

Short communication

Solvent-free synthesis of new open-framework metal oxalates with different 4-connected topologies

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ABSTRACT

Three open-framework metal oxalates, formulated as $(\text{Hdbu})[\text{In}_2(\text{OH})(\text{ox})_3]$ (**1**), $(\text{Hthfa})[\text{Eu}_2(\text{Hthfa})(\text{H}_2\text{O})(\text{ox})_4] \cdot 3\text{H}_2\text{O}$ (**2**), and $(\text{Hepc})[\text{Bi}(\text{ox})_2]$ (**3**), were prepared under solvent-free conditions, where dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene, ox = oxalate, thfa = tetrahydrofurfurylamine, and epc = 4-ethylpiperazine-1-carbaldehyde. Topological analyses reveal that these compounds have different 4-connected networks with sra (for **1**), lon (for **2**), and dia (for **3**) topologies. Compound **2** displays a bright red luminescence as a result of excitation at 397 nm.

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Open-framework metal oxalates have been intensively studied because of their diverse structures and appealing physical properties such as luminescence, magnetism, and proton conduction [1–3]. These crystalline compounds are usually synthesized under hydrothermal and solvothermal conditions [4–6]. Recently, we have developed a new approach for preparing metal oxalates and related hybrid-framework solids without the addition of water as a solvent [7,8]. By eliminating the effect of solvent on the framework structures, this synthetic route shows great potential in the creation of new open-framework compounds. An illustrative example is the solvent-free synthesis of an fsh-type hybrid framework $(\text{C}_{10}\text{N}_3\text{H}_{28})_{0.5} \cdot \text{Mn}_2(\text{H}_2\text{PO}_4)_{1.5}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ that is normally not accessible by hydrothermal approach because it is highly unstable in water [9].

From the viewpoint of structural chemistry, the use of different metal ions with various charges and coordination numbers as framework cations is highly desirable for the formation of new coordination polymers [10–12]. Previously, we reported the solvent-free synthesis of several transition metal oxalates with chain-like, layered, and three-dimensional structures [7,13]. Yet the influence of main group metals and rare earth elements on the metal oxalate structures has not been investigated under solvent-free conditions. Here we report the solvent-free synthesis of three new metal oxalates, namely, $(\text{Hdbu})[\text{In}_2(\text{OH})(\text{ox})_3]$ (**1**), $(\text{Hthfa})[\text{Eu}_2(\text{Hthfa})(\text{H}_2\text{O})(\text{ox})_4] \cdot 3\text{H}_2\text{O}$ (**2**), and $(\text{Hepc})[\text{Bi}(\text{ox})_2]$ (**3**), where dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene, ox = oxalate, thfa = tetrahydrofurfurylamine, and epc = 4-ethylpiperazine-1-

carbaldehyde. Structural analyses reveal that these compounds display different 4-connected networks with sra (for **1**), lon (for **2**), and dia (for **3**) topologies, respectively [14]. To the best of our knowledge, compound **1** represents the first example of an open-framework metal oxalate with a zeolitic sra topology.

Colorless crystals of compound **1** were obtained by heating a mixture of $\text{In}(\text{OH})_3$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and 1,8-diazabicyclo[5.4.0]undec-7-ene at 150 °C for 5 days. The asymmetric unit of **1** contains 32 non-hydrogen atoms, of which two indium atoms are crystallographically independent. Each indium atom is seven coordinated by six oxalate oxygen atoms and one hydroxyl group with the In–O bond lengths in the range of 2.093(4)–2.273(4) Å. Each oxalate ligand has a typical chelating bis-bidentate coordination mode. The bridging oxygen atom between two indium atoms is a hydroxyl group, which is confirmed by the presence of a sharp IR band at 3610 cm^{-1} for $\nu_{\text{O-H}}$ stretching frequencies. The linkages between indium atoms and oxalate ligands create hcb-type layers parallel to the *bc* plane, which are further connected by hydroxyl groups to give rise to a three-dimensional structure (Fig. 1a). The framework of **1** can be simplified into a rare zeolitic sra topology by regarding each indium site as a 4-connected node (Fig. 1b) [15]. Prior to this work, only the indium oxalate NKB-1 with a zeolitic gis topology was known [16]. Other 4-connected metal oxalates often adopt dia and qtz topologies [17,18].

Viewed along the [001] direction, the structure of **1** shows regular 14-ring channels delimited by eight InO_7 polyhedra and six oxalate ligands. The square-like 14-ring window has a pore size of $9.4 \times 9.4\text{ \AA}^2$ (measured from the distance between two carbon atoms across the window). The Hdbu cations are well ordered within the large channels

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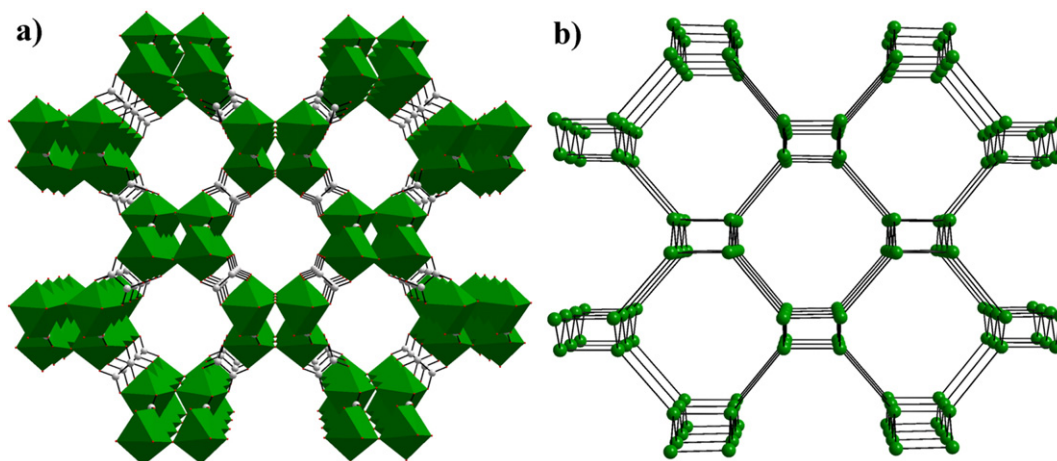


Fig. 1. (a) A view of the framework structure of **1** contains large 14-ring channels. (c) Compound **1** with a zeolitic sra topology.

of **1**. A void space analysis performed by using the program *PLATON* indicates that these organic cations occupy 54.0% of the unit cell volume [19].

