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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 bismuth-based coordination $[(CH_3)_2NH_2][Bi(pdc)(bdc)]\cdot 2DMF,$ novel polymers, $[(CH_3)_2NH_2][Bi(tdc)_2] \cdot 1.5DMF$ and $[Bi(bpdc)_2H_2O]$ ·xGuest (compounds **1–3**) (H₂pdc = 3,5pyridinedicarboxylic acid, $H_2bdc = 1,4$ -benzenedicarboxylic acid, $H_2tdc = 2,5$ -thiophenedicarboxylic acid, H_2 bpdc = 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 Bi³⁺, feature three-dimensional structures with hms and dia topology, respectively. However, 5-coordinated Bi³⁺ based compound **3** is a two-dimensional layered structure. Compound **1** can tune emissive performance by doping different lanthanide ions Tb³⁺, Eu³⁺ and Dy³⁺. Furthermore, detection of nitro explosives is investigated. All of the compounds are characterized by elemental analysis, IR spectrum and thermogravimetric analysis.

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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 Bi³⁺, which possess a lone pair of electrons, are rarely reported [4].

Due to its geometrically flexible coordination environments, the Bi³⁺ 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 Bi³⁺ ion is generally distorted, which is different from common octahedron and tetrahedron and so on [5]. From the perspective of coordination number, Bi³⁺ 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

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http://dx.doi.org/10.1016/j.inoche.2017.06.018 1387-7003/© 2017 Published by Elsevier B.V. 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 fluorescencebased 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, 3,5pyridinedicarboxylic acid (H₂pdc), 1,4-benzenedicarboxylic acid (H₂bdc), 2,5-thiophenedicarboxylic acid (H₂tdc) and 4,4'biphenyldicarboxylic acid (H₂bpdc), 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 $\mathbf{1}$ 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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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 C2/c space group. The purity of compound **2** is confirmed by PXRD patterns (Fig. S1b). The Bi³⁺ ion is eight-coordinated with eight oxygen atoms from four tdc²⁻ 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, tdc²⁻ 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_2 bpdc under solvothermal conditions at 85 °C [11]. Single crystal X-ray diffraction analysis reveals that compound **3** crystallizes in tetragonal system, space group *P4/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 Bi³⁺ ion in compound **3** connects four bpdc²⁻ 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 Bi³⁺ 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 H₂tdc 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_2 bpdc 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

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Fig. 4. (a) Emission spectra of compound 1 excited at 313 nm in solid state at room temperature; (b) Tb, Eu, Dy doped compound 1 excited at 330 nm in solid state at room temperature.

decomposition of ligands. The final residue of 31.6% is attributed to Bi_2O_3 powder (calcd: 28.6%). For compound **2**, the initial weight loss below 230 °C belongs to the removal of guest molecules. Upon further heating, the weight loss between 230 and 540 °C belongs to the decomposition of ligands. The final residue of compound **2** at 800 °C is attributed to Bi_2O_3 powder. For compound **3**, the weight loss below 600 °C can be attributed to the loss of guest molecules, coordinated water molecules and organic ligands. The final residue at 800 °C is attributed to Bi_2O_3 powder.

Wavelength/nm

(a)

ntensity/a.u.

The luminescent properties of compound **1** were investigated. The solid-state emission spectra of compound **1** reveals that it emits blue light when excited at 313 nm (Fig. 4a). The doped samples are synthesized by doping Tb^{3+} , Eu^{3+} and Dy^{3+} during the synthesis process [12]. As shown in Fig. S4, PXRD patterns indicates that the structure of compound **1** don't change after doping lanthanide ions. Tb^{3+} , Eu^{3+} and Dy^{3+} doped compound **1** emit intense green, red and blue luminescence when excited at 330 nm, respectively (Fig. 4b), which reveals that doping lanthanide ions into bismuth-based MOFs is an effective way to tune the luminescent performance.

Taking into account the strong luminescent properties of compound **1** and the electron transfer between π -electron-rich fluorescent compounds and electron-deficient analyte in the fluorescence quenching processes, we further investigate the detection of nitro explosives. Emission spectra of compound **1** dispersed in DMF exhibits intense emission at 414 nm when excited at 313 nm (Fig. S5). However, the fluorescent quenching is observed by the addition of 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol

(2,4-DNP) and 4-nitrophenol (4-NP) (Fig. 5). The fluorescent quenching efficiency was analysed by using the Stern-Volmer (SV) equation $(I_0 / I) = 1 + K_{sv}[Q]$, where K_{sv} is the quenching constant (M^{-1}) , [Q] is the molar concentration of the explosives, I_0 and I are the luminescence intensities of compound **1** before and after the addition of the explosives, respectively. As shown in Fig. S6, the SV plots are almost linear at low concentration range. Compound **1** has the high K_{sv} values of $4.91 \times 10^4 \text{ M}^{-1}$ toward TNP, $4.57 \times 10^4 \text{ M}^{-1}$ toward 2,4-DNP and $3.70 \times 10^4 \text{ M}^{-1}$ toward 4-NP, respectively. The different quenching efficiencies can be attributed to electron and energy transfer and electrostatic interactions in the host-guest systems [13].

