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Lead(II) coordination polymers based on rigid-flexible 3,5-bis-oxyacetate-benzoic acid: Structural transition driven by temperature control

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ABSTRACT

Three Pb(II) complexes $\{[Pb_3(BOABA)_2(H_2O)]\cdot H_2O\}_n$ (**1**), $\{[Pb_4(BOABA)_2(\mu_4\text{-}O)(H_2O)_2]\cdot H_2O\}_n$ (**2**), and $[Pb_3(BOABA)_2(H_2O)]_n$ (**3**) (H_3BOABA=3,5-bis-oxyacetate-benzoic acid) were obtained under the same reaction systems with different temperatures. Complexes **1** and **2** are two dimensional (2D) networks based on Pb-BOABA chains and $Pb_4(\mu_4\text{-}O)(COO)_6$ SBUs, respectively. Complex **3** presents an interesting three dimensional (3D) framework, was obtained by increasing the reaction temperature. Structural transition of the crystallization products is largely dependent on the reaction temperature. Moreover, the fluorescence properties of complexes **1**–**3** have been investigated.

1. Introduction

Up to now, as an emerging class of crystalline materials, coordination polymers (CPs) have witnessed the explosive growth owing to their intriguing structures, and potential applications in a wide range of fields [1–3]. Thus, the area of CPs (especially for metal-organic frameworks, MOFs) has become one of the fastest growing fields in chemistry [4]. So far, the majority of work in this area is still focused on the controllable assemblies of CPs, expecting to achieve products with targeted structural features and predesigned functions in the realm of crystalline materials [5]. However, how to rationally control and realize the desirable CPs, and how to interpret the law of self-assembly still remains a realistic and fundamental scientific challenge.

For the self-assembly processes of CPs, two primary topics (the reaction conditions and the synthesis systems) ought to be highly considered. As we all known, if the synthesis system (including metal ion and ligand) is well defined, the reaction condition would play a key role in the formation of the resulting materials. Generally, with regard to the reaction condition, many factors, such as temperature, pH values, solvents, and template agents can affect the formation and topology of CPs bearing the same metal ion and ligand [6]. Among the various reaction conditions, the reaction temperature is one of the most effective ways to synthesize new materials with predictable structural transition and function [7–9]. So the investigation on the reaction condition can help us directly and accurately reveal the relationships between the structure and properties.

In addition, multi-carboxylates have been intensively investigated in the field of CPs with an intriguing variety of topologies and potential applications [10–12]. While, numerous investigations mainly focused on the entirely rigid or flexible multi-carboxylate coordination systems [13–16], very few were performed on mixed rigid-flexible multi-carboxylic acid ligands. As a good tripodal ligand with two highly flexible arms and one rigid carboxyl group, 3,5-bis-oxyacetate-benzoic acid (H_3BOABA), has not been well explored to date [17–22], especially in the presence of Pb(II) as the center ion. Pb(II) complexes, a subfamily of CPs, are excellent candidates as photoluminescence materials because their large ionic radius of lead(II) induces a wide range of coordination numbers and the presence of 6 s^2 outer electrons [23–25]. Hence, we selected H_3BOABA as the primary ligand and adopted the “temperature control” strategy to construct Pb(II) CPs, and three new complexes were obtained. Complexes **1** and **2** feature 2D networks based on different secondary building units (SBUs). Whereas, **3** shows a 3D framework formed by Pb–O–C rods and BOABA ligands.

