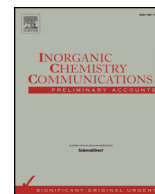




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Short communication

## Extra-large-pore metal sulfate-oxalates with diamondoid and zeolitic frameworks

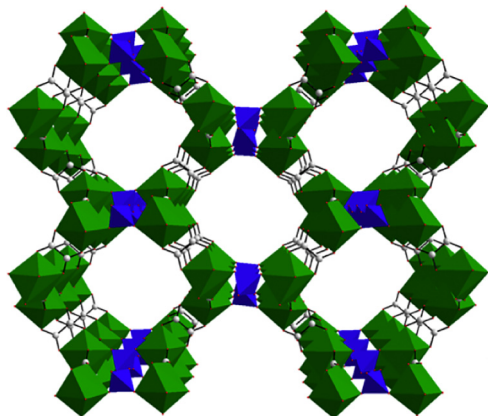


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## GRAPHICAL ABSTRACT

Two metal sulfate-oxalates were prepared under solvent-free conditions. They have 4-connected nets with diamondoid and zeolitic ABW topologies. The temperature dependence of the magnetic susceptibility of the diamondoid framework was also investigated.



## ARTICLE INFO

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## ABSTRACT

Presented here are two new open-framework metal sulfate-oxalates, formulated as  $H_2hpiP-Mn_2(SO_4)(C_2O_4)_2(H_2O)$  (SCU-14) and  $(Hthfa)_2In_2(SO_4)(C_2O_4)_3 \cdot 2H_2O$  (SCU-16), where hpip = homopiperazine and thfa = tetrahydrofurfurylamine. SCU-14 has a diamondoid framework with extra-large 14-ring channels. SCU-16 has a zeolitic ABW topology with extra-large 16-ring channels. The temperature dependence of the magnetic susceptibility of SCU-14 was also investigated.

Open-framework inorganic-organic hybrid solids are an important class of solid state materials that are usually assembled from metal ions, inorganic anions, and organic ligands [1–3]. These crystalline materials have well-defined structures with appealing properties such as luminescence, proton conduction, and catalysis [4–6]. During the past years, considerable attention has been paid to the synthesis of open-framework metal phosphate-oxalates [7–10]. A notable example is extra-large-pore NTHU-6 emitting yellow luminescence [7]. Hybrid

frameworks containing other inorganic anions, such as arsenate, sulfate, selenite, phosphite, and sulfite, have also been investigated [11–16]. These inorganic-organic hybrid solids are generally prepared by hydrothermal and solvothermal methods. Recent developments show that solvent-free synthesis offers an alternative way to prepare hybrid framework materials [17,18]. This synthetic method not only eliminates the safety concerns associated with high reaction pressure under hydrothermal and solvothermal conditions, but also opens up

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exciting opportunities to make new open-framework materials [19–22]. For example, several transition metal sulfate-oxalates that are sensitive to hydrolysis have been successfully isolated under solvent-free conditions by using different amines as the structure-directing agents [23–26]. These inorganic-organic hybrid solids display some interesting framework topologies, such as dia, hcb, kgd, and mog. Given the large pool of amine molecules, we expect that new open-framework structures, especially those with extra-large pores, will be potentially accessed under similar solvent-free conditions in this compositional domain. During the course of such investigations, two open-framework metal sulfate-oxalates, formulated as  $\text{H}_2\text{hpip}\cdot\text{Mn}_2(\text{SO}_4)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})$  (SCU-14) and  $(\text{Hthfa})_2\cdot\text{In}_2(\text{SO}_4)(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}$  (SCU-16), were obtained as good quality single crystals, where *hpip* = homopiperazine and *thfa* = tetrahydrofurfurylamine. The two compounds have three-dimensional structures with extra-large 14-ring and 16-ring channels, respectively [27]. Topological analyses reveal that SCU-14 has a diamondoid net while SCU-16 has a zeolitic ABW net [28]. As far as we know, the zeolitic ABW topology has been observed for the first time in hybrid frameworks containing both oxalate ligands and inorganic oxoanions (e.g., phosphate and sulfate).

In a typical synthesis, a mixture of MnO (0.071 g),  $\text{H}_2\text{SO}_4$  (98%, 53  $\mu\text{L}$ ),  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  (0.252 g), and homopiperazine (105  $\mu\text{L}$ ) was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 8 days. The autoclave was subsequently allowed to cool to room temperature. Yellow crystals of SCU-14 were recovered from the resulting product by sonification, washed with methanol (the crystals are highly unstable in water), and dried in air (42% yield based on manganese). SCU-16 was prepared under similar synthetic conditions. The phase purity of the two compounds was confirmed by powder X-ray diffraction.

SCU-14 crystallizes in the orthorhombic space group  $P2_12_12_1$  (no. 19). The asymmetric unit contains two manganese atoms, one  $\text{SO}_4$  unit, two oxalate ligands, one water molecule, and one  $\text{H}_2\text{hpip}$  cation. Each manganese atom is octahedrally coordinated by six oxygen atoms with the Mn–O bond length in the region of 2.134(3)–2.360(4) Å. The manganese atoms are bridged by oxalates ligands to give rise to double-chain substructures running along the [100] direction. These manganese oxalate chains are further assembled by sulfate groups to produce a three-dimensional structure (Fig. 1a). Viewed along the [100] direction, SCU-14 displays extra-large 14-ring channels delimited by eight  $\text{MnO}_6$  octahedra, four  $\text{SO}_4$  tetrahedra, and two oxalate ligands. Intersecting this channel are two different 10-ring channels running along the [001] and [111] directions. The  $\text{H}_2\text{hpip}$  cations reside within the intersecting channels and interact with the framework oxygen atoms through extensive hydrogen bonds. The closest N...O distances vary from 2.681(6) to 2.779(5) Å. A void space analysis employing PLATON indicates that the organic cations occupy 34.2% of the unit cell volume [29].

