Inorganic Chemistry Communications xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Three novel bismuth-based coordination polymers: Synthesis, structure and luminescent properties

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ARTICLE INFO

Article history:
Received 16 May 2017
Received in revised form 8 June 2017
Accepted 10 June 2017
Available online xxxx

Keywords:
Coordination polymer
Bismuth
Luminescence
Fluorescence quenching
Nitro explosives

ABSTRACT

Three novel bismuth-based coordination polymers, $[(CH_3)_2NH_2][Bi(pdc)(bdc)]\cdot 2DMF$, $[(CH_3)_2NH_2][Bi(tdc)_2]\cdot 1.5DMF$ and $[Bi(bpdc)_2H_2O]\cdot xGuest$ (compounds **1**–**3**) (H_2pdc = 3,5-pyridinedicarboxylic acid, H_2bdc = 1,4-benzenedicarboxylic acid, H_2tdc = 2,5-thiophenedicarboxylic acid, H_2bpdc = 4,4′-biphenyldicarboxylic acid), have been successfully synthesized under solvothermal conditions and characterized by single crystal X-ray diffraction. Compounds **1** and **2**, which are constructed by 9-coordinated or 8-coordinated Bi^{3+}, feature three-dimensional structures with *hms* and *dia* topology, respectively. However, 5-coordinated Bi^{3+} based compound **3** is a two-dimensional layered structure. Compound **1** can tune emissive performance by doping different lanthanide ions Tb^{3+}, Eu^{3+} and Dy^{3+}. Furthermore, detection of nitro explosives is investigated. All of the compounds are characterized by elemental analysis, IR spectrum and thermogravimetric analysis.

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), which consist of metal ions and organic ligands, have received much attention during recent years due to their various architectures [1], tunable pore size [2] and attractive properties [3]. However, most of the works are mainly focused on transition metals which are usually 4-coordinated or 6-coordinated or lanthanides due to their unique properties in fluorescence and catalysis, while MOFs constructed by main group metals, such as Bi^{3+}, which possess a lone pair of electrons, are rarely reported [4].

Due to its geometrically flexible coordination environments, the Bi^{3+} ion can be regarded as a novel node in the construction of MOFs. From the viewpoint of coordination angle, the presence of the lone pair of electrons affects the coordination angle of bismuth, so that the polyhedral of Bi^{3+} ion is generally distorted, which is different from common octahedron and tetrahedron and so on [5]. From the perspective of coordination number, Bi^{3+} ion commonly has a variety of coordination numbers (as shown in Table S1), which leads to unpredictability and diversity of bismuth-based structures. For example, Norbert Stock and co-workers reported an 8-coordinated bismuth-based MOF constructed from simple building units, it reveals unprecedented topological complexity with only one unique node [6].

Moreover, bismuth-based MOFs always exhibit noticeable optical and catalytic properties. Some of them can be treated as lanthanide hosts to tune the emissive performance by doping different lanthanide ions into the structures due to similar radius, charges and coordination numbers [7]. In addition, porous Bi-containing MOFs with fluorescent properties can be used for fluorescence-based detection.

In light of the above, in order to study the effect of coordination configuration of bismuth on the structure and their luminescent properties, we choose four simple organic ligands with higher symmetry, 3,5-pyridinedicarboxylic acid (H_2pdc), 1,4-benzenedicarboxylic acid (H_2bdc), 2,5-thiophenedicarboxylic acid (H_2tdc) and 4,4′-biphenyldicarboxylic acid (H_2bpdc), to construct novel bismuth-based coordination polymers. Herein, three novel bismuth coordination polymers have been synthesized and structurally characterized [8]. We further explore the luminescent properties of compound **1** as lanthanide host and effective detection of nitro explosive.

Compound **1** is synthesized by $Bi(NO_3)_2\cdot 5H_2O$, H_2pdc and H_2bdc under solvothermal conditions at 105 °C [9]. Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in hexagonal system with *P*-62*m* space group and features a three-dimensional (3D) structure composed of H_2pdc and H_2bdc mixed ligands. Powder X-ray diffraction (PXRD) pattern of compound **1** confirms high purity of the synthesized samples (Fig. S1a). As shown in Fig. 1a, each Bi^{3+} ion is nine-coordinated with one nitrogen atom from pdc^{2-} anion and eight oxygen atoms from four carboxylic acid groups, to form a distorted hexahedron geometry. The Bi—O and Bi—N distances are in the range of 2.354–2.740 Å, which are similar to the reported results. Fig. 1a clearly shows the process of construction of 3D structure by using mixed ligand strategy. Each pdc^{2-} anion connects three Bi^{3+} ions through two carboxylic acid