Wavelength/nm

In summary, three novel coordination polymers based on bismuth have been successfully synthesized under solvothermal conditions. The high coordination number metal bismuth-based compounds **1** and **2** feature 3D structures, but compound **3** based on 5-coordinated bismuth is a 2D layer structure. It was found that the lone pair of electrons and various coordination numbers of bismuth have significant effects on the construction of complex bismuth-based MOFs. In addition, compound **1** can be used for detection of TNP, 2,4-DNP and 4-NP, and doping lanthanide ions into bismuth-based compounds is also an effective way to obtain functional luminescent materials.

Acknowledgment

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 21373095).



Fig. 5. Effect on the emission spectra of compound 1 dispersed in DMF upon incremental addition of a selected explosive (1 mM, 20 µL addition each time; inset: SV plots of selected explosive).

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

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Appendix B. Supplementary material

CCDC 1545100–1545102 containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif, Single-crystal structure analysis, Powder XRD patterns, TG curve, IR spectra, Emission spectra, and the SV plots at low concentration range can be found online at doi: http://dx.doi.org/10.1016/j. inoche.2017.06.018.

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- [8] Single-crystal structure analysis: Crystallographic data for three compounds were collected on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure of compound 2 was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97, the structure of compounds 1 and 3 were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-2014. All the metal atoms were located first, and then the oxygen, carbon, nitrogen and sulfur atoms of the compound were subsequently found in difference Fourier maps. The hydrogen atoms of the ligand were placed geometrically. All non-hydrogen atoms were refined anisotropically.
- [9] Synthesis of compound 1: Bi(NO₃)₃·5H₂O (5 mg, 0.010 mmol), H₂pdc (4 mg, 0.024 mmol), H₂bdc (4 mg, 0.024 mg), DMF (1 mL) and methanol (0.5 mL) was sealed in a 20 mL vial and heated at 105 °C for 24 h, then cooled to room temperature gradually. Colorless crystals were collected (yield 55% based on Bi). The as-synthesized sample was characterized and formulated by elemental analysis, thermogravimetric analysis and single-crystal X-ray diffraction studies as [(CH₃)₂NH₂][Bi(pdc)(bdc)]·2DMF. Elemental analysis (wt%) for 1. Calcd: C, 37.80; H, 3.97; N, 7.67. Found: C, 37.54; H, 3.97; N, 7.49.
- [10] Synthesis of compound 2: Bi(NO₃)₃·5H₂O (12 mg, 0.025 mmol), H₂tdc (20 mg, 0.116 mmol), DMF (2 mL) and methanol (1.5 mL) was sealed in a 20 mL vial and heated at 115 °C for 3 days, then cooled to room temperature gradually. Colorless crystals were collected (yield 60% based on Bi). The as-synthesized sample was characterized and formulated by elemental analysis, thermogravimetric analysis and single-crystal X-ray diffraction studies as [(CH₃)₂NH₂][Bi(tdc)₂]·1.5DMF. Elemental analysis (wt%) for 1. Calcd: C, 31.51; H, 3.19; N, 4.96. Found: C, 31.91; H, 3.17; N, 5.03.
- [11] Synthesis of compound 3: Bi(NO₃)₃·5H₂O (2 mg, 0.004 mmol), H₂bpdc (5 mg, 0.020 mmol), NaBF₄ (16 mg, 0.146 mmol), DMF (1 mL), benzylalcohol (0.1 mL) and acetic acid (25 µL) was sealed in a 20 mL vial and heated at 85 °C for 24 h, then cooled to room temperature gradually. Colorless crystals were collected (yield 65% based on Bi).
- [12] Synthesis of doped compound 1: Bi(NO₃)₃·5H₂O (5 mg, 0.010 mmol), H₂pdc (4 mg, 0.024 mmol), H₂bdc (4 mg, 0.024 mg), DMF (1 mL), methanol (0.5 mL) and 100 µL Tb(NO₃)₃ solution (5.3 mM) was sealed in a 20 mL vial and heated at 105 °C for 24 h, then cooled to room temperature gradually. Colorless crystals were collected. The same synthetic conditions are used for the preparation of Eu³⁺ and Dy³⁺ doped compound 1 except with Eu(NO₃)₃ and Dy(NO₃)₃ instead of Tb(NO₃)₃.
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