fig. 1). The lengths of  $Pb\text{--}O$  bonds are in the range of 2.458 (8)–2.657(8)  $\text{\AA}$ , which are similar to those  $Pb^{II}$ -based CPs involved carboxylate ligands [4].

The 1,2-pda anion in 1 shows the *cis* coordination fashion and acts as a tetradentate ligand, where one carboxylate adopts a chelating bidentate mode, and the other is a bis-monodentate bridging mode (Scheme 1a). Therefore, the *cis*-1,2-pda ligands coordinate with  $Pb^{II}$  ions to result in a 1D chain-like structure, as depicted in Fig. 2. Because of the existence of weak  $Pb \cdots O$  interaction ( $Pb1 \cdots O2^a=2.747\text{ \AA}$ , symmetry codes:  $a: x+1, y, z$ ) between the adjacent 1D chains, an undulating 2D layer is thus formed by the neighboring 1D chains, which displays a binodal *sql* topological framework with short Schläfli symbol of  $(4^4.6^2)$ , as shown in Fig. 3. Lastly, the neighboring layered networks are further assembled into a 3D supramolecular framework *via* the  $\pi \cdots \pi$  stacking interlocks of the two phenyl rings of 1,2-pda ligands, where the distance of the centroid-to-face is ca.  $3.639\text{ \AA}$ .

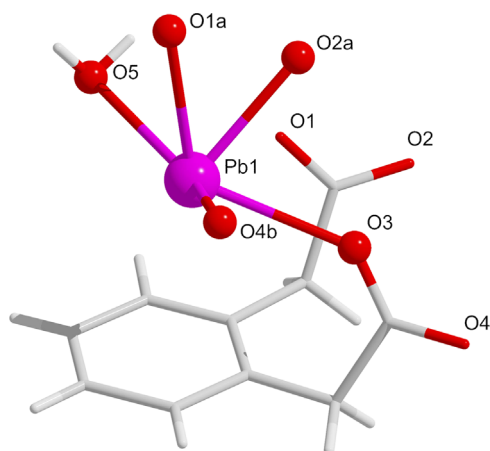


Fig. 1. The coordination environment of  $Pb(II)$  ion in 1. Symmetry codes: a:  $1-x, -y, 1-z$ ; b:  $1-x, 1-y, 1-z$ .

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