Colorless crystals of compound **2** were obtained by heating a mixture of Eu_2O_3 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and tetrahydrofurfurylamine at 150°C for 6 days. The asymmetric unit of **2** contains two crystallographically independent europium atoms, each of which resides in a distorted tricapped trigonal prismatic environment with the $\text{Eu}-\text{O}$ bond lengths in the range of $2.364(4)$ – $2.698(5)$ Å. Each oxalate ligand in the structure links two europium atoms in a chelating bis-bidentate coordination mode. The linkages between europium atoms and oxalate ligands create a three-dimensional structure (Fig. 2a). The whole framework can be simplified into a 4-connected net with a symbol of lon by regarding each europium site as a 4-connected node (Fig. 2b). Viewed along the [100], [010], and [101] directions, compound **2** possesses multidirectional 12-ring channels. There are two types of organic cations in the structures. A type I organic cation resides within 12-ring channel and acts as a structure-directing agent. A type II organic cation attaches to the framework through $\text{Eu}-\text{O}$ bond. It plays a dual role by acting a ligand to metal center as well as a charge-balancing agent containing one monoprotonated amino group. The organic cations form extensive hydrogen bonds with framework oxygen atoms and lattice water molecules. The shortest $\text{N}\cdots\text{O}$ distances are in the region of $2.807(9)$ – $2.979(9)$ Å.

Colorless crystals of compound **3** were obtained by heating a mixture of Bi_2O_3 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and 1-ethylpiperazine at 130°C for 7 days. There are one bismuth atom, two oxalate ligands, and one monoprotonated epc cation in the asymmetric unit of **3**. The bismuth atom is coordinated by eight oxalate oxygen atoms with the $\text{Bi}-\text{O}$ bond lengths in the range of $2.293(10)$ – $2.731(12)$ Å. Each bismuth atom links four adjacent neighbors through bridging oxalate ligands, forming a three-dimensional structure (Fig. 3a). The framework can be topologically represented as a 4-connected dia net by regarding each bismuth site as a 4-connected node. It should be noted that a hydrated bismuth oxalate, $(\text{C}_3\text{N}_2\text{H}_5)_2[\text{Bi}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, also adopts this net [20]. However, each bismuth atom in this compound has a nine-coordinated geometry, which is different from that in compound **3**. Viewed along the [111] direction, compound **3** displays large 12-ring channels with a pore size of 8.8×11.3 Å². The Hepc cations orderly reside within the channels, which occupy 54.6% of the unit cell volume. Different from the directly used amines in compounds **1** and **2**, the structure-directing agent in compound **3** is generated *in situ* from the reaction between 1-ethylpiperazine and oxalic acid. A possible mechanism for the formation of this organic molecule is shown in Fig. 3b. First, a condensation reaction between oxalic acid and 1-ethylpiperazine occurred to form an amide molecule. Then, the carboxylate group in the amide molecule was removed at elevated temperature. As far as we know, the Hepc cation was observed for the first time in an

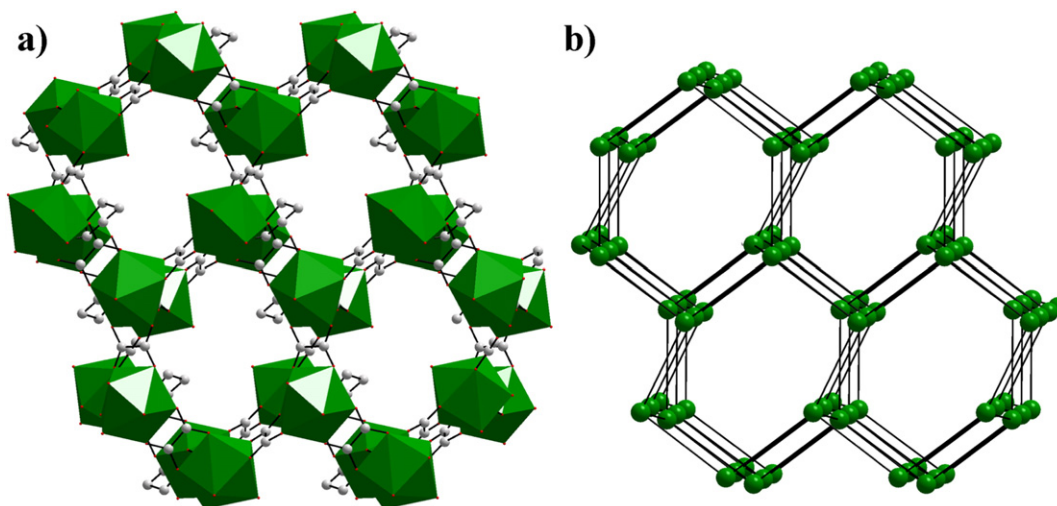


Fig. 2. (a) A view of the framework structure of **2** contains large 12-ring channels. (b) Compound **2** with a lon topology.

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