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http://dx.doi.org/10.1016/j.inoche.2017.06.018
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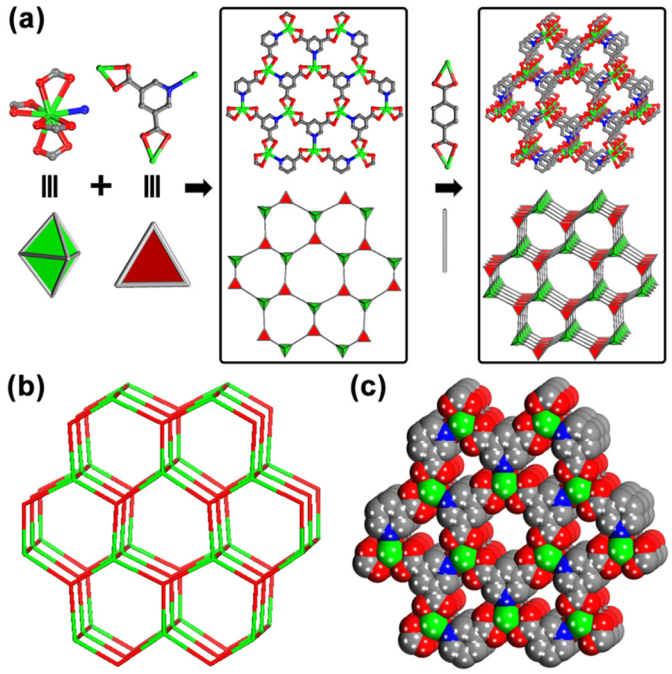

Fig. 1. Description of the structures of compound **1**: (a) the formation of a 3D framework by mixed ligands strategy; (b) the (3, 5) connected *hms* topology; (c) the 1D channels along [001] direction. Color code: carbon: gray; nitrogen: blue; oxygen: red; bismuth: green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

groups and one nitrogen atom, generating a two-dimensional (2D) honeycomb layer. The 2D layer is further connected by bdc^{2-} ligand to form a 3D framework. From a topological point of view, the Bi^{3+} can be regarded as a 5-connected node, pdc^{2-} ligand can be regarded as a 3-connected node and bdc^{2-} ligand can be regarded as a 2-connected node, compound **1** adopts (3, 5) connected *hms* topology (Fig. 1b). Compound **1** possesses two types of channels with diameters of 2.5 and 4.5 Å excluding the van der Waals radius, respectively (Fig. 1c).

Compound **2** is synthesized by the solvothermal reaction of $Bi(NO_3)_3 \cdot 5H_2O$ with H_2tdc in the mixture of dimethylformamide (DMF) and methanol [10]. Single crystal X-ray diffraction analysis reveals that it crystallizes in monoclinic system with *C*2/*c* space group. The purity of compound **2** is confirmed by PXRD patterns (Fig. S1b). The Bi^{3+} ion is eight-coordinated with eight oxygen atoms from four tdc^{2-} ligands respectively. The Bi—O distances are in the range of 2.243–2.700 Å, these bond parameters are close to those in other reported complexes. To better understand the structure of compound **2**, the Bi^{3+} ion can be regarded as a 4-connected node, tdc^{2-} ligand can be regarded as a 2-connected node (Fig. 2a), therefore, the framework of compound **2** can be described as a 2-fold interpenetrated *dia* topology (Fig. 2c). There are two kinds of channels in the structure of compound **2**, the size of the channels are about 5 × 6 and 6 × 6 Å excluding the van der Waals radius, respectively (Fig. 2d and e).

