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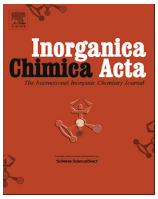

Note

Two metal–organic coordination polymers assembled from a flexible iodo-dicarboxylate ligand and N-donor ancillary ligands

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ABSTRACT

Two metal–organic coordination polymers, namely, $\{[Zn(L)(4,4'\text{-bpy})_{1.5}(H_2O)]\cdot H_2O\}_n$ (**1**) and $[Zn(L)(bpe)]_n$ (**2**), have been hydrothermally synthesized through the reaction of 5-iodo-benzene-1,3-dioxyacetic acid (H_2L) with divalent zinc salts in the presence of ancillary nitrogen ligands (4,4′-bpy = 4,4′-bipyridine, bpe = 1,2-bis(4-pyridyl)ethylene) and structurally characterized by elemental analysis, IR and X-ray diffraction. Complex **1** shows a metal–organic chain structure, the adjacent chains are further linked by hydrogen bonds and C—I···O halogen bonding to form a 3D supramolecular structure. Compound **2** contains interesting threefold parallel interpenetrated two-dimensional (2D) → two-dimensional (2D) network motifs which are united together to yield a 3D supramolecular structure through inter-layer C—H···O interactions. In addition, thermal analysis and photoluminescent properties of the complexes have also been investigated.

1. Introduction

The rational design and construction of coordination frameworks have been rapid developed in the last decades stemming from their intriguing structural motifs as well as their potential applications in catalysis, nonlinear optics (NLO), magnetism, ion exchange, crystal plasticity, adsorption, luminescence, and nanomaterials [1–5]. A variety of coordination frameworks with fascinating structures have been successfully synthesized in the self-assembly of organic building blocks and metal ions [6–11]. As we all know, the aromatic multicarboxylate ligands are good candidates in the assembly of multi-dimensional coordination polymers due to their abundant coordination modes to metal ions [12–20]. The exploration of a new kind of multi-topic ligands containing certain features like flexibility and different functional groups have recently attracted considerable attention. In our latest works, a series of coordination polymers based on 5-iodo-isophthalic acid and ancillary nitrogen ligands have been synthesized, in which 1D or 2D structures are expanded to 3D supramolecular architectures through I-related and other supramolecular interactions [21]. Compared to rigid ligands, flexible ones can adopt additional different conformations and geometrical freedom to meet the requirements of assembly process, which facilitate the formation of more interesting topological structures [22,23]. As a continuation of our studies, we designed a flexible iodo-dicarboxylate ligand, 5-iodo-benzene-1,3-dioxyacetic acid (H_2L), in which one iodine atom and two carbomethoxy groups are located in the meta position of the benzene ring. Owing to the nonlinear flexibility around etheric oxygen and the distortion between the aromatic ring and the carboxylate groups, a variety of coordination modes and conformations for the ligand should be expected. In addition, the iodine atom has potentially capability of partaking in oxygen (or nitrogen)···I halogen bonding and related I···π and I···I interactions to result in remarkably different 3D supramolecular structures.

Here, we report two metal coordination polymers, $\{[Zn(L)(4,4'\text{-bpy})_{1.5}(H_2O)]\cdot H_2O\}_n$ (**1**) and $[Zn(L)(bpe)]_n$ (**2**), assembled from 5-iodo-benzene-1,3-dioxyacetic acid (H_2L) ligand in the presence of the auxiliary N-containing ligands 4,4′-bpy or bpe. Their photoluminescent properties were studied as well. To the best of our knowledge, this is the first time to report the metal–organic frameworks constructed from 5-iodo-benzene-1,3-dioxyacetic acid.

2. Experimental

2.1. Materials and general procedures

The ligand 5-iodo-benzene-1,3-dioxyacetic acid (H_2L) was synthesized according to the literature [24,25]. All other starting materials were of analytical grade and obtained from commercial sources without further purification.