By regarding  $\text{Mn}_2\text{O}_{11}$  dimers as 4-connected nodes, the framework structure of SCU-14 can be represented as a diamondoid net with a point symbol of  $6^6$  (Fig. 1b). It should be noted that such a 4-connected net is also found in another metal sulfate-oxalate, namely,  $\text{H}_2\text{dmen}\cdot\text{Mn}(\text{SO}_4)(\text{ox})$  [25]. However, careful analyses of the two structures reveal some interesting differences. SCU-14 has extra-large 14-ring channels containing  $\text{Mn}_2\text{O}_{11}$  dimers as structural nodes, while  $\text{H}_2\text{dmen}\cdot\text{Mn}(\text{SO}_4)(\text{ox})$  has 12-ring channels with  $\text{MnO}_6$  octahedra as 4-connected nodes. Previously we demonstrated that the use of a larger building unit as the structural node will thicken the inorganic walls of a pcu-type hybrid framework [30]. In this work, the larger building unit in SCU-14 is the key factor to enlarge the pore size of a diamondoid net from 12-membered ring to 14-membered ring.

SCU-16 crystallizes in the monoclinic space group  $P2_1/c$  (No. 14). The asymmetric unit consists of two indium atoms, three oxalate ligands, one  $\text{SO}_4$  unit, two water molecules, and two *Hthfa* cations. Each indium atom is surrounded by seven oxygen atoms from three oxalate ligands and one sulfate anion. Each oxalate ligand serves as a cross-linker between two adjacent indium atoms. The linkages between indium atoms and oxalate ligands result in the formation of honeycomb-like layers parallel to the *ab* plane. They are packed along the [001] direction in an ABAB sequence. The indium oxalate layers are further pillared by sulfate ions to form a three-dimensional structure (Fig. 2a). Viewed along the [100] direction, the compound shows regular 16-ring channels delimited by eight  $\text{InO}_7$  polyhedra, six oxalate ligands, and two  $\text{SO}_4$  tetrahedra. The diameter of the 16-ring window is nearly 10.5 Å, calculated from the distance between two oxygen atoms across the window. Furthermore, there are 12-ring channels along the [001] and [111] direction. *Hthfa* cations and water molecules are orderly within the intersecting channels, which occupy 48.9% of the unit cell volume.

The framework structure of SCU-16 can be represented as a zeolitic ABW net by regarding indium atoms as 4-connected nodes (Fig. 2b). Prior to this work, a variety of framework topologies (e.g., dia, fsc, fsd, fsh, ins, kgd, lon, mmt, mog, pcu, and ths) have been observed in metal phosphate/phosphite/sulfate oxalates. However, none of them have 4-connected zeolitic nets. Therefore, SCU-16 is the first metal sulfate-oxalate with a zeolitic net. We believe that the high coordination numbers of indium atoms is beneficial for the formation of 4-connected nets in oxalate-based hybrid frameworks.

Thermogravimetric analyses for SCU-14 and SCU-16 were carried out in a flow of  $\text{N}_2$  with a heating rate of 10 °C/min. Each compound shows a three-step weight loss in the measured region. For SCU-14, the first loss between 170 and 240 °C is caused by the departure of water molecules (observed: 3.52%; expected: 3.59%). The second loss between 300 and 490 °C is assigned to the decomposition of organic cations and oxalate ligands (observed: 51.35%; expected: 52.22%). The last loss, which is continuous up to 610 °C, is attributed to the departure

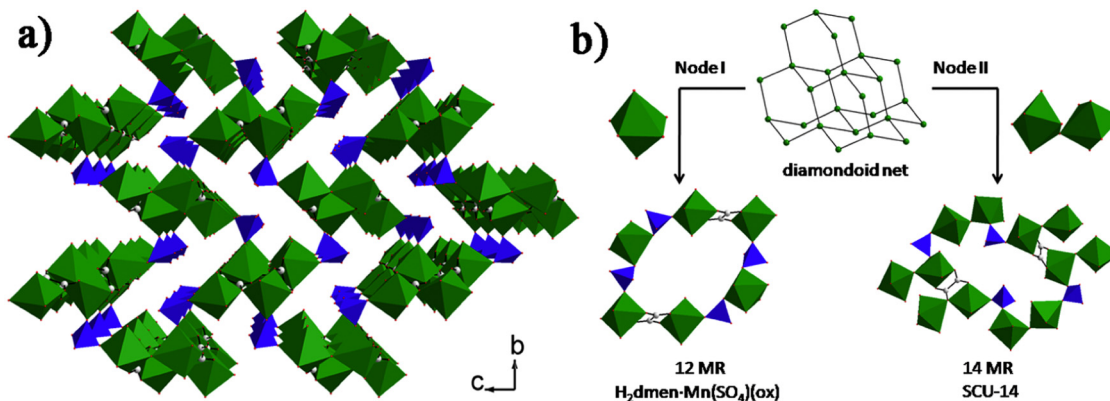


Fig. 1. (a) View of the framework structure of SCU-14 with 14-ring channels. (b) Two different structural nodes in metal sulfate-oxalates with a diamondoid net: SCU-14 has 14-ring channels with  $\text{Mn}_2\text{O}_{11}$  dimers as the nodes, while  $\text{H}_2\text{dmen}\cdot\text{Mn}(\text{SO}_4)(\text{ox})$  has 12-ring channels with  $\text{MnO}_6$  octahedra as the nodes.

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