

Synthesis and characterizations of a magnesium metal–organic framework with a distorted (10,3)-a-net topology

Shengqian Ma^a, Jacqueline A. Fillinger^a, Michael W. Ambrogio^a,
Jing-Lin Zuo^b, Hong-Cai Zhou^{a,*}

^a Department of Chemistry and Biochemistry, Miami University, Oxford, OH, 45056, USA

^b Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

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Abstract

A magnesium metal–organic framework with a distorted (10,3)-a-net topology has been synthesized under solvothermal conditions, and characterized by X-ray structure determination, thermogravimetric analysis, X-ray powder diffraction, IR, and nonlinear optical studies.

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Metal–organic frameworks (MOFs) have attracted a great deal of attention because of their fascinating topologies [1–3] and potential applications such as catalysis, separation, non-linear optics, magnetism, and gas storage [4–17]. In the gas storage studies, one of the important directions is to construct MOFs with reduced density for the enhancement of gravimetric storage capacity. MOFs formed by light main group metals such as Mg²⁺, and Al³⁺ may play an important role in this endeavor [17]. However, most studies in the literature have focused on MOFs assembled from d- or f-block elements [18–20]. MOFs based on main-group metals, in particular, light main group metals are very rare [21–23].

Recently, we became interested in constructing MOFs with the (10,3)-a-net topology, which can be reliably built using three-connected organic bridging ligands and inorganic nodes [24–29]. One of the reasons for such an interest is that the (10,3)-a-net is chiral and the studies may lead to chiral MOFs built from achiral components. Most (10,3)-a MOFs reported thus far are based on trigonal-planar

ligands and divalent metal ions, such as Co²⁺, Ni²⁺, Zn²⁺, and Cd²⁺ [25,26]. Herein, we report a distorted (10,3)-a magnesium MOF built from 1,3,5-benzenetricarboxylate (BTC).

Mg₂(BTC)(CH₃COO)(C₄H₉NO)₃·H₂O, MOF **1**, was obtained under solvothermal conditions from a reaction of Mg(NO₃)₂·6H₂O and BTC in dimethylacetamide (DMA).¹ Single crystal X-ray analysis² revealed that MOF **1** crystallizes in a noncentrosymmetric space group *P*2₁2₁2₁. There are two crystallographically independent magnesium atoms (Mg1 and Mg2, Fig. 1) in the 3D framework. Mg1 is coordinated by four O atoms from carboxyl-

¹ A mixture of H₃BTC (0.01 g, 4.76 × 10⁻⁵ mol), Mg(NO₃)₂·6H₂O (0.020 g, 7.8 × 10⁻⁵ mol) in 1.5 mL dimethylacetamide (DMA) was sealed in a Pyrex tube and heated to 130 °C at which it stayed for 24 h, and then cooled to room temperature with a decreasing rate of 0.2 °C/min. The colorless block crystals obtained were washed with DMA to give pure MOF **1** with a formula of Mg₂(C₉H₃O₆)(CH₃COO)(C₄H₉NO)₃·H₂O (yield: 65% based on BTC ligand). Elemental analysis calcd (%) for the compound: C 46.49, H 5.93, N 7.07; found: C 46.61, H 5.72, N 7.21.

² X-ray crystal data for MOF **1**: C₂₂H₃₃N₃O₁₁Mg₂, *M*_r = 576.14, orthorhombic, *P*2₁2₁2₁, *a* = 12.537(5) Å, *b* = 14.977(5) Å, *c* = 15.404(6) Å, *V* = 2892.3(18) Å³, *Z* = 4, *T* = 213 K, ρ_{calcd} = 1.323 g/cm³; *R*₁ (*I* > 2σ(*I*)) = 0.060, *wR*₂ = 0.15, GOF = 1.09.

* Corresponding author. Tel./fax: +1 513 529 8091.

E-mail address: zhouh@muohio.edu (H.-C. Zhou).