Compound **3** is synthesized by $Bi(NO_3)_2 \cdot 5H_2O$ and H_2bpdc under solvothermal conditions at 85 °C [11]. Single crystal X-ray diffraction analysis reveals that compound **3** crystallizes in tetragonal system, space group *P*4/*nmm* with a 2D framework. The agreement between the as-synthesized and simulated PXRD patterns indicates the phase purity of the product (Fig. S1c). Different from compounds **1** and **2**, each Bi^{3+} ion in compound **3** connects four $bpdc^{2-}$ anions through carboxylic acid groups and one solvent molecule in the axial direction (Fig. 3a). With the additional influence of lone pair of electrons, the spatial configuration of the four Bi—O bonds tends to be flat, so Bi^{3+} can be regarded as a quadrilateral node, forming a 2D structure eventually with a *sql* topology (Fig. 3b). With the -AA-

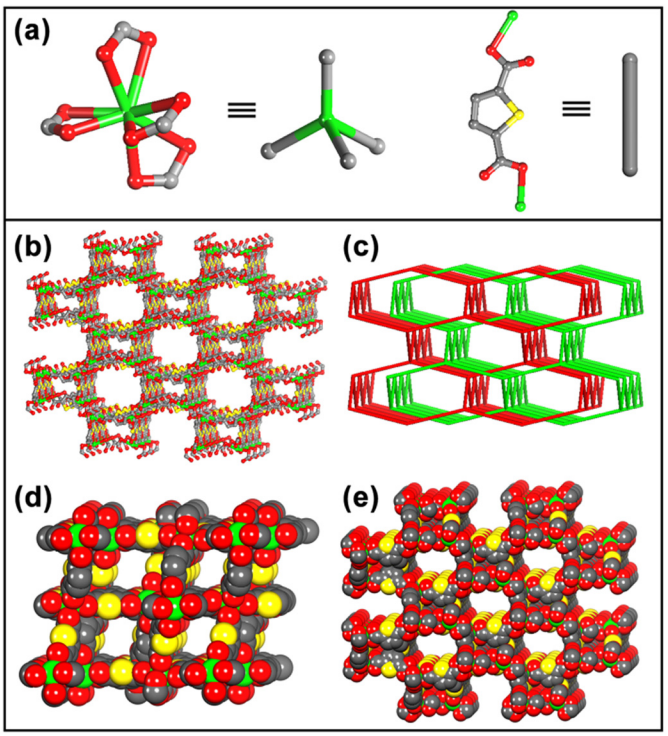

Fig. 2. Description of the structures of compound **2**: (a) Bi^{3+} ion viewed as a 4-connected node with distorted tetrahedron, the ligand H_2tdc viewed as a 2-connected node; (b) the 3D framework of compound **2**; (c) the 2-fold interpenetrated 4-connected *dia* topology; (d) the 1D channels along [010] direction; (e) the 1D channels along [001] direction. Color code: carbon: gray; nitrogen: blue; oxygen: red; sulfur: yellow; bismuth: green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stacking of the 2D layers, compound **3** possesses one type of channel with diameters of 11 × 11 Å excluding the van der Waals radius.

The thermal stabilities of compounds **1–3** are investigated by thermogravimetric analysis (TGA) (Fig. S2). For compound **1**, the first step weight loss of 26.4% below 335 °C belongs to the removal of dimethylamine cation and DMF molecule (calcd: 26.3%). Upon further heating, the weight loss between 335 and 480 °C belongs to the

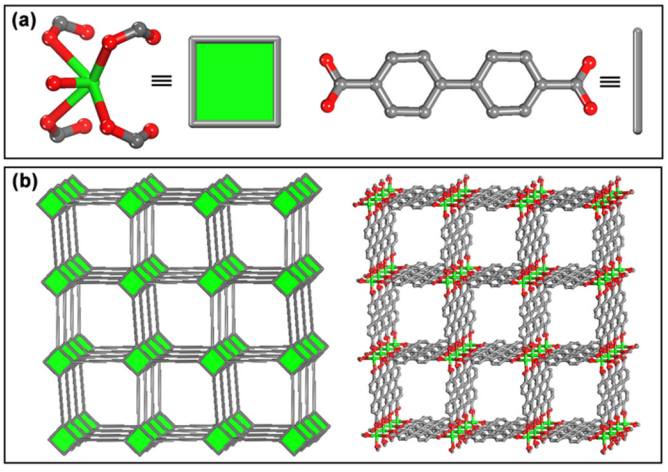

Fig. 3. Description of the structures of compound **3**: (a) Bi^{3+} ion viewed as a 4-connected quadrilateral node, the ligand H_2bpdc viewed as a 2-connected node; (b) schematic representation of the topology and the 2D layer along [001] direction. Color code: carbon: gray; nitrogen: blue; oxygen: red; bismuth: green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article as: L. Kan, et al., Three novel bismuth-based coordination polymers: Synthesis, structure and luminescent properties, Inorg. Chem. Commun. (2017), http://dx.doi.org/10.1016/j.inoche.2017.06.018