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2.2. Synthesis

*2.2. 1. {[Zn(L)(4,4′-bpy)$_{1.5}$(H$_2$O)]·H$_2$O}$_n$ (**1**)*

A mixture of H_2L (0.0176 g, 0.05 mmol), 4,4′-bipyridine (0.0078 g, 0.05 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.0149 g, 0.05 mmol), and NaOH (0.0040 g, 0.1 mmol) in distilled water (7 mL) was placed in a Teflon-lined stainless steel container, heated to 130 °C for 3 days, and then cooled to room temperature. Colorless prism crystals of **1** were obtained in 68% yield based on zinc. *Anal.* Calc. for $C_{25}H_{23}IN_3O_8Zn$ (685.73): C, 43.79; H, 3.38; N, 6.13. Found: C, 43.65; H, 3.32; N, 6.07%. IR/cm^{-1} (KBr): 3430 (s), 1610 (vs), 1589 (vs), 1419 (s), 1403 (s), 1270 (m), 1164 (s), 1064 (m), 832 (w), 813(w), 554(w).

*2.2.2. [Zn(L)(bpe)]$_n$ (**2**)*

Compound **2** can be obtained following the same synthetic procedures as that of **1** except using 1,2-bis(4-pyridyl)ethane (bpe) (0.0091 g, 0.05 mmol) instead of 4,4′-bipyridine as the starting material, and the colorless block single crystals were collected in 81% yield based on zinc. *Anal.* Calc. for $C_{22}H_{17}IN_2O_6Zn$ (597.65): C, 44.21; H, 2.87; N, 4.69. Found: C, 44.30; H, 2.81; N, 4.62%. IR/cm^{-1} (KBr): 3062 (w), 2931 (w), 1612 (s), 1567 (m), 1403 (s), 1303 (m), 1260 (w), 1164(s), 1051 (m), 1028 (m), 835 (s), 804 (m), 720 (w), 553 (s).

2.3. Physical measurements

Elemental analysis for C, H, and N were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm^{-1} on a Bruker VECTOR 22 spectrometer. Thermal analyses were performed on a SDT 2960 thermal analyzer from room temperature to 800 °C at a heating rate of 20 °C/min under nitrogen flow. Powder X-ray diffraction (PXRD) for compounds **1–7** were measured at 293 K on a Rigaku D/max-3B diffractometer (Cu Kα, λ = 1.5406 Å). The crushed single crystalline powder samples were prepared by crushing the crystals and scanned from 5 to 50 °C with a step of 0.1°/s. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

3. Results and discussion

3.1. Crystal structure

*3.1.1. {[Zn(L)(4,4′-bpy)$_{1.5}$(H$_2$O)]·H$_2$O}$_n$ (**1**)*

X-ray crystallographic analysis revealed that both complexes 1 and 2 crystallized in triclinic space group $P\bar{1}$.[1] The asymmetric unit of **1** contains one crystallographically independent Zn(II) atom, one L^{2-} anion, one and a half bpy ligands, one coordinated and one solvent water molecules. Each metal atom is six-coordinated by three carboxylate oxygen atoms from two L^{2-} anions, one oxygen atom from water molecule and two nitrogen atoms from two bpy ligands, and displays distorted octahedral geometry (Fig. 1a). N3, O1, O2 and O3A atoms comprise the equatorial plane, while N1 and O1W occupy the axial positions. The Zn–O/N bond distances are in the range of 2.019–2.264 Å. The whole ligand acts as a μ_2-bridge linking two Zn1 atoms *via* one chelating and one monodentate carboxylate groups, while the etheric oxygen atoms do not take part in the coordination. Two Zn(II) ions are connected by two L^{2-} ligands to generate a rectangular 24-membered macrocycle with dimensions of *ca.* 7.715 × 6.382 Å (Fig. 1b).

The bpy ligands adopt two kinds of coordination mode. One acts as a bidentate ligand linking two Zn(II) atoms from two macrocycles to form a 1D ribbon; the other one acts as monodentate ligand hanging from the ribbon with only one terminal N atom binding Zn(II) atom, just like outstretched arms, as shown in Fig. 1c. The other N end of the monodentate bpy ligand is connected with O2W through hydrogen bond [26–28] (O2W–N2a, 2.876(8) Å). The free water molecule O2W serves not only as donor but also as acceptor, whereas the coordination water molecule O1W serves only as donor in the interactions (Table 1). The 1D infinite ribbons are expanded to 2D layer through O(2W)–H(2WB)···N(2)a and O(1W)–H(1WB)···O(2W)b hydrogen bonds, as shown in Fig. 1d. In addition, the weak inter-chain $\pi\cdots\pi$ interactions [29,30] between the adjacent pyridine rings can contribute to the stability of the layer. The ring normal and the vector between the ring centroids form an angle of about 31° up to centroid–centroid distances of 4.323 Å [31]. It is noteworthy that the distance of the nearest O and I atoms is only 3.121 Å, which is shorter than the sum of the van der Waals radii of the two atoms (*ca.* 3.50 Å) [32], indicating the existence of O···I halogen bonding. Then the supramolecular layers are connected into a 3D supramolecular structure through the inter-layer O···I interactions (Fig. 1d).