2. Experimental

2.1. Materials and general methods

All the chemicals used for synthesis were of analytical grade and commercially available. H_3BOABA was synthesized according to the literature [17]. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Thermogravimetric (TG) analysis was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min^{-1}

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from ambient temperature to 800 °C, an empty Al_2O_3 crucible was used as reference. Fluorescent spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

2.2. Synthesis of complexes

$$\{[Pb_3(BOABA)_2(H_2O)]\cdot H_2O\}_n \tag{1}$$

A mixture of $Pb(NO_3)_2$ (0.066 g, 0.2 mmol), H_3BOABA (0.02 g, 0.1 mmol), and NaOH (1.5 mL, 0.2 mol/L) in 10 mL deionized water was sealed in a 25 mL Teflon-lined autoclave and heated to 140 °C for 3 days. After the autoclave was cooled to room temperature at 10 °C h^{-1}, colorless block crystals were collected by filtration, washed with 3×10 mL of deionized water and air-dried. Yield 35% based on H_3BOABA. Anal. Calc. for $C_{22}H_{18}O_{18}Pb_3$: C, 22.17; H, 1.52%. Found: C, 22.14; H, 1.56%. IR (KBr, cm^{-1}): 3345w, 2358 m, 2341 m, 1575 s, 1515 s, 1406 s, 1370 s, 1301 m, 1162 s, 1069 s, 785 s, 720 m, 676w.

$$\{[Pb_4(BOABA)_2(\mu_4{-}O)(H_2O)_2]\cdot H_2O\}_n \tag{2}$$

This complex was synthesized by a procedure similar to that of **1** except that the temperature was 160 °C. Yield 42% based on H_3BOABA. Anal. Calc. for $C_{22}H_{20}O_{20}Pb_4$: C, 18.44; H, 1.41%. Found: C, 18.41; H, 1.43%. IR (KBr, cm^{-1}): 3327w, 2358 s, 2336 m, 1598 s, 1532 s, 1384 s, 1336 s, 1169 s, 1070 m, 778 s, 721 m, 673w.

$$[Pb_3(BOABA)_2(H_2O)]_n \tag{3}$$

This complex was synthesized by a procedure similar to that of **1** except that the temperature was 180 °C. Yield 26% based on H_3BOABA. Anal. Calc. for $C_{22}H_{16}O_{17}Pb_3$: C, 22.51; H, 1.37%. Found: C, 22.49; H, 1.40%. IR (KBr, cm^{-1}): 3324w, 2361 s, 2334 m, 1563 s, 1536 s, 1381 s, 1332 s, 1163 s, 1075 m, 773 s, 724 m, 677w.

2.3. X-ray crystallography

X-ray single-crystal diffraction data of all complexes were collected on a Rigaku SCX-mini diffractometer with graphite monochromatic Mo-Kα radiation (λ=0.71073 Å). The program Crystal Clear was used for integration of the diffraction profiles [26]. An empirical absorption correction was applied using the SADABS program [27]. All structures were solved by direct methods using the SHELXS program of the SHELXTL package [28] and refined by full-matrix least-squares methods with SHELXL [29]. Metal atoms were located from the *E*-maps and other non-hydrogen atoms excluded in conterions were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The H atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The diffuse electron densities resulting from these residual solvent molecules of complex 2 were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated [30]. All the crystal data and structure refinement details for three complexes are given in Table 1. The data of relevant bond distances and angles are listed in Table S1. CCDC 1501256 (1), 1501257 (2) and 1501258 (3).

3. Results and discussion

3.1. Description of the crystal structures

$$\{[Pb_3(BOABA)_2(H_2O)]\cdot H_2O\}_n \tag{1}$$

Single-crystal X-ray analysis indicates that complex **1** crystallizes in space group P$\bar{1}$ (see Table 1). The selected bond lengths and angles are summarized in Table S1, (Supporting information, SI). Complex **1** reveals a 2D layer structure based on the Pb-BOABA secondary building units (SBUs). There are three crystallographically independent Pb(II) ions assuming different coordination geometry. As shown in Fig. 1, Pb(1) ion is hexa-coordinated by six oxygen atoms belonging to BOABA ligands (Pb–O 2.417(11)–2.765(11) Å). The Pb(2) ion is also hexa-coordinated, whereby five oxygen atoms from BOABA ligands, one oxygen atom from one water molecule (Pb–O 2.308(11)–2.815(11) Å). The Pb(3) ion sits in an irregular penta-coordinated environment accomplished by five oxygen atoms from three separated BOABA ligands with the Pb–O bond lengths ranging from 2.372(12) to 2.771(11) Å. All three Pb(II) ions are in hemidirected coordination spheres. In **1**, all BOABA ligands adopt μ_5-η^1:η^2:η^1:η^1:η^1:η^2 and μ_5-η^1:η^1:η^1:η^1:η^1:η^2 coordination modes (Scheme 1a and b). Pairs of BOABA ligands acts as a hexa-connector to link the neighboring Pb(II) ions to form a 1D chain substructure (Fig. 2a). Furthermore, these 1D chains are interconnected by BOABA ligands to afford a 2D network (Fig. 2b).