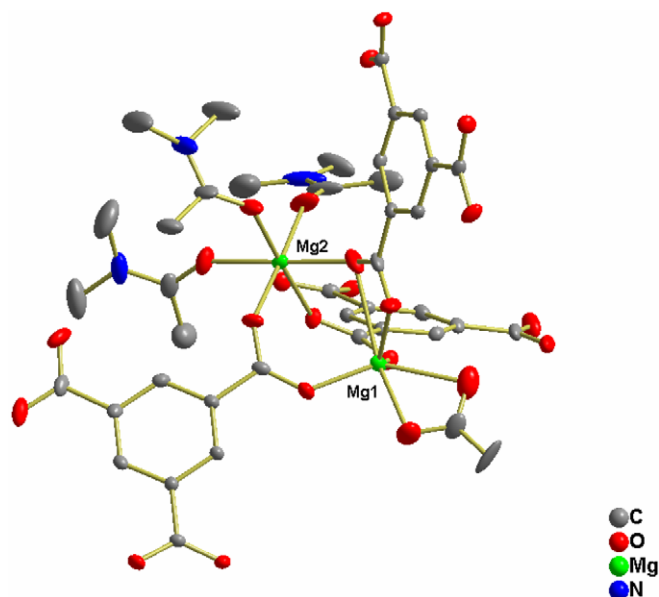


Fig. 1. A structural unit of MOF 1 containing a secondary building unit (SBU) and three BTC ligands.

ate groups of three BTC ligands, and two O atoms from an acetate group, resulting from DMA decomposition [30]. Mg1–O distances vary from 1.961 to 2.626 Å. The coordination environment of Mg1 is distorted octahedral with the *cisoid* angles being 54.2–115.6° and *transoid* angles being 128.1–160.4°. Mg2 is octahedrally coordinated by three O atoms from three BTCs, and three O atoms from three DMAs. The Mg2–O distances vary from 2.030 to 2.082 Å, the *cisoid* angles from 86.6° to 96.2°, and *transoid* angles from 176.0° to 177.7°.

The difference between the coordination environments of Mg1 and Mg2 results in a secondary building unit (SBU) with C_1 symmetry (Fig. 1), which in turn propagates throughout the 3D network to form a chiral net. In each SBU, two of the BTC carboxylate groups adopt a symmetric bridging mode and the third, a chelating–bridging mode, connecting the two Mg atoms (Fig. 1). Thus, each BTC ligand connects three SBUs and every SBU binds three BTC ligands to form a distorted (10,3)-a-network (Fig. 2).

In MOF 1, there are two types of three-connected nodes: one corresponds to the SBU, the other represents the BTC ligand. Different from the usual (10,3)-a-net epitomized by its 4_1 or 4_3 helices that run in three perpendicular directions [27–29], in MOF 1 the $4_1/4_3$ symmetry was lowered by distortion to 2_1 , as shown in Fig. 2. X-ray diffraction studies on a multiply twinned crystal gave rise to a Flack parameter of 0.1(5). The unusually large value of estimated standard deviation gives uncertainty on whether there is an *enantiomeric excess* (ee) in the crystal or not. Circular dichroism and vibrational circular dichroism studies on the single crystal for diffraction studies or bulk samples of MOF 1 suggested that MOF 1 may have a net ee, but the experimental evidence was inconclusive. There is also no apparent reason