*3.1.2. [Zn(L)(bpe)]$_n$ (**2**)*

As shown in Fig. 2a, compound **2** consists of one kind of Zn(II) ion, one kind of L^{2-} anion, and two kinds of bpe ligands. At first glance, metal center takes a tetrahedral geometry: two oxygen atoms from two L^{2-} ligands and two nitrogen atoms from two different kinds of bpe ligands. However, the distance of 2.641 Å between Zn1 and O1 suggests there are non-negligible interactions. Thus, the Zn1 center can be regarded as a distorted trigonal bipyramid geometry. The L^{2-} ligand links two Zn atoms with one carboxylate group in monodentate fashion and the other one in chelating fashion to form an infinite chain in which the Zn···Zn distance is 13.318 Å. Adjacent chains are bridged by the two kinds of μ_2-bpe ligands in *ABAB* mode with the Zn···Zn distance being 13.378 Å and 13.399 Å, respectively, to give a 2D net with (4,4) topology, in which metal atoms at each corner and the L^{2-} and bpe ligands at each edge, respectively (Fig. 2b). The two pyridyl rings of the same ligand are in the same plane, and the dihedral angle between the planes of the two kinds of the bpe ligand is 36.6°. In addition, the distance between the iodine atom and the adjacent ethylene group is 3.804 Å, indicating exist of the weak I···π interactions [33,34], which can contribute to the stabilization of the layer. It should be noticed that the layer is not complanate but quite corrugated, which allows other two equivalent nets to fill the voids *via* mutual interpenetration leading to the formation of an unusual threefold interpenetrated two-dimensional (2D) → two-dimensional (2D) sheet, as depicted in Fig. 2c. Generally speaking, 3D interpenetrated nets can be more easily constructed than 2D and 1D ones and twofold interpenetrations are common. Such threefold 2D interpenetrating network is still rare. Additionally, the C18–H18···O1e (Fig. 2e, Table 1) interactions are observed between adjacent sheets, which result in a 3D supramolecular structure of 3-fold interpenetration [35,36].

According to the above structural description of the two coordination polymers, there are two different conformations of the L^{2-} ligand (Fig. 3). Due to the presence of the $-OCH_2-$ groups between the aromatic ring and the carboxylate groups, the whole ligand is more flexible than rigid ligands. Upon the ligand being coordinated as a bridge, its freedom to rotate around the etheric oxygen atom is restrained and the ligand can be locked in a twisted conformation.

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[1] Crystallographic data for **1** ($C_{25}H_{23}IN_3O_8Zn$): Mr = 685.73, space group $P\bar{1}$, a = 7.5071(15) Å, b = 13.077(3) Å, c = 13.528(3) Å, α = 83.00(3)°, β = 88.99(3)°, γ = 82.75(3)°, V = 1307.6(5) Å^3, Z = 2, ρ = 1.742 g cm^{-3}, μ = 2.174 mm^{-1}, T = 296(2) K, reflections collected: 12151, independent reflections: 4569, S = 1.063, R_1 = 0.0479, wR_2 = 0.1126. Crystallographic data for **2** ($C_{22}H_{17}IN_2O_6Zn$): Mr = 597.65, space group $P\bar{1}$, a = 8.0493(2) Å, b = 10.738(3) Å, c = 13.318(3) Å, α = 76.78(3)°, β = 74.11(3)°, γ = 83.85(3)°, V = 1076.6(4) Å^3, Z = 2, ρ = 1.844 g cm^{-3}, μ = 2.617 mm^{-1}, T = 296(2) K, reflections collected: 10870, independent reflections: 3787, S = 1.062, R_1 = 0.0380, wR_2 = 0.0694.