Table 1
Crystal data and structure refinement summary for complexes.

Complex	1	2	3
Formula	$C_{22}H_{18}O_{18}Pb_3$	$C_{22}H_{20}O_{20}Pb_4$	$C_{22}H_{16}O_{17}Pb_3$
Fw	1191.93	1433.14	1173.92
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
crystal size/mm	0.32×0.30×0.28	0.35×0.33×0.29	0.31×0.29×0.27
a [Å]	10.235 (2)	8.9756 (18)	9.1255 (18)
b [Å]	11.354 (2)	11.556 (2)	11.542 (2)
c [Å]	12.597 (3)	15.721 (3)	23.556 (5)
α [°]	88.53 (3)	100.02 (3)	90
β [°]	74.14 (3)	102.77(3)	97.81 (3)
γ [°]	67.91 (3)	97.23 (3)	90
V ($Å^3$)	1299.9 (5)	1542.9 (5)	2458.1 (8)
Z	2	2	4
$D_{calcd}/mg\cdot m^{-3}$	3.045	3.085	3.172
F(000)	1080	1280	2120
Reflections collected/ unique	11361/4576	13345/5416	24578/5362
θ range/◦	3.14–25.00	3.00–25.00	3.03–27.00
μ/mm^{-1}	19.471	21.844	20.588
R/wR [$I > 2\sigma(I)$][a]	0.0560/0.1393	0.0567/0.1019	0.0487/0.0668
R indices (all data)	0.0806/0.1550	0.0956/0.1121	0.0746/0.0724
GOF on F^2	0.926	0.864	0.993
completeness	99.7%	99.6%	99.8%

[a] $R=\Sigma(||F_0| - |F_C||)/\Sigma|F_0| wR_2=[\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$

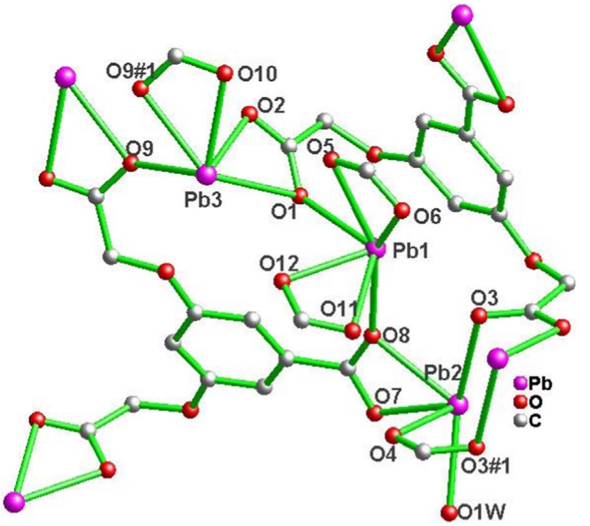

Fig. 1. The coordination environment of Pb(II) in complex **1**, Hydrogen atoms and the disordered solvent molecules have been omitted for clarity (similarly hereafter). #1: −x +1,−y+1,−z+1

$$\{[Pb_4(BOABA)_2(\mu_4{-}O)(H_2O)_2]\cdot H_2O\}_n \tag{2}$$

Complex **2** also crystallizes in the triclinic space group P$\bar{1}$, and the