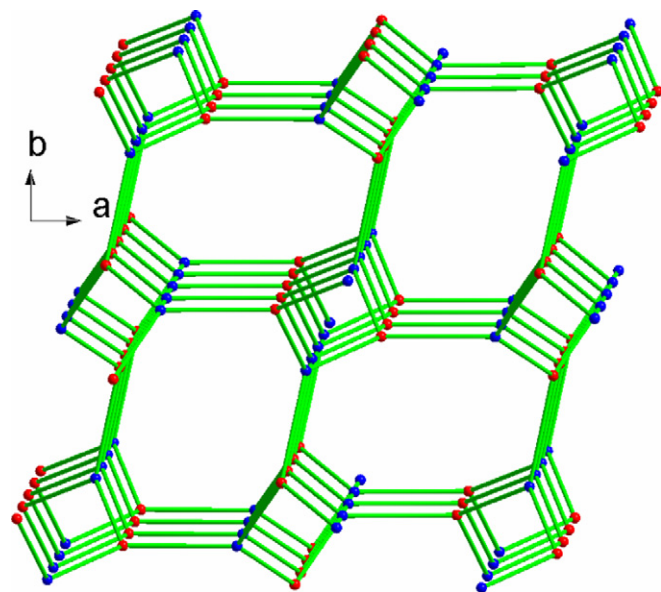


Fig. 2. The distorted (10,3)-a-network viewed down *c*-axis. Red spheres represent the SBUs; blue ones represent the BTC ligands. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

to let one to believe such an ee because no chiral factors were introduced during the solvothermal reaction procedure. However, at this stage we cannot completely exclude such a possibility.

Although the channels of the framework are blocked by coordinated solvent molecules on Mg atoms, consistent with the low surface area of MOF 1 revealed by a nitrogen adsorption measurement, applying larger ligands at similar assembly conditions should lead to porous MOFs containing chiral channels.

In an IR spectrum of MOF 1, the disappearance of the band at 1698 cm^{-1} indicates that all the carboxylic acid groups are deprotonated during the solvothermal reaction. The bands at 1384 and 1618 cm^{-1} are attributed to C=O stretch vibrations, while the bands at 1273 and 1112 cm^{-1} originate from the skeleton vibrations of the aromatic benzene rings of the BTC ligands [31,32].

Thermal gravimetric analysis (TGA) shows that the compound is stable to $200\text{ }^\circ\text{C}$, as confirmed by X-ray powder diffraction (XRPD, Fig. 3). In the TGA plot, The first weight loss of 3.2% from 50 to $200\text{ }^\circ\text{C}$ corresponds to the loss of one water guest (calcd: 3.0%). The second weight loss of 54.1% from 200 to $530\text{ }^\circ\text{C}$ agrees with the loss of the three coordinated DMA molecules and the coordinated CH_3COO (calcd: 53.9%). The BTC ligand starts to decompose from 530 to $600\text{ }^\circ\text{C}$ with an overall weight loss of 29.4% (calcd: 29.5%). The remaining 13.2% weight corresponds to that of a white MgO residue (calcd: 13.5%).

It is well known that a noncentrosymmetric space group assignment can be confirmed by the second harmonic generation (SHG) [10]. A crystalline sample of MOF 1 displays a SHG response five times that of KDP, demonstrating potentials for non-linear optical applications.

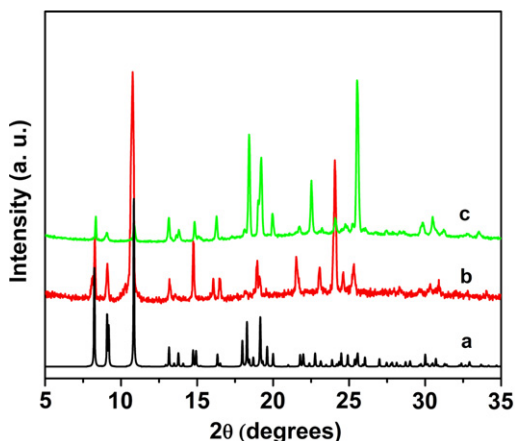


Fig. 3. X-ray powder diffraction patterns: (a) simulated; (b) experimental; (c) heated at 200 °C for 2 h.

In conclusion, a magnesium MOF with a distorted (10,3)-a-net topology and moderate SHG response is presented. Future work will focus on the construction of porous MOF with light-weight main-group metals and large ligands. The construction of MOFs containing chiral channels from achiral ligands is also in progress in our laboratory.

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with Cambridge crystallographic data center as supplementary publication No. CCDC 620573 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data containing a TGA plot and an IR spectrum associated with this communication can be found, in the online version, at [doi:10.1016/j.inoche.2006.10.010](https://doi.org/10.1016/j.inoche.2006.10.010).

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