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Zinc(II) and lead(II) metal-organic networks driven by a multifunctional pyridine-carboxylate building block: Hydrothermal synthesis, structural and topological features, and luminescence properties

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ABSTRACT

4-(5-Carboxypyridin-2-yl)isophthalic acid (H_3L) was applied as a flexible, multifunctional *N*,*O*-building block for the hydrothermal self-assembly synthesis of two novel coordination compounds, namely 2D $[Zn(\mu_3\text{-}HL)(H_2O)]_n \cdot nH_2O$ (**1**) and 3D $[Pb_2(\mu_5\text{-}HL)(\mu_6\text{-}HL)]_n$ (**2**) coordination polymers (CPs). These compounds were obtained in aqueous medium from a mixture containing zinc(II) or lead(II) nitrate, H_3L, and sodium hydroxide. The products were isolated as stable crystalline solids and were characterized by IR spectroscopy, elemental, thermogravimetric (TGA), powder (PXRD) and single-crystal X-ray diffraction analyses. Compound **1** possesses a 2D metal-organic layer with the **fes** topology, which is further extended into a 3D supramolecular framework via hydrogen bonds. In contrast, compound **2** features a very complex network structure, which was topologically classified as a binodal 5,6-connected net with the unique topology defined by the point symbol of $(4^7.6^3)(4^9.6^6)$. Compounds **1** and **2** disclose an intense blue or green luminescent emission at room temperature.

1. Introduction

The design of novel coordination polymers (CPs) or metal-organic frameworks (MOFs) has seen a tremendous development in last decade, owing to unusual structural features and notable functional properties of such materials [1–9]. Although many factors can influence the structural characteristics and properties of metal-organic networks, a particular research direction concerns the search for new multifunctional organic building blocks and their use toward the generation of CPs or MOFs [10–15]. In this regard, diverse multicarboxylic acids containing both pyridine and additional aromatic carboxylate functionalities are especially attractive multifunctional building blocks in self-assembling intricate metal-organic networks [16–20]. This is primarily governed by their ability to adopt a large diversity of coordination modes depending on the reaction pH and degree of deprotonation, to show high thermal stability in the course of hydrothermal reactions, and to participate in strong H-bonding and weak supramolecular interactions thus allowing an additional stabilization of coordination networks [16,21–24].

Aiming at further exploring various pyridine-carboxylate building blocks for the hydrothermal self-assembly generation of CPs [16,23,25], we focused on 4-(5-carboxypyridin-2-yl)isophthalic acid (H_3L) as a multifunctional ligand, based on the following considerations. First, H_3L can be an excellent spacer for the construction of CPs due to the presence of pyridyl N and different carboxylate O binding sites, variable degree of deprotonation of COOH groups, and flexible conformation wherein both aromatic

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rings can rotate around the C–C bond. Second, H_3L has been almost unexplored in coordination chemistry as attested by a search of the Cambridge Structural Database [26], which only revealed a very limited number of compounds [16]. Hence, we report herein the self-assembly synthesis, full characterization, crystal structures, topological classification, thermal stability, and luminescent properties of two novel metal-organic networks, $[Zn(\mu_3\text{-}HL)(H_2O)]_n\cdot nH_2O$ (**1**) and $[Pb_2(\mu_5\text{-}HL)(\mu_6\text{-}HL)]_n$ (**2**), derived from H_3L.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were of A.R. grade and used without further purification. 4-(5-Carboxypyridin-2-yl)isophthalic acid (H_3L) was prepared according to a published procedure [14]. Elemental (C, H, N) analyses were performed on an Elementar Vario EL elemental analyzer. IR spectra were recorded in KBr pellets on a Bruker EQUINOX 55 spectrometer. UV/Vis absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under N_2 atmosphere with a heating rate of 10 °C/min on a LINSEIS STA PT1600 thermal analyzer. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-$K\alpha$ radiation ($\lambda = 1.54060$ Å), in which the X-ray tube was operated at 40 kV and 40 mA. Excitation and emission spectra of solid samples were recorded at room temperature on an Edinburgh FLS920 fluorescence spectrometer.

2.2. Synthesis of $[Zn(\mu_3\text{-}HL)(H_2O)]_n\cdot nH_2O$ (**1**)

$Zn(NO_3)_2\cdot 6H_2O$ (0.089 g, 0.30 mmol), H_3L (0.073 g, 0.30 mmol), and NaOH (0.024 g 0.60 mmol) were mixed in H_2O (10 mL) with continuous stirring at room temperature for 15 min (the pH value of the obtained reaction mixture was ~5.0), and then sealed in a 25 mL Teflon-lined stainless steel vessel. This was heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Colorless block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 75.4 mg, 65% based on zinc(II) nitrate. Anal. Calcd (%) for $C_{14}H_{11}ZnNO_8$: C, 43.49; H, 2.87; N, 3.62. Found, C, 43.69; H, 2.89; N, 3.58. IR (KBr, cm^{-1}): 3466 (m), 3060 (w), 1704 (s), 1624 (s), 1594 (w), 1560 (m), 1508 (w), 1430 (s), 1348 (s), 1306 (m), 1272 (w), 1244 (w), 1170 (w), 1140 (w), 1106 (w), 1060 (m), 1026 (m), 962 (m), 870 (m), 849 (w), 790 (m), 776 (m), 710 (m), 664 (w), 501 (w).

2.3. Synthesis of $[Pb_2(\mu_5\text{-}HL)(\mu_6\text{-}HL)]_n$ (**2**)

This product was synthesized in the similar way as that described for **1**, except that $Zn(NO_3)_2\cdot 6H_2O$ was replaced by $Pb(NO_3)_2$ (0.30 mmol, 99.4 mg); the pH value of the reaction mixture before hydrothermal synthesis was ~5.0. Colorless block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 177.3 mg, 60% based on lead(II) nitrate. Anal. Calcd (%) (%) for $C_{28}H_{14}Pb_2N_2O_{12}$: C, 34.15; H, 1.43; N, 2.84. Found: C, 34.37; H, 1.45; N, 2.82. IR (KBr, cm^{-1}): 1658 (m), 1594 (m), 1560 (s), 1416 (m), 1278 (w), 1226 (w), 1176 (w), 1146 (w), 1042 (w), 854 (w), 824 (w), 796 (w), 778 (w), 750 (w), 728 (m), 636 (w), 526 (w).

2.4. Crystallography

The single-crystal data for compounds **1** and **2** were collected at 293(2) K on an Bruker APEX-II CCD diffractometer with Cu-Kα radiation ($\lambda = 1.54184$ Å). The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (except for those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations at the final stage of full-matrix least-squares refinement. The hydrogen atoms of the water molecules were located by difference maps and constrained to ride on their parent O atoms. All calculations were performed using the SHELXTL-97 system [27]. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table S1, whereas hydrogen bonds are given in Table S2 (supplementary information).

3. Results and discussion

3.1. Hydrothermal self-assembly synthesis

Compounds **1** and **2** were synthesized by hydrothermal self-assembly reactions under the same reaction conditions (160 °C, 3 days, Scheme 1), except for the type of metal nitrate used [$Zn(NO_3)_2\cdot 6H_2O$ for **1** and $Pb(NO_3)_2$ for **2**]. The structural differences of the obtained products indicate that the assembly process is metal ion-dependent, thus resulting in a 2D metal-organic layer structure in **1** and a 3D metal-organic network in **2**. Both compounds were isolated as stable crystalline solids and were characterized by standard methods, namely by elemental analysis, IR spectroscopy, thermogravimetric analysis, single crystal and powder X-ray diffraction (PXRD) analyses. In the IR spectra of HL^{2-}, the absorption bands at 1704 and 1658 cm^{-1} are attributed to the asymmetric stretching vibration of uncoordinated carboxylic groups in **1** and **2**. The asymmetric stretching and symmetric stretching bands of the coordinated carboxylate groups appear at 1624, 1348 cm^{-1} and 1594, 1416 cm^{-1} for **1** and **2**, respectively. The middle and broad peak at 3466 cm^{-1} can be assigned as the characteristic peak of the ν_{O-H} vibration of the lattice and coordinated water molecules in **1**. In fact, the PXRD patterns for the as-synthesized bulk samples of **1** and **2** are in good agreement with the simulated ones from the single crystal X-ray diffraction data (Figs. S1 and S2, supplementary information), thus confirming the phase purity of the obtained materials.

3.2. Crystal structure of compound **1**

The crystal structure of **1** is composed of one Zn(II) atom, one μ_3-HL^{2-} block, one coordinated and one lattice H_2O molecules per formula unit (Fig. 1a). The Zn1 center is five-coordinated and possesses a distorted square-pyramidal $\{ZnNO_4\}$ environment, filled by three O and one N atoms from the three different μ_3-HL^{2-} spacers, and one O atom from the coordinated H_2O molecule. The Zn–O [1.9827(15)–2.4131(19) Å] and Zn–N [2.0402(17) Å] bond distances are in good agreement with those observed in some related Zn(II) compounds [16,28–30]. Although one of the Zn–O 2.4131(19) Å distances is somewhat elongated, it is still well below the sum of the van der Waals radii for Zn and O atoms [2.90 Å]. In **1**, the HL^{2-} block acts as a *N*,O_2-ligand and exhibits a μ_3-coordination mode (Scheme 2, mode I), in which the two deprotonated carboxylate groups show the η^1:η^0 monodentate and η^1:η^1 bidentate modes. The dihedral angle between the pyridyl and phenyl rings in the μ_3-HL^{2-} ligand is 69.28°. The μ_3-HL^{2-} spacers alternately link the adjacent Zn(II) centers to form a 2D metal-organic sheet (Fig. 1b). It should be mentioned that only one Zn(II) derivative bearing L^{3-} ligand was reported before [16], namely $[Zn_2(\mu_4\text{-}L)(\mu_2\text{-}bpdc)_{0.5}(py)_2]_n$ {H_2bpdc = 4,4′-biphenyldicarboxylic acid, py = pyridine}. In contrast to **1**, this mixed-ligand 3D coordination polymer shows two types of Zn(II) atoms, namely